

New Routes for Functionalised Nanoparticles for Polymer Nanocomposites



Céline Shepherd
University of Oxford
St Anne's College

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Abstract

Polymer nanocomposites represent a class of advanced, multifunctional materials, combining the attractive features of both nanomaterials and polymers. The level of dispersion of the nanoparticles directly controls the extent to which nanocomposites can maximize the unique attributes of their nano-scale fillers. However, as a consequence of the tendency of nanofillers to agglomerate, the anticipated superior properties of polymer nanocomposites are yet to be realised, and remain merely a theoretical prediction. As a result, the surface chemistry of nanofillers is often tailored to reduce the attractive interparticle interactions that promote agglomeration. This modification can also be used to enhance the interfacial interactions between the nanofiller and polymer matrices to achieve improved filler dispersion. Accordingly, this thesis addresses this challenge in nanocomposite technology by investigating the chemical surface functionalisation of various nanoparticles in order to produce polypropylene (PP) nanocomposites with superior electrical, mechanical and thermal properties.

Part I describes covalent modification of nanosilica, microsilica, furnace Carbon Black (CB), acetylene black (ACB) and carbon nanotube (CNT) nanomaterials by carbene insertion and azo-coupling reactions, in a series of studies, in order to tailor their surfaces for application in polypropylene (PP) nanocomposites. The surface characterisation of the modified nanomaterials was assessed in detail using XPS, CHN, SSNMR, BET, ATR-IR and thermal analysis techniques. The surface grafting densities were estimated to be of the order of 10^{13} and 10^{14} molecules/cm² and additionally, SSNMR provided direct evidence of the diarylcarbene reaction to the silica surface. Following nanocomposite production with PP by solvent mixing methods, the macroscopic properties were studied demonstrating altered electrical, mechanical and thermal properties following assessment of the DC conductivity, dielectric properties, thermal analysis (TGA, DSC, DMA) and morphological measurements. In particular, the introduction to the CB surface of a diaryl complex with terminal dodecyl hydrocarbon chains demonstrated substantial improvements to the DC electrical and dielectric properties of the PP nanocomposites.

Part II explores the non-covalent surface functionalisation of CB and ACB by the physisorption of the non-ionic surfactant Triton-X-100. Various protocols were developed in which an optimal surface loading for CB was determined by treatment at 0.024 mM(aq). In addition, the modification procedure was combined with the granulation protocol of ACB in an effort to evaluate the potential for industrial applications. The degree of surface functionalisation was extensively characterised by BET, XPS, thermal analysis, UV-Vis and ATR-IR analyses. PP nanocomposites produced by solvent and melt mixing methods demonstrated similar conductive properties following the nano-scale modification, however morphological, dielectric and thermal analysis indicated altered interfacial interactions demonstrating improved mechanical properties.

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List of Abbreviations

Ac	Acetyl
ACB	Acetylene black
Ar	Aryl
aq	Aqueous
ATR-IR	Attenuated total internal reflectance infra-red
Av	Avagadro's constant
B.E.	Binding energy
BOC	<i>tert</i> -butoxycarbonyl
br.	Broad
C	Celsius
CB	Carbon Black
Conc.	Concentrated
CHN	Combustion analysis
cm ⁻¹	Wavenumber
CNT	Carbon nanotube
D	diameter
δ_H	Proton (¹ H) NMR chemical shift
δ_C	Carbon (¹³ C) NMR chemical shift
d	Doublet
DCM	Dichloromethane
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTG	Differential thermogravimetric curve
Eq	Equivalents
ESI	Electrospray ionisation
Et	Ethyl

List of Abbreviations

Ether	Diethylether
eV	Electron volt
FT	Fourier transform
FWHM	Full width at half maximum intensity
g	Grams
GP	Graphene
hrs	Hours
HRMS	High resolution mass spectrometry
Hz	Hertz
IMFP	Inelastic mean free path
IR	Infra-red
<i>J</i>	Coupling constant
Lit.	Literature value
M	Multiplet
[M+H] ⁺	Protonated molecular ion
Me	Methyl
Min	Minutes
MWCNT	Multi-walled carbon nanotube
Mol	Moles
μm	micrometer
Mp	Melting point
MP	Microparticle
MS	Mass spectroscopy
m/z	Mass/charge ratio
NBS	<i>N</i> -bromosuccinimide
NC	Nanocomposite
Nm	Nanometer
NMR	Nuclear magnetic resonance
NP	Nanoparticle

List of Abbreviations

Ph	Phenyl
Ppm	Parts per million
PP	Polypropylene copolymer with ethylene as co-monomer
Q	Quartet
R	Alkyl
RT	Room temperature
S	Singlet
sat.	Saturated
SEM	Scanning electron microscopy
S.D.	Standard deviation
T	Triplet
T _g	Glass transition temperature
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
TLC	Thin layer chromatography
Triton	Triton X-100
UHV	Ultra-high vacuum
UV	Ultra-violet
$\nu_{\max}$	Infrared wavenumber adsorption
w/w	Weight/weight
Wt. %	Weight percentage addition
XPS	X-ray photoelectron spectroscopy

1. Introduction

1.1. General Introduction to Polymer Nanocomposites

Nanocomposites exploit the unique properties of both nanomaterials and polymers, and are emerging as an important class of multifunctional materials with superior electrical,¹ thermal,² mechanical,³ optical,⁴ antibacterial,⁵ gas barrier⁶ and fire retardancy⁷ functionalities. Consequently, they exhibit substantial potential for cheaper, lighter and stronger advanced materials and as such are already in commercial use in the aerospace, marine coating, automobile and construction industries and are expected to become dominant in the engineering sector. Nanocomposites therefore promises to, and to a certain extent already have, become a feature of our everyday lives.⁸⁻¹⁰

Recent innovations in nanomaterial science has meant that traditional micron size filler particles in composites have been replaced by advanced fibres and particles at the nanomeric scale, dramatically enhancing the properties which can be introduced at low weight additions to the polymer matrix. Accordingly, the formal definition of a nanocomposite is that it is a multiphase material, in which at least one phase is at the nano-scale. The material can be ceramic, metal or a polymer, the subject of this work.¹¹

In the early 1990s, the first polymer nanocomposite was developed using nylon 6 reinforced with the layer silicate montmorillonite,¹² stimulating a surge in research and commercial investment into these types of clay polymer nanocomposites using layered silicates but also clay nanoparticles, such as silica and alumina. The development of materials ensued with increased mechanical performance, as well as important thermal and barrier properties.^{13, 14} Whilst for elastomers (rubber), reinforcing clay fillers have proved less effective, and rather Carbon Black (CB) as an additive is widely used. In fact, the discovery of the reinforcing ability of CB to natural rubber has shaped the automotive industry, imparting major improvements to the modulus, tear strength and ultimately the

service life of tyres.^{15, 16} More recently, fibrous carbon-based nanofillers (Carbon Nanotubes and Carbon Fibre) or inorganic nanowires have been used to improve the mechanical properties of polymers.^{17, 18}

These mechanical property enhancements are achieved because of the direct reinforcing properties the selected rigid or fibrous filler can impart to the polymer matrix, due to their specific modulus, size and shape. Equally, other properties (gas barrier, flammability and others) can be introduced to the polymer according to the innate properties of the selected nanofiller. However, the mechanical properties can also be indirectly improved, because the distribution of a nanofiller into the polymer matrix can alter the crystallisation behaviour and the ultimate morphology of the material. The success of this is determined by the strength of the filler-filler and filler-polymer interactions.¹⁹

Increasingly electrical conductive properties are also being demanded from conventional polymers, which are typically insulating materials, to vastly broaden their application in engineering and advanced technologies. This can be realised through the addition of conducting nanofillers (carbon-based or metallic powders and fibres) to polymers.²⁰ Depending on the magnitude of the conductivity, in accordance with the properties and quantity of the nanofiller, semi-conductive or conductive nanocomposites can be used for numerous applications (Figure 1.1). Examples include for anti-static, dissipation of electrostatic discharge (ESD), electromagnetic or radio frequency interference (EMI/RFI) shielding applications. Further, conductive plastics demonstrate potential for use in the production of fuel cells, batteries, capacitors and sensors, amongst other devices in the electronic industries.²¹

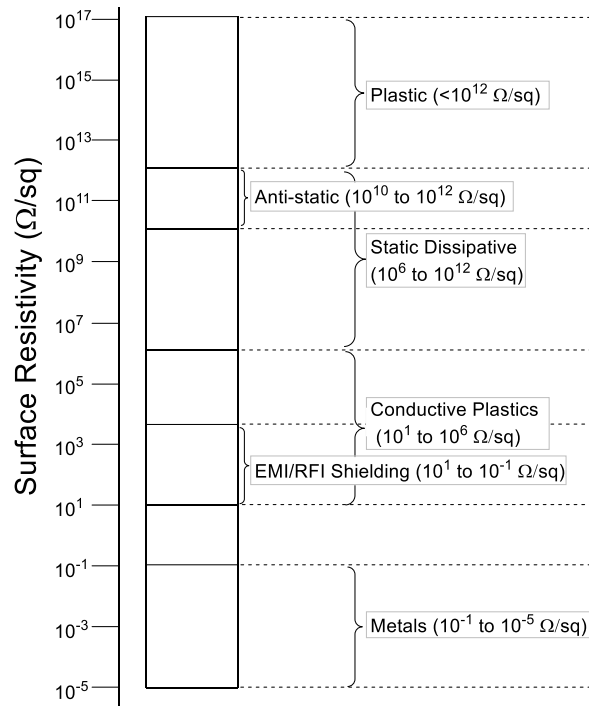


Figure 1.1: Potential applications of electrically conductive polymer nanocomposites according to their surface resistivity. Adapted with permission from John Wiley and Sons © 2013.²²

1.1.1. Key Challenges

The application of this promising technology is however compromised by the tendency of nanomaterials to agglomerate and disperse poorly in the polymer matrix. As a result, large filler additions are required to achieve the desired properties, for example for highly conductive polymer nanocomposites, further augmenting agglomeration in the system as a consequence. Significantly, this negates the unique nano-scale attributes of the nanofillers, and in some cases nanofiller agglomeration can impair the innate mechanical properties of the original polymer.²³ Agglomeration in polymer nanocomposites is governed by attractive interactions between the nanofillers, for example Van der Waals interactions or hydrogen bonding. Importantly, these interactions are more influential as the nanofiller size decreases, concomitant with the increasing surface areas. Further, agglomeration can often be further promoted by poor compatibility between the filler and the polymer matrix.

Similarly, for a nanofiller to impart its intrinsic reinforcement, amongst other properties, to the polymer matrix, strong interfacial interactions are required between the two components. In more detail, the interface defines in two-dimensional terms the boundary between the different chemistry and/or microstructure between the nanoparticle and polymer matrix. However, chemical interactions between the nanofiller and the polymer chains, which are of similar sizes, mean there is a three-dimensional region where the polymer chains surrounding the nanofiller have a different mobility to polymer chains in the bulk polymer matrix.²⁴ This new polymer phase is therefore referred to as the ‘bounded polymer layer’ or the interphase. The properties and thickness of the bounded polymer layer will have a significant impact upon the properties of the eventual polymer nanocomposite material.^{25, 26} The presence of this interfacial region mean that there is a gradual change between the properties between the two components, rather than a sharp change, as would be introduced by a direct interface. Importantly, an effective interfacial region in polymer nanocomposites is also dependent upon the degree of the nanofiller agglomeration in the polymer matrix, both of which will dictate the polymer nanocomposite properties.²⁴

The agglomeration and interfacial region, and therefore the global properties, of polymer nanocomposites are largely influenced by the fabrication method as well as the properties and level of compatibility of the selected nanomaterial and polymer. With some success, efforts have been made to optimise these parameters in the pursuit of producing polymer nanocomposites with low loadings of dispersed nanofillers. However, functionalisation of the components or the addition of additives has been more widely employed as the method to control the agglomeration and improve the interfacial region in polymer nanocomposite technology.²⁷ Accordingly, this introduction aims to broadly present the general important parameters that govern polymer nanocomposite properties, and to

describe the general functionalisation approaches used in an effort to confront this challenge.

1.2. Fabrication of Polymer Nanocomposites

First, the method used to prepare the nanocomposite will directly influence the dispersion and distribution of the nanomaterial in the polymer matrix, influencing the interfacial interactions between the components. Typically, nanocomposites are prepared by melt compounding and solvent blending (methods used in this work) as well as *in situ* polymerisation methods. Additional steps including sonication, micro-bead milling and ball milling are often also used to aid the separation of the nanomaterials as they are mixed with the polymer during processing.²⁸⁻³⁰

1.2.1. Solvent Mixing

Generally, the solvent mixing or solvent blending method entails the dissolution of the polymer in a selected solvent, combination with the nanofiller, also dispersed in the same or a different solvent, before drying to produce the polymer nanocomposite as a thin film or powder.²² The low viscosity of the polymer solution often means good nanofiller dispersion can be more easily achieved by this method, compared to others.³¹ However, the addition of a sonication step is often also employed to further inhibit nanofiller agglomeration.³²

1.2.2. Melt Mixing

Melt mixing or melt compounding is generally the preferred method for nanocomposite research due to its relative simplicity, low cost and viability in the polymer industry. In this method, the nanofiller can be dispersed in the polymer matrix at high temperatures by a number of methods including mechanical and shear mixing, extrusion and injection or blow moulding techniques.^{27, 33} However, compared to solution mixing, nanofiller

dispersion is generally less effective and high sheer mixing has been shown to damage nanofillers, reducing their aspect ratio and likewise, the properties of the resulting polymer nanocomposite. Additionally, preparation of high filler additions can be challenging, demanding longer processing time as the viscosity of the sample increases.³⁰

1.3. Polymers

1.3.1. Background

Polymeric materials have substituted many natural materials due to their economic practicality, easy fabrication and processability, low density, and exceptional durability – which stems from their high chemical resistance to corrosion, solvents and moisture exposure. As a result, application of polymers in construction, domestic appliances, textiles, medical devices and packaging are vast, amongst other important technical and engineering applications, forming a ubiquitous role in our everyday lives. Nonetheless, these exemplary materials do possess disadvantages, such as poor mechanical strength, a relatively short lifespan and poor thermal stability. Therefore, the opportunity to improve these properties, and introduce new ones (such as electrical conductivity), by the addition of nanofillers presents a strategy to further advance these materials.³⁴ The chemistry of the selected polymer chosen for nanocomposite preparation, including its type, polarity, degree of crystallinity and viscosity, all contribute to the control of the overall properties.³⁵ Therefore, this section aims to briefly introduce the different types of polymeric materials and general definitions, as well as present detailed information on Polypropylene (PP), the selected polymer for the nanocomposites in this work.

1.3.2. Types

Polymers are macromolecules formed by the linking of several small molecules (monomers) by polymerisation processes. Synthetic polymers are usually prepared by

condensation and addition polymerisation reactions and generally classified into three main types, namely fibres, plastics and elastomers. The strength or flexibility of polymeric materials are determined but the structure (linear, branched, network) associated with the species present in the polymer backbones chains (for example aromatic rings, double or single bonds). Further they are broadly classified according to whether they are a thermoset or thermoplastic. Thermosets, are cured irreversibly, generally as a result of cross-linking, into the desired shape during heating at the end of processing. Thermoplastics on the other hand, can be remoulded and shaped in the melt after initial processing, although reprocessing can degrade the polymer and therefore stabilisers (antioxidants and/or heat stabilisers) are often added during initial processing to negate these effects.

Following this point, it is worth emphasising that in commercial production, polymers can often be regarded as complex mixtures comprised of macromolecules as well as a number of additives, in addition to the stabilisers mentioned for thermoplastics and fillers in the production of polymer composites. Examples of other common additives included in the manufacture are process aids, such as lubricants, and other modifiers, including pigments, blowing agents (for polymer foams), viscosity modifiers, mould release agents, antimicrobial additives and plasticisers. Additionally, polymers can be produced from different monomers, termed copolymers, combining the properties of prevalent polymers at set ratios for improved blended properties. For example, ethylene monomer can be selectively added into polypropylene in order to improve rheological, mechanical and optical properties. Different types exist according to the ordering of the monomer units: alternating copolymer, in which the monomer arrangement is completely regular (-ABABABAB-); block copolymers, linked sequences of sections of the homopolymer (-AAABBBBBBAA-); graft copolymer, which are branched block copolymers

(AAAAAAA-BBBBBBBB) and random copolymers, for which there are no set monomer arrangements (-ABBBAABABB-). Otherwise, polymers can also be combined in immiscible or miscible polymer blends, in accordance with the compatibility of the different polymers at the molecular level, to exhibit combined, modified properties.^{34, 36}

1.3.3. Polypropylene (PP)

The work in this thesis is concerned with the semi-crystalline, apolar thermoplastic polyolefin, polypropylene (PP) copolymer with ethylene as a co-monomer, prepared at approximately a 90:10 ratio between the two monomers, propylene and ethylene respectively. The main production method for polypropylene (PP) uses Ziegler-Natta and metallocene catalysis, first developed in 1957, not long after the commercialisation of polyethylene (PE) in 1939.³⁷ PP exhibits a good balance of polymer properties, as a chemically inert, non-toxic, recyclable polymer, and demonstrates moderate mechanical and thermal stability at a sensible cost and ease of processing.^{38, 39} For all these reasons, PP is already established as one of the most widely used commodity thermoplastics, in packaging, household items as well as for advanced engineering applications in the automotive sector and aviation.⁴⁰ As such, PP is an excellent candidate for nanocomposite research as there exists a huge potential to widen PP applications, especially in engineering.⁴¹ Additionally, the introduction of electrical conductivity properties has proven to be most successful in nonpolar, semi-crystalline polymers associated with the good dispersion of carbon-based nanofillers in these polymer types.²² Further, the addition of reinforcing nanofillers could be an attractive solution to some of the limiting properties of PP, namely its poor thermal and UV stability – the tertiary C-H group along the polymer backbone renders PP susceptible to free radical attack.³⁶ Another drawback is PP's low compressive strength and low resistance to crack propagation, mechanical properties that could both be enhanced by nanofiller addition.¹⁰

1.4. Nanomaterials

1.4.1. Background

The selection of the nanoparticle will dictate the functionality of the polymer nanocomposite, for example by the introduction of new or improved electrical, mechanical and thermal stability properties to the polymer matrix. Nonetheless the specific properties of the selected nanofiller, such as the specific surface chemistry, aspect ratio, surface area, porosity, and morphology will also contribute to the likelihood of the nanocomposite acquiring these desired properties.⁴²

There are a number types of nanomaterials, classified according to the number of dimensions exhibited outside the nano-scale range (>100 nm). For example, different carbon-based nanomaterials, Carbon Black, carbon nanotube (CNT) and graphene, are classified as 0D, 1D and 2D nanomaterials (Figure 1.2).

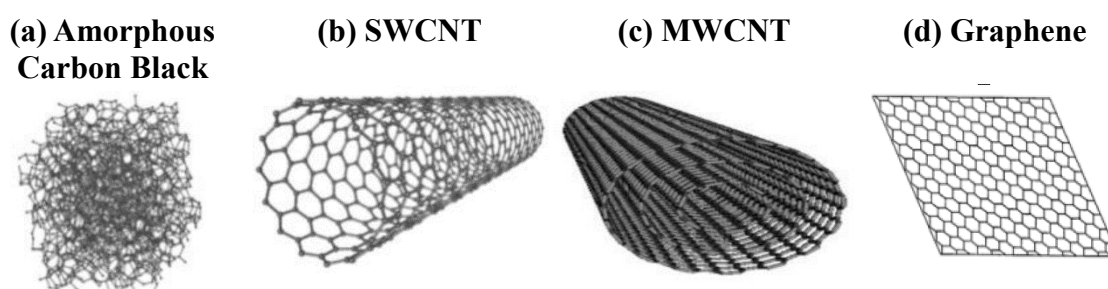


Figure 1.2: Carbon nanomaterials exist in many different forms including (a) 0D amorphous Carbon Black nanoparticles (b) 1D single-walled nanotubes (SWCNTs) (c) 1D multi-walled nanotubes (MWCNTs) and (d) 2D graphene. This figure was adapted from © 2015 Robert Săndulescu, Mihaela Tertiș, Cecilia Cristea and Ede Bodoki; originally published under CC BY 3.0 license. Available from:10.5772/60510.⁴³

As an overview, zero-dimensional (0D) nanomaterials are composed of a particle entirely at the nano-scale range (1-100 nm), and are commonly referred to as nanoparticles, or nanofillers in reference to nanoparticles used in polymer nanocomposites. Examples include inorganic nanomaterials (silica, CaCO_3 ⁴⁴), metals (Ag, Au), metal oxides (Al_2O_3 , ZnO, TiO_2), and carbon-based nanomaterials (CB). A one-dimensional (1D) nanomaterial has one physical dimension outside the nano-scale range and tends to have a needle-like

structure. 1D nanomaterials are classified according to four categories: nanotubes, nanowires, nanobelts and nanorods. Key examples of 1D nanomaterials in nanocomposites are carbon nanotubes (CNTs), which can be single-walled (SWCNT) or multi-walled (MWCNT), and carbon fibre (CF). Two-dimensional (2D) nanomaterials are plate-like shapes. They are composed of two dimensions that are not limited to the nanoscale range, and the main types include nanowalls, nanoprisms, nanodisks and nanosheets. Topical examples of 2D nanomaterials for nanocomposites are layered silicates⁴⁵ and graphene. Finally, three-dimensional nanomaterials (3D) are bulk nanomaterials which consist of nanocrystalline structures arranged at different orientations within three dimensions beyond the nanometric range, for example dispersions of nanoparticles (0D) or bundles of needle-like nanomaterials (1D).⁹ The work in this thesis focuses primarily on silica and carbon-based 0D nanoparticles as well as 1D carbon nanotubes.

1.4.2. Silica

Silica (SiO_2) is a highly versatile, chemically stable compound which exists in crystalline and amorphous forms both in nature as well as synthetically. As an integral feature to a number of technologies it is central to our everyday lives. For example, it is present in optical fibres, electronic microcircuits, glass, ceramics, food additives and catalysts in oil refineries.⁴⁶ Further, it is already a key component in a number of industrial products and materials including plastics, elastomers, concrete, insulation material, adhesives, paints and coatings. A key focus in nanocomposite technology is to extend to polymers the highly attractive qualities of silica – high rigidity, exceptional thermal stability and optical properties. As a result, materials with the potential of enhanced optical and mechanical properties, such as increased impact and tensile strength, can be produced.⁴⁷

The two classes of synthetically prepared amorphous silica are wet process silica (sol-gel and precipitate silica) and pyrogenic silica, also referred to as fumed and thermal silica.⁴⁸ The sol-gel process was first performed by the acidic gelation of sodium silicate (Na_2SiO_3) solution.⁴⁹ Later the Stöber method was established, in which the hydrolysis of tetraethyl orthosilicate (TEOS) using a basic solution of ammonium hydroxide in ethanol produced monodispersed amorphous silica at a range of sizes (200-1500 nm).⁵⁰ Further, smaller sized silica (25-80 nm) have also be produced by adapting the Stöber reaction to water-in-oil in microemulsion methods.^{51, 52} For the other type of wet silica, the treatment of silicates with mineral acids, followed by precipitation in alkaline conditions, produces colloidal silica often referred to as precipitate silica.⁵³ Alternatively, fumed silica powder, is produced by the vapour phase hydrolysis of silicon tetrachloride in an oxygen/hydrogen flame.⁵⁴ Fumed silica is attractive for nanocomposite applications and surface modification research, as it is produced as powder and its general high surface area and low porosity surface encourages good interactions in the polymer matrix.^{55, 56}

The basic properties of amorphous silica are largely governed by the production methods, by which the surface area, porosity, particle size, surface chemistry and purity are all determined. Nonetheless, common to all amorphous silica nanoparticles is the bulk unordered arrangement of the core SiO_4 tetrahedron units and the presence of siloxane (Si-O-Si) and various silanol groups ($-\text{Si-OH}$) surface groups (Figure 1.3).

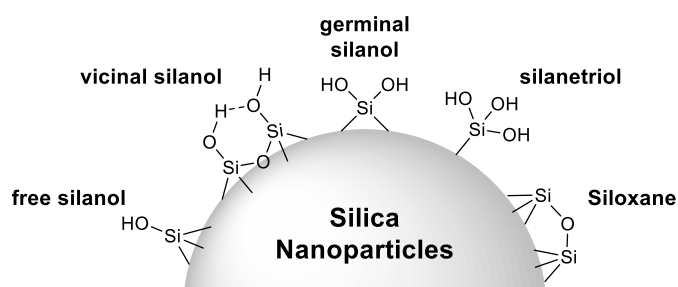


Figure 1.3: The surface chemistry of silica nanoparticles. The Figure is adapted from reference with permission Elsevier © 2000.⁵⁷

The most reactive surface groups are the isolated silanols, however if adjacent silanol groups are present, hydrogen bonding can result in the less reactive vicinal silanol surface groups. Additionally, silanediol or germinal silanol, and more rarely silanetriols, can be found at the surface. The concentration and distribution of these functional group will vary however, altering the hydrophilicity, with important consequences as fillers for nanocomposites.^{57, 47} This is largely because silica has a tendency to agglomerate as a result of the strong hydrogen bonding interactions between the polar siloxane and free silanol surface groups on adjacent silica aggregates. Therefore, in nanocomposites these interactions can dominate if the compatibility is poor between the silica and polymer, especially in the case of a non-polar polymers such as PP, unfortunately promoting poor filler dispersion.⁵⁸

1.4.3. Carbon-Based Nanomaterials

Carbon-based nanomaterials have dominated nanocomposite material research as reinforcement, electrical and thermal conductive fillers, amongst which, Carbon Black (CB), carbon nanofibers (CF), carbon nanotubes (CNTs) and graphene have attracted the most attention.²² Carbon Black (CB) has been selected in this thesis as the principal nanomaterial in the pursuit of conductive PP nanocomposites. It is already mass-produced and importantly it is also a relatively inexpensive conductive carbon nanofiller compared to other types. However, some work has also focused on CNTs due to the high amount of research effort worldwide which has invested into this high quality and especially promising nanocarbon.

1.4.3.1. Carbon Black (CB)

CB has been used in a variety of applications and is indeed has an established history, traditionally used as a pigment in inks and paints. More recently, it has been widely used as reinforcement in the rubber industry, a breakthrough in the automotive industry in

dramatically enhancing the service life of tyres.¹⁶ Today, CB is still used in tyres, inks, paints and coatings as well as in plastics to impart electrical conductivity, for reinforcement or as a stabiliser against degradation from UV radiation.²²

CB is a particulate form of carbon which as a nanofiller for polymer nanocomposites has exhibited electrical conductivity in the region of $\sim 10^2 \text{ Scm}^{-1}$.²² There are a number of types of CB, depending on the production method used: Furnace Black, Thermal Black, Acetylene Black, Lampblack and Channel Black. The manufacture method comprises of the thermal decomposition or incomplete combustion of liquid or gaseous hydrocarbon compounds before cooling by water and any further processing. The production method largely dictates the CB properties, including the surface area, specific surface chemistry, porosity, aspect ratio and morphology (structure type). The quality of CB according to each of these parameters is important because as a nanofiller they will influence the polymer nanocomposite properties.

The most common CB type is Furnace Black, which is manufactured by the incomplete combustion of hydrocarbons. It is prepared in a continuous process in a closed system, first by the pre-heating of heavy aromatic oils (coal tar or crude oil), termed the feedstock, at controlled temperature (200-250 °C) and pressure conditions. Next, a hot gas stream (usually natural gas) is introduced to the reactor, or 'furnace', the feedstock is vaporised followed by partial pyrolysis, and elemental carbon is formed. Steam or water spays are used to control and quench the reaction, and from the reactor the CB cools as it flows through heat exchangers before collection into bags or for further processing, such as granulation to increase the bulk density.¹⁶ Lampblack is also produced by an incomplete combustion process but uses oil or pine wood as the feedstock, in a process unsuitable for mass production. Channel Black, formerly the main production process before Furnace Black, but is now more or less obsolete, used natural gas as the feedstock

and following contact with Channel Steel at elevated temperatures produced CB in an open system. Alternatively, Thermal Black and Acetylene Black, using natural gas and acetylene gas respectively as the feedstock, are manufactured in closed systems by thermal decomposition processes. For these Carbon Black types, the feedstocks are added to the reactor, in the absence of air, where they thermally decompose into carbon and hydrogen before cooling by water sprays to produce the CB product.^{16, 22, 36, 59}

The primary particle is the smallest unit of CB, typically (5-100 nm). The size, shape, graphitic content and crystallinity determine the colour, conductivity and UV protection performance properties of the CB. Generally CB primary particles are spherical,⁶⁰ however the size is variable, and importantly directs the specific surface area, which can range from 10 m²/g to 200 m²/g for CB.⁵⁸ The surface area is a critical component of a nanofiller in polymer nanocomposites. The larger the surface area, the greater the filler-polymer interfacial region present in the polymer nanocomposite, permitting greater compatibility between the two components. A large surface area of a nanofiller can therefore assist the effective translation of the filler properties to the polymer matrix. Commenting further on the surface chemistry, CB has an amorphous structure with graphitic regions similar to graphite. This paracrystalline nature of CB means it has a morphological roughness, but also an inhomogenous energetic surface, structural features which can also affect polymer-filler interactions.⁵⁸ Additionally, dependent on the manufacture process and the quality of the feedstock used, hydrogen and oxygen groups can decorate the surface of CB at the edges of the graphitic basal planes of the crystallites. These functional groups range from carboxylic to hydroxyl groups as well as carbonyls, ketones, lactones, phenols, quinones and pyrones, amongst others, as demonstrated in Figure 1.4.⁶¹

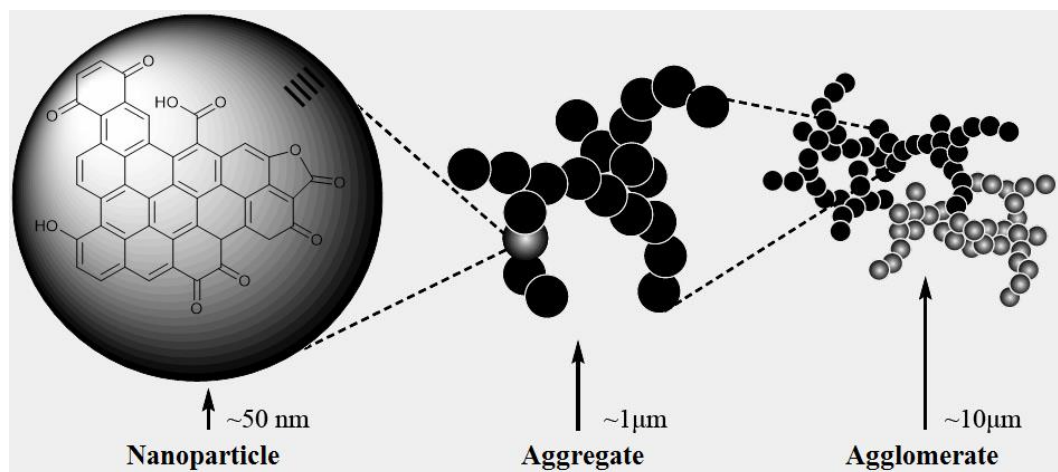


Figure 1.4: Schematic drawing of a Carbon Black nanoparticle and the aggregate and agglomerate formation. This figure was adapted from © 2013 Malin Liu; originally published under CC BY 3.0 license. Available from:10.5772/55651.⁶² The surface chemistry on the CB nanoparticle was adapted with permission from Elsevier © 2002.⁶¹

Figure 1.4 also exhibits another important property of CB, especially with regards to nanocomposite technology, which is the ‘structure’ of the CB. This term describes the defined units of fused primary CB nanoparticles, which can vary in size and shape, as well as the number of particles present. Their irreversible formation is controlled by the manufacturing process. The CB structure type can be described in terms of the void volume between aggregates, in which ‘low structure’ represents CB aggregates with a small number of primary particles and a linear or compact type structure, and therefore a low void volume. Alternately, ‘high structure’ denotes CB aggregates with a larger number of primary particles and displays a large degree of branching, which is porous as a result, exhibiting high void volumes. The ‘high structure’ form of CB is often described as grape-like bundles. Attractive Van der Waals interactions between aggregates also promotes the formation of CB super-agglomerates (1-40 μm), but unlike CB aggregates, these can be broken down by shear force or sonication.⁵⁸ In terms of polymer nanocomposites, it is the presence of CB aggregates in polymer matrices which enables electrical conductivity at lower loadings than are otherwise predicted for a system with separate primary spherical particles.⁶³ Further, smaller, high structure aggregates have

been shown to be the best types for CB conductive fillers.¹⁶ However, poor compatibility of CB with polymer matrices often promotes further CB agglomeration, in addition to the attractive CB-CB interactions already present. Unfortunately, this is unfavorable for high performance nanocomposites, as first high filler loadings are required to achieve electrical conductivity in the polymer nanocomposite and second, a high degree of agglomeration can compromise the intrinsic high performance mechanical and processability properties of the polymer²³

1.4.3.2. Carbon Nanotubes (CNTs)

Following their discovery by Iijima in 1991,⁶⁴ an extensive research effort has explored the use of CNTs as fillers for high performance polymer nanocomposites due to their superior electronic, structural, mechanical and thermal properties.⁶⁵ CNTs are 1D nanomaterials, hollow cylindrical tubes composed of a single or multiple layers of graphene sheets, in the case of single-walled or multi-walled CNTs (Figure 1.2). Unfortunately, one major drawback for this extraordinary nanomaterial is still the challenge of large-scale production of high quality, well defined CNTs at low cost. The most common production method is by Chemical Vapor Deposition (CVD), in which CNTs are grown in the presence of metal catalysts after the thermal decomposition of hydrocarbon vapor at high temperatures (~600-1200 °C). Similar to CB, the properties of the CNTs, such as the diameter, length and quality, can be directed by the production methods in relation to the selected hydrocarbon vapor, catalyst and temperature amongst other parameters.⁶⁶ High-pressure carbon monoxide (HiPCO)⁶⁷ is one example, in which the CO is used as the carbon source for the production of nanotubes with particularly small diameters.⁶⁸ Additionally, the two other major synthetic methods in use are arc discharge⁶⁹ and laser ablation.⁷⁰ The extraordinary properties of CNTs, associated with their high aspect ratio, mean that at extremely low filler additions, compared to other

nanomaterials, their properties can be effectively translated to polymer matrices.^{22, 71}. However, similar to CB, the promise of CNTs as a nanofiller is unfortunately undermined by their tendency to exist in bundles due to strong Van der Waals intermolecular forces. This is particularly significant for CNTs due to their anisotropic 1D structure and high surface areas.⁷²

1.5. Functionalisation

As detailed in the sections above, the properties of the selected nanomaterial and polymer, their synergy, and the processing methods and conditions used to produce the nanocomposite will all contribute to its eventual properties. Accordingly, many studies have been devoted to investigating and optimising these parameters. Ultimately, however good filler dispersion and distribution in polymer matrices remains the principal challenge in nanocomposite technology in order to achieve properties concomitant with theoretical predictions. Functionalisation has therefore been employed as the principal strategy to improve nanofiller dispersion by enhancing the filler-matrix interfacial interactions through the inhibition of unfavourable agglomeration.²⁷ Consequently, functionalisation approaches have been developed, principally for nanofillers, by both covalent or non-covalent methods. For example different methods investigated to modify CNTs can be seen in Figure 1.5.⁶⁸

In response to the challenge for polymer nanocomposites, posed by poor nanomaterial dispersion, this thesis aims to investigate covalent and non-covalent methods to functionalise nanofillers. The generalities of each functionalisation approach are broadly described in this section.

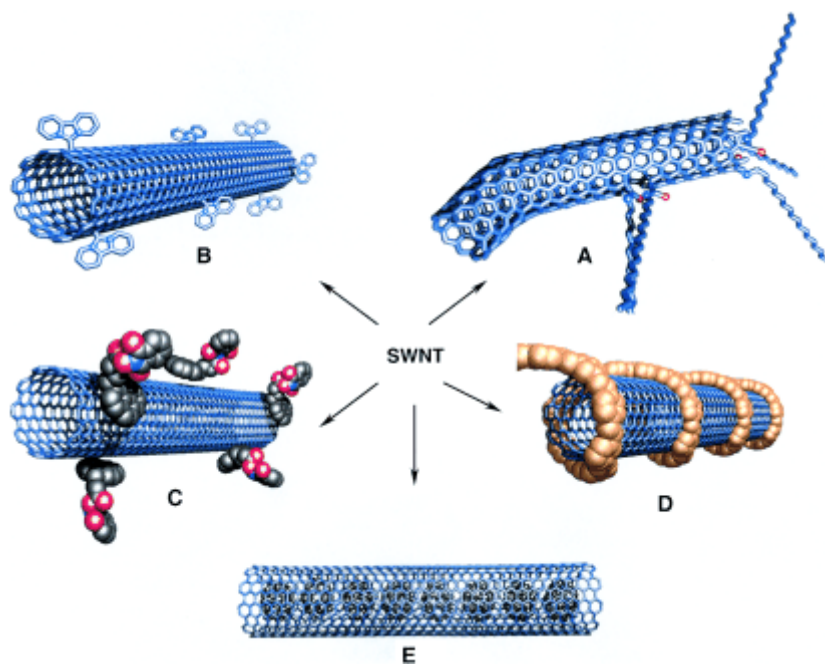


Figure 1.5: A schematic displaying examples of different functionalisation possibilities for SWCNTs by (a) defect group (b) sidewall covalent (c) surfactants (d) polymer and (e) endohedral functionalisation approaches. Adapted with permission from John Wiley and Sons © 2002.⁶⁸

1.5.1. Covalent Functionalisation

This method entails the modification of the surface of nanofillers by chemical methods using modifier agents or polymer grafting. A common method for the modification of silica surfaces is by the covalent grafting of the free surface silanol groups using commercially available alkoxy silane or halosilane coupling reagents. Secondary modifications can then be performed to further derivatise the surface chemistry, for example using linker chemistry or Click reactions.⁷³ Additionally, polymerisation reactions to the pre-modified silica surface has been widely investigated, typically characterised into two major methods, referred to as ‘grafting to’ and ‘grafting from’ approaches.⁷⁴ ‘Grafting to’ polymerisation refers to the addition of prepared polymers with reactive end-functionalised groups to the activated silica substrate, whereas ‘grafting from’ entails the addition of monomers which subsequently polymerise, initiated by the silica surface.⁷⁵ The latter approach tends to be preferred, as the ‘grafting to’ often delivers a low graft density to the silica substrate as dictated by the steric hindrance of the

pre-made macromolecules.^{76, 77} However, routes to surface modify silica at low loading additions are also being pursued in order to achieve polymer nanocomposites with an optimal interfacial region, effective so as to reduce silica agglomeration and improve compatibility with the polymer, but equally the interfacial region should not be too large, as this can ‘dilute’ the transfer of the valuable rigid properties of the silica nanoparticles to the polymer matrix.⁷⁸

In terms of covalent modification methods commonly used for carbon-based nanoparticles, one of the standard approaches is to oxidise the surface by acid treatment ($\text{H}_2\text{SO}_4/\text{HNO}_3$) to generate functional groups ($-\text{COOH}$, $-\text{OH}$, $-\text{C}=\text{O}$) which can then be used in secondary reactions to further manipulate and derivatise the surface.⁷⁹ However, these harsh oxidising conditions are non-selective and can be destructive to the structure of the nanofillers.⁸⁰ In particular for CNTs, aggressive covalent functionalisation approaches such as these have been shown to dramatically reduce their valuable conductive properties.^{81, 82} This is because aggressive covalent side-wall functionalisation routes have been shown to introduce defects, inhibiting the long range π conjugation of the nanotubes and ultimately deteriorating the usual excellent intrinsic conductivity properties.⁸³ Therefore, milder approaches are being explored, for example the electron properties of CNTs have been shown to remain intact following cycloaddition reactions $[2 + 1]$ using carbenes⁸⁴ and nitrenes⁸⁵ and also following functionalisation with alkyl radicals.⁸⁶

In this context, the introduction of desired functionalities using diarylcarbene insertion reactions and the azo-coupling reactions of diazonium salts, represents a useful strategy for the surface modification of nanofillers and will be the covalent route assessed in this thesis. Previously, diarylcarbene derivatives, extensively developed in the Moloney group, have provided a direct, versatile method for the irreversible introduction of desired

functionality into materials. Examples include the surface modification of single-walled carbon nanotubes (SWCNTs),⁸⁷ fullerenes,⁸⁸ hydrogen-terminated diamond,⁸⁹ silica⁹⁰ as well as a comprehensive range of polymers.^{91, 92} This approach permits changes to the surface chemistry, which allows for the introduction of colour,⁹³ biocidal activity,⁹⁴ biocompatibility⁹⁵ as well as altered surface wettability.⁹⁶ Surface modification using diarylcarbenes is particularly promising, due to their high chemical stability, compared to other carbene species, and almost limitless functionality can be introduced to materials of low reactivity, at a relatively low cost and material requirement. The functionalisation approach, displayed in Figure 1.6, entails the thermolytic or photochemical decomposition of the diazo-precursor compound to the reactive carbene species. Subsequently, the substrate surface is irreversibly modified *via* C-C, X-H (X= O, N or S) insertion reactions and C=C addition reactions.⁹⁰ The functionality of the diaryldiazo precursor can be adapted, as shown in Figure 1.6, at the positions of the R groups before performing the modification reaction to the selected material surface.

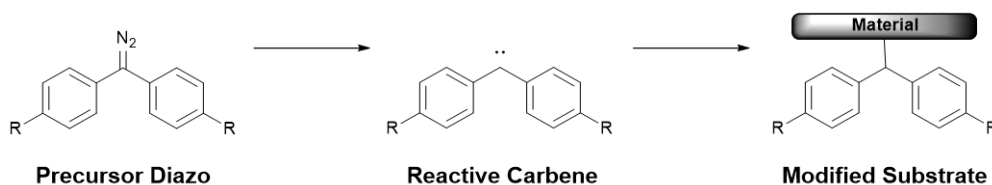


Figure 1.6: A schematic displaying the general method for the surface modification using diaryl carbene chemistry.

Further, diaryl carbene surface modification can be combined with a second step azo-coupling reactions with diazonium salts, in order to further manipulate a material's surface. Reaction with diazonium salts has also proved an effective route for the direct surface functionalisation of different nanofiller types.^{97, 98, 99}

1.5.2. Physical Functionalisation

Physical functionalisation, usually using surfactants or polymers, has been employed to both organic and inorganic nanofillers to construct nanocomposites with improved macroscopic properties.⁹ For example, polymers, such as polystyrene, have been used to modify CNTs by wrapping around the tubes as a result of the attractive Van der Waals interactions and π - π stacking interactions, which exist between the components (Figure 1.5(d)).^{100, 101} Likewise, Surfactants – amphiphilic compounds with both polar and apolar components – can absorb onto the surface of particles, (Figure 1.5(c)) promoting stable dispersions in aqueous and organic solutions. A major advantage of this broadly applicable functionalisation route is that it does not damage the structure of the nanofillers, especially important for nanofillers with higher aspect ratios, such as CNTs as discussed above. Further, physical modification generally requires simple procedures and many surfactants are also commercially produced.¹⁰² For these reasons, non-covalent nanofiller modification by surfactant adsorption will be the subject of the second part of the work in this thesis.

In aqueous media, the hydrophobic region of surfactants is typically referred to as the ‘tail’ group and the hydrophilic component the ‘head group’, whose charge denotes the surfactant type: cationic, anionic, zwitterionic or non-ionic.¹⁰³ Common commercially available surfactants that have been used for the adsorption of nanofillers include the cationic surfactants, cetyl trimethylammonium bromide (CTAB) and cetylpyridinium chloride (CPC), anionic surfactants, polystyrene sulfonic acid sodium salt (PSS) and sodium dodecyl sulfate (SDS), and the non-ionic surfactants, polyoxyethylene 8 lauryl ether and Triton X-100 (Figure 1.7).^{100, 104-106 107}

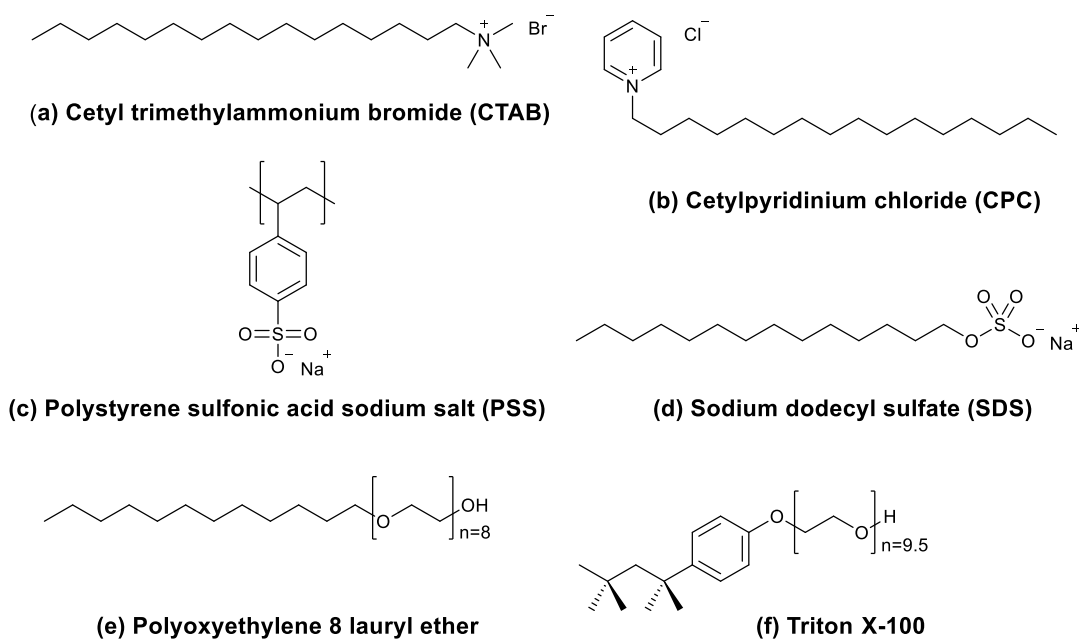


Figure 1.7: The chemical structures of commonly used surfactants for nanofiller modification.

The adsorption interaction between the nanoparticle and the surfactant is driven by the selected types as well as the media chosen for the dispersion. The uptake of ionic surfactants, for example, onto a charged particle surface in an aqueous solution is promoted by Coulombic attractions. Alternatively, the adsorption of non-ionic surfactants is driven by the hydrophobic/hydrophilic attractions between the surfactant and the particle, assisted by the solvent media in some cases.^{83, 103} This adsorption mechanism can be directed by the selection of the hydrophilic groups or chain lengths. For example, for carbon-based nanomaterials, an increased chain length, higher degree of branching, the presence of unsaturated carbon bonds or the inclusion of benzene rings have all been reported to demonstrate an improved degree of surface adsorption.^{108, 109} In viable systems, by these mechanisms the surfactant will adsorb onto the nanoparticle surface. Micellisation is expected to occur above the Critical Micelle Concentration (CMC), at which point the surfactants self-organise at the surface, and spontaneously in the solvent media.¹⁰³ As such, this simple modification approach has been extensively used to aid the stabilisation of colloidal dispersions of nanomaterials, in water and organic solvents,

relevant to a number of research areas including cosmetics, printing inks, paints, detergents, and the pharmaceutical industry.¹¹⁰ Improved compatibilisation between the components is achieved by the reduced surface tension at the interface. Further good nanofiller dispersion is also stabilised by electrostatic repulsive or steric effects between particles with the ionic or non-ionic surfactant modified surfaces respectively, inhibiting the attractive Van der Waals interactions which usually govern agglomerate formation.¹¹¹ The extent of the stability of the dispersion is dominated by the strength of the adsorption interaction accompanied by the degree of surface coverage, but also by the hydrodynamic thickness of the surfactant layer on the particle.¹¹¹ More recently a few studies have extended this dispersive approach using surfactant chemistry from colloidal dispersions in aqueous and organic media to polymeric solutions.^{108, 112, 113} Following some promising results as a dispersant for nanoparticles in non-polar organic solvents as well as in nanocomposite research, the non-ionic surfactant Triton X-100 (Figure 1.7(f)) was selected as the non-covalent modification candidate in this work.^{104, 109, 114}

1.6. Scope of this Thesis

The thesis aims to investigate functionalisation strategies for silica and carbon-based nanofillers in order to produce polypropylene nanocomposites with associated enhanced multifunctional properties.

Tailored methodologies by covalent and adsorption routes have been developed and optimised for the surface property control of selected nanomaterials. This is necessary to improve the interfacial interactions between the nanofillers and the polypropylene (PP) matrix in order to reduce agglomerate formation. Filler dispersion directly controls the extent to which nanocomposites can exploit the unique nanoparticle properties, and as a consequence determines the degree to which superior electrical, mechanical, thermal and optical properties can be translated into the system.

Accordingly, the Results and Discussion of this work has been divided into two sections: Part I (Chapters 3-5) describes covalent modification routes and the ensuing PP nanocomposites, and includes published work adapted with permission from the American Chemical Society © 2016.¹¹⁵ Part II (Chapters 6 and 7) investigates the non-covalent, physical adsorption nanofiller modification route, and the resultant PP nanocomposites.

Chapter 3 introduces carbene and diazonium coupling covalent routes for the introduction of a hydrophobic, nitrogen label functionality to the surface of silica and Carbon Black (CB). Extensive nanoparticle surface analysis methods, in particular using XPS, CHN, thermal analysis, SSNMR and ATR-IR techniques, were developed and used to provide evidence of the surface functionalisation and to estimate the degree of the surface loading.

Chapter 4 optimised the carbene technology to tailor the surface of a broader range of nanoparticles, namely nanosilica, microsilica, CB, acetylene black (ACB) and multi-walled nanotube (MWCNT), by the introduction diaryl units terminated in steric stabilising hydrocarbon chains of various lengths. Thermal analysis techniques were used to investigate the modification step and additional surface analysis, including XPS, SSNMR, ATR-IR and BET, were used to study the changed nanofiller surface chemistry.

Chapter 5 describes the production by solvent mixing methods of PP nanocomposites with the modified nanosilica, microsilica and CB nanoparticles, prepared and investigated in Chapter 4. The macroscopic properties were analysed in detail by thermal analysis, DC conductivity, dielectric analysis and morphological measurements in order to determine the altered electrical and mechanical properties as a result of the nano-scale modification.

Chapter 6 explored an alternative, simpler surface modification method for CB by the physisorption of the surfactant Triton X-100. The CB functionalisation protocol was optimised at several stages and the functionalised surface confirmed by thermal analysis,

XPS, BET, ATR-IR measurements, as well as by UV-Vis analysis of the supernatant solution extracted from the modification procedure. Triton X-100 modified CB/PP samples were prepared by solvent and melt mixing methods and extensive macroscopic property characterisation was employed to investigate the effect of the CB modification.

Chapter 7 further extends the Triton X-100 investigation for improved PP nanocomposite properties by the functionalisation of the higher quality ACB carbon-based nanoparticles, combining the modification protocol with a granulation procedure typically used in the manufacture of Carbon Blacks.

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2. Experimental: Theory and Techniques

The complementary use of a number of characterisation techniques were required to produce the modified polypropylene nanocomposites in this work. Each project consisted of four main steps to achieve this:

1. Nanoparticle functionalisation;
2. Characterisation of the nanoparticles;
3. In house preparation methods of the solvent and melt-mixed PP nanocomposites;
4. Evaluation of the resulting nanocomposite properties.

For step 1, the modification procedures of the nanoparticles are discussed in detail in the appropriate sections of the thesis, Chapters 3, 4 and 6, and additional preparation conditions and compound characterisation of the organic compounds is included in the Appendix-Organic Experimental. Following the functionalisation procedures, the nanomaterials were characterised (Step 2) using a selection of procedures listed below:

- X-ray photoelectron spectroscopy (XPS);
- Simultaneous thermal analysis (STA);
- Solid-state nuclear magnetic resonance (SSNMR);
- Combustion analysis (CHN);
- Brunauer-Emmett-Teller (BET) surface area analysis;
- Attenuated total reflectance-infrared spectroscopy (ATR-IR);
- Ultraviolet-visible spectroscopy (UV-Vis);
- Transmission electron microscopy (TEM);
- Scanning electron microscopy (SEM).

In Step 3 the nanocomposites were prepared by solvent and melt mixing nanocomposite procedures using developed, set protocols according to the selected nanomaterial. As required for certain analysis methods, the nanocomposite samples were then processed, into compression moulded plaques ($1 \times 1 \times \sim 0.1 \text{ cm}^3$) and films ($D = 26 \text{ mm}$) of variable

thicknesses (15-500 μm). The specifics of these procedures have been included in the appropriate sections of the thesis (Chapters 5, 6 and 7).

Finally, in Step 4, the prepared nanocomposites were characterised by an assortment of: TEM, SEM and STA, volume electrical conductivity measurements, dielectric analysis and dynamic mechanical analysis (DMA).

Accordingly, this chapter aims to present the general background theory and experimental methods of the main techniques employed to characterise the nanofillers and nanocomposites prepared in this thesis.

2.1. X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is an excellent surface analysis technique used to reveal the chemical and electronic state of elements and the chemical composition at the surface of a material.

2.1.1. Background Theory

This technique analyses the surface using X-ray photoemission processes to liberate low-energy electrons ($\sim 20\text{-}2000$ eV), whose detected emission and energy presents a ‘fingerprint’ that can be used to identify the chemical nature of the material. The usual set-up includes the sample, a source of ‘soft X-rays’ radiation (often $\text{AlK}\alpha$ (1253.6 eV) or $\text{MgK}\alpha$ (1486.7 eV) and an electron energy analyser. These are all encased in an ultra-high vacuum (UHV) chamber.¹ The underlying process in XPS is the photoelectric effect, first observed by Heinrich Hertz,² and later explained by Albert Einstein.³ The photoelectric effect describes the transfer of the energy of photons ($h\nu$), which results in the emissions of electrons, referred to as photoelectrons, from a material. Accordingly, in XPS, the core level electrons, photoionized by the X-rays at the surface of the sample are subsequently emitted as photoelectrons and detected (see Figure 2.1(a)).

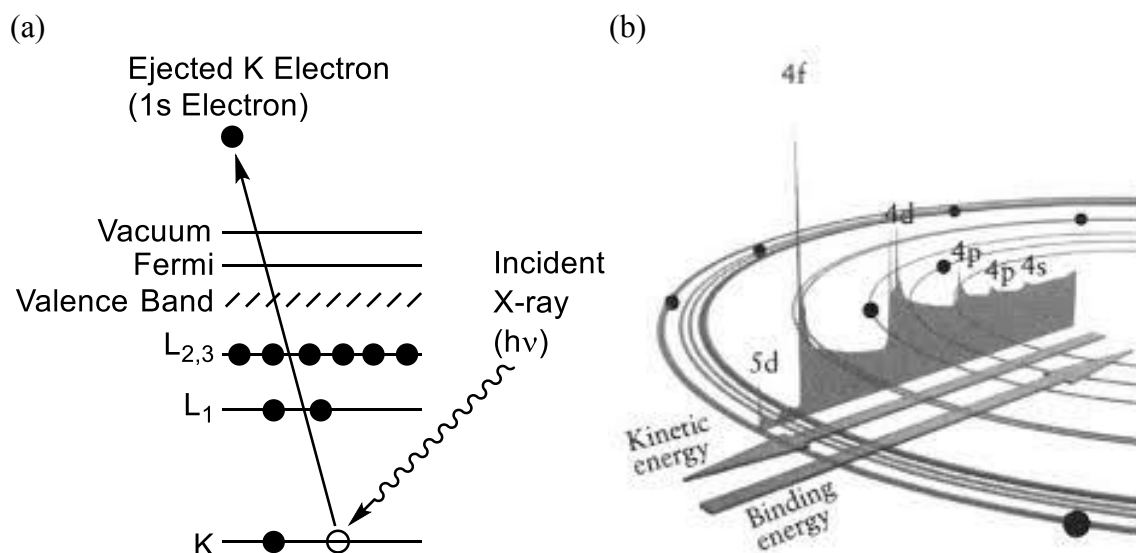


Figure 2.1: Diagrams of the XPS processes displaying (a) the X-ray excitation of a 1s shell electron and (b) the ejection of electrons from different orbitals in the electronic structure, contributing to the discrete peaks or background noise of the output photo electron spectrum. Used with permission from John Wiley and Sons © 2005.¹

Accordingly, the output photoelectron spectrum (Figure 2.1(b)) displays the photoelectron energy distribution (number of detected electrons ‘N(E)’ as a function of their kinetic energy. The detected kinetic energy of the photoelectrons is dependent upon the photon energy of the instrument used. However, the kinetic energy can be related to the more useful intrinsic property that identifies the element and atomic energy level, the binding energy (E_B) calculated *via* the following equation:

$$E_B = h\nu - E_k - \phi \quad (\text{Equation 2.1})$$

where E_B is the binding energy of the core level of the emitted photoelectron (with respect to Fermi level), $h\nu$ is the photon energy, E_k is the kinetic energy and ϕ is the spectrometer work function, the energy required to expel the photoelectron from the Fermi level into the vacuum.

For a photoelectron to be ejected from the sample it must first have a binding energy and work function below that of the photon energy. Secondly, for the excited photoelectron to be successfully detected and characterised, it must be ejected without energy loss. Some of the excited photoelectrons, however, cannot be characterised, either because they never

reach the surface or the excited photoelectron reaches the detector, but has lost some energy in the process. This latter case is called inelastic scattering and contributes to the background noise of the spectrum. Therefore, although the X-rays can penetrate the surface by some degree ($\sim 1\ \mu\text{m}$), XPS is regarded a surface sensitive technique, as the emission of photoelectrons without energy loss can generally only happen close to the surface ($< 1\ \text{nm}$).¹

2.1.2. XPS Quantification

The XPS analysis in this thesis comprised of the surface characterisation of the unmodified and modified nanofillers. A number of spectral features can be observed by XPS analysis; however, only the ones relevant to the sample analysis performed for this thesis, have been include in detail here.

The XPS spectrum is obtained by first measuring a survey scan (or wide scan) of the sample, in which the binding energy ($\sim 0\text{--}1200\ \text{eV}$) is plotted against measured intensity (usually counts per second). The binding energy is element specific and therefore the identity of the main elements present in the sample is determined by the binding energies of the high intensity peaks in the photoelectron spectrum (as displayed in Figure 2.1(b)). High resolution scans are then performed at specified binding energies for the detected elements of interest. High resolution scans permit the evaluation of small shifts, namely chemical shifts, compared to the expected elemental core level binding energy. These binding energy shifts can originate from initial-state effects, namely due to the surrounding chemical environment. For example, elements of higher oxidation states, a high number of substituent chemical groups and the presence of electronegative neighbouring atoms all contribute to a chemical shift to a higher binding energy. Binding energies can also shift as a result of final-state effects that follow photoelectron emission. For example, the polarisation of surrounding ions and relaxation of the electron orbitals

will affect also contribute to the observed chemical shifts. Next, the elemental peaks in the high resolution XPS spectra are deconvolved (peaks fitted) according to the observed chemical shifts, standard binding energies of which are widely referenced.⁴

Shake-up satellites are another feature common to aromatic organic samples (and are observed in the C 1s spectra of the carbon-based nanofillers in this thesis). These peaks occur due to collisions between an outgoing photoelectron and a valence electron, which is as a result excited to a higher-energy level. In the case of C 1s spectra of an aromatic sample (such as carbon-based nanofillers) this process occurs between the bonding and anti-bonding transition of the π molecular orbital (π - π^* transition). This results in a reduction of the emitted core photoelectron's detected kinetic energy, which is manifested in the spectrum as a satellite structure at reduced intensity to the main C 1s peak.

The relative peak areas of the detected and fitted, elemental and chemical states is dependent upon several factors. These include the concentration of the detected species, the photoemission-cross section (probability of photoemission occurring for the individual core level), the inelastic mean free path ((IMFP) electron attenuation length) and the instrument response (the ability of the spectrometer to detect the emitted photoelectrons as a function of kinetic energy). Accordingly, the following expression describes the intensity (I) of a photoelectron peak:

$$I = J\rho\sigma K\lambda \quad \text{(Equation 2.2)}$$

where J is the photon flux, ρ is the concentration of the detected species, σ is the photoemission cross-section, K represents the instrumental response and λ is the IMFP.⁵ However, this expression is generally simplified using sensitivity factors (F) which are experimentally determined and take into account the σ , K and λ factors of the expression, in addition to some other characteristic features of the analysis. Tabulated sensitivity values can be found in the literature.⁶ Accordingly, the sensitivity factor and the

calculated peak intensity – determined by integrating the peak area after subtraction of the selected background (linear, shirely, step) – can be used to calculate the relative concentrations of the peaks of interest by the following expression:

$$[A] = \{(I_A/F_A)/\Sigma(I/F)\} \times 100 \quad (\text{Equation 2.3})$$

where $[A]$ is the atomic % of A present in the sample, I_A the intensity of the peak of A , F_A is the sensitivity factor of A and $\Sigma(I/F)$ is the sum of all the detected peak intensities divided by the relevant sensitivity factors. The assumptions of this calculation includes, the expectation that the X-ray flux will remain constant during the sample analysis, as well as the homogeneous composition of the analysed sample within the sampling depth of the XPS. This second assumption is rarely achieved, although this is the most regularly used method for the comparison of similar samples.⁷

2.1.3. Experimental

XPS samples were prepared in a pellet press, and affixed to the sample stub using double-sided carbon tape. Analysis was performed using a VG – Escalab X-Ray Photoelectron Spectrometer VGX900 using Al K α radiation with an energy of 1486.6 eV at an operating pressure $<1 \times 10^{-8}$ mBar. The Pass Energy was set at 50 eV for the wide scan of the sample, and 20 eV for high resolution scans of specific areas; C 1s, N 1s, O 1s and Si 2p. Casa XPS peak fitting software was used to analyse the XPS spectra and a reference charge correction of 284.5 eV for C 1s applied. The error of the binding energies of the devolved peaks is included in the discussion for each set of analysed samples. The area under the elemental peaks and standard sensitivity factors (C, 1; O, 2.93; N, 1.8; Si, 0.817)^{6, 8} were used to calculate relative percentage elemental abundance within the surface and near-surface sampling depth of the XPS.

2.2. Simultaneous Thermal Analysis

Thermal analysis was extensively performed on the nanofillers and PP nanocomposites in this thesis, in which a range of properties (weight loss, heat flow and moduli) were assessed as a function of temperature. For the nanomaterial analysis this meant the decomposition/evaporation temperatures of the surface functionalisations could be established as well as inspection of the colour changes to the samples following heating. Furthermore, the weight loss data (TGA) was used to determine the degree of the functionalisation loading. In this work, the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured using a simultaneous thermal analyser (STA), which could concurrently measure the weight changes and thermal effects of the sample in the thermobalance. The two thermal analysis techniques, DSC and TGA, are presented in more detail below.

2.2.1. Dynamic Scanning Calorimetry

DSC measures the energy transferred as heat to or from a sample (ΔP) as it is heated, cooled or kept in isothermal conditions as a result of a chemical or physical transformation. The measurement generates a heat flow (mW) signal as a function of temperature ($^{\circ}\text{C}$) or time. The two categories of DSC include power-compensation DSC and heat-flux DSC. The former has the sample and reference (typically an empty pan) in separate, small, identical furnaces and both are subjected to a pre-set thermal program. Then, during a thermal transition power compensation is supplied to the required furnace to maintain the set program rate and the change in heat flow (ΔP) is directly measured in mW or J/s. The thermograms produced by this technique are typically presented endo-up. Alternatively, heat-flux DSC, involves the use of a single furnace for both the sample and the reference pans. In this set-up, the temperature difference (Δt) created between the two samples is measured during the pre-set program. This produces a differential thermal analysis (DTA) signal (in $^{\circ}\text{C}$), which can be converted to power (ΔP) by a calibrated

instrument, permitting calculation of the enthalpies.⁹ Typically for this instrument type the thermograms will be represented as endo-down, this convention has been applied in this thesis as the STA used has a single furnace design.

A number of specific experimental conditions can be selected in the instrument set up, for example the selected pan type, scan rates and purge gas, all influence the DSC results. Pan types for DSC are available in a vast range of pan sizes, material types (alumina, aluminium, gold, copper and steel pans) as well as different means of encapsulation (crimped shut, hermetically sealed, pin holed, vented or open) according to different samples, temperatures and pressure requirements. The amount of sample loaded in the pan is dependent on the sample type and experiment; however, for repeated sample runs or for sample comparison purposes, similar samples masses should be tested. Good, uniform contact with the bottom of the sample pan is also important.

Purge gases are used to prevent STA instrument contamination during analysis as well as to remove as-produced volatiles. Inert purge systems, often nitrogen, are generally used, but air and oxygen can also be selected, for example for oxidative testing.

Scan rates for DSC can range from 0.001 and 500 °C/min, however 10 °C/min is typically employed. Selecting the rate is balance between a high sensitivity measurement by a fast scan rate, or a high peak resolution measurement by a slow scan rate. Furthermore, considerations of the speed of the event being analysed as well as the available time for analysis also determine the rate for the measurement. A number of DSC techniques have been developed. One example is Modulated DSC, in which slow heating rates are used to separate ‘reversible’ events (T_g) and ‘irreversible’ events (solvent loss), or a second is Fast Scan DSC, where scan rates at ~ 500 °C min⁻¹ are used to increase the size of endo/exotherms and for the analysis of small samples (10-500 μ m). Additionally, DSC

can be combined with FT-IR, MS or Raman attachments for additional analysis of the chemical changes to the samples.

Considering all the different options for heating rates, pan types and purge gases with different thermal conductivities (N₂, O₂, air, He, Ar), calibration is required for the results to be independent of these factors. Some commonly used industry standards include indium, lead, zinc and silver for the instrument calibration.

At the beginning of a DSC run there is often an endothermic peak before the flat baseline can be established. This initial period of instability, as the energy transmitted to the sample and reference chamber/s reaches the set heating rate, is referred to as the 'transient'. Events can then be recorded including melting, glass transition, cure reactions, recrystallisation and decomposition.

2.2.2. Thermogravimetric Analysis

This technique evaluates the mass of a sample as a function of time or temperature. Experiment parameters can be set depending on the aim of the analysis. For example, the temperature program can be constant (isothermal), linear or non-linear temperature programs can be used. Equally, the atmosphere (N₂, O₂, air) for the experiments can be selected or switched mid-analysis for inert, oxidising or reactive conditions, as required. The output thermogram will display the TGA curve as plot of the mass (or %), as a function of temperature or time. The result can also be displayed using the first derivative of the TGA, giving the differential thermogravimetric (DTG) curve. This presents the rate of the mass loss and often permits a more detailed analysis of the weight loss profiles. Sample mass changes can occur for a variety of reasons, such as by evaporation, gas desorption or adsorption, thermal decomposition (N₂), oxidative decomposition (air or O₂) or chemical reactions amongst others.

2.2.3. STA (DSC-TGA) Experimental

TGA and DSC measurements were conducted using a Perkin Elmer Simultaneous Thermal Analyser, STA6000. All the experiments used samples (~12 mg) loaded in an open alumina pan and a nitrogen gas flow selected. The alumina pans were reused for STA experiments; after being cleaned by sonication in HCl (5 % conc.) for 1 hr, and dried in an oven overnight (~80 °C), the pans were conditioned in the STA (30-850 °C at a ramp rate of 30 min⁻¹). For carbene insertion analysis, the sample was heated at a ramp rate of 10 °C min⁻¹ and a sigmoidal baseline was used to evaluate the reaction enthalpy. For nanoparticle analysis, samples were heated from 30-800 °C at a ramp rate of 20 °C min⁻¹. For PP and nanocomposite analysis, samples were subjected to a heating run (30-250 °C) to remove the thermal history, followed by a cooling cycle (250-30 °C), and then heated beyond the decomposition of PP (30-850 °C), all at a ramp rate of 20 °C min⁻¹. The machine is calibration to the accuracy of ±1 J/g for the enthalpy, ±1 °C for onset temperature measurements and ± 0.05 mg for weight measurements. Where possible, STA experiments have been repeated, the S.D. values are included as appropriate in the results and discussion sections.

2.3. Solid-State NMR Spectroscopy

Solution NMR is routinely used for the characterisation of organic compounds, as it has for this thesis, and is arguably the most important analysis technique for organic chemists.¹⁰ Nevertheless, application of the same basic concepts in solid-state NMR have proved pivotal in the characterisation of the covalent modified silica in this thesis. Nuclear magnetic resonance (NMR) is a radiofrequency technique, which under the conditions of a strong magnetic field observes the frequency at which point the nuclei spin resonates with the electromagnetic field. Application of this technique to solid-state (as opposed to in solution), however, means spectra are produced at a lower resolution and with broad line-widths, often requiring a high power of radio frequency radiation to achieve saturation. Additionally, molecular rotation generally does not occur in SSNMR, resulting in long spin-lattice relaxation times, but equally shortened spin-spin relation times. This means that pulse experiments used to aid the resolution, require lengthy delays (several seconds) between consecutive pulses to allow for the equilibrium to re-establish each time.

In more detail, line-broadening effects arise in the SSNMR spectra are due to anisotropic interactions present in the sample measured as a solid. These include dipole-dipole interactions, chemical shift anisotropy and the electric quadrupole interaction. However, all these interactions have an orientation dependence of $1-3\cos^2\theta$, where θ is the angle of the applied field and the principal axis of the molecule. One technique, Magic Angle Spinning (MAS), minimises these line-broadening anisotropic interactions by spinning the sample at high speeds at the 'magic angle' of 54.74° to the applied field, whereby $1-3\cos^2\theta = 0$. Under these conditions, the dipolar-dipolar interactions and anisotropies average to zero. Otherwise, decoupling techniques are also used to decrease linewidths by reducing the dipolar field of the electrons.¹¹

2.3.1. Experimental

The SSNMR experiments were run by Dr Nicholas Rees (NMR facility at the CRL, Oxford). The SSNMR were recorded on a Varian Chemagnetics CMX Infinity 200 (4.7T) spectrometer operating at 39.8 and 50.32 MHz for ^{29}Si and ^{13}C respectively. Dry nitrogen was used for all gas requirements and the spinning speed of 4 kHz was used in all experiments. ^{29}Si NMR samples were packed in 7.5 mm zirconia rotors. A double resonance MAS probe was used for all measurements.

^{13}C CP/MAS NMR spectra were obtained using 7.5 mm O.D. rotors containing 300 mg of sample. A cross-polarization sequence with a variable X-amplitude spin-lock pulse and phase modulated proton decoupling was used. 13000 transients were acquired using a contact time of 1 min, an acquisition time of 40 min (1024 data points zero filled to 16 K) and a recycle delay of 30 s. All ^{13}C spectra were referenced to adamantane (the upfield methine resonance was taken to be at $\delta = 29.5$ ppm on a scale where δ (TMS) = 0) as a secondary reference.

^{29}Si CPMAS spectra were acquired with a cross-polarization sequence and phase-modulated proton decoupling. 2000 transients were acquired using a contact time of 1.0 min, an acquisition time of 40-60 min (1024 data points zero filled to 32 k) and a recycle delay of 5 s. DPMAS ^{29}Si spectra were acquired with a one-pulse sequence and phase-modulated proton decoupling. 2000 transients were acquired with an acquisition time of 30 min (1024 data points zero filled to 32 k) and a recycle delay of 30 s. All ^{29}Si spectra were externally referenced to kaolinite (taken to be at $\delta = -91.7$ ppm on a scale where δ (TMS) = 0) as a secondary reference.

2.4. Combustion Analysis

The CHN results were used to evaluate the elemental composition of the modified nanomaterials. Following the carbene modification with the nitrogen-label, the CHN results also presented the opportunity to evaluate the surface loadings of the functionalisations introduced to the nanofiller sample. By this technique, samples are oxidized by ‘flash combustion’ from which the resulting combustion products (CO_2 , H_2O , NO_2 , O_2) are passed through a reduction furnace before separation by column chromatography (CO_2 , H_2O , N_2). Finally, the components are detected using a thermal conductivity detector (TCD).¹²

2.4.1. Experimental

Samples (5 mg) were submitted to MEDAC Ltd. for combustion analysis (CHN). The results are presented as elemental percentages of the carbon, oxygen and nitrogen content, for which the detection limit is $<0.1\%$ and the accuracy is $\pm 0.3\%$.¹² Additionally, the relative error of the nitrogen loading for one repeated samples (CB_5.5) was calculated at 25% (See Appendix-Chapter 3).

2.5. Brunauer-Emmett-Teller Surface Analysis

BET (Brunauer-Emmett-Teller) analysis is one of the most commonly used methods to determine the surface area and additionally provides further information, such as the porosity, pore sizes, pore volumes and the pore distributions at the surface. An extension of the Langmuir theory (monolayer adsorption), the BET theory was developed by Stephen Brunauer, Paul Emmett and Edward Teller.¹³ By the BET theory, the adsorption isotherm for the multilayer physisorption of gas molecules (N_2 , Ar, Kr) on a substrate can be described by the following expression:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_0} \quad (\text{Equation 2.4})$$

where V is the volume of physisorbed gas, V_m is the volume of physisorbed gas at a monolayer coverage, P is the equilibrium pressure, P_0 is the saturation pressure of the gas at the absolute temperature of the system and C is the BET constant and is related to the heat of adsorption. A plot of $P/(V(P_0 - P))$ against P/P_0 is called the BET plot and the intercept and slope reveals the BET constant (C) and the volume at which the monolayer surface coverage is attained (V_m). The key assumptions of the BET theory are that the Langmuir theory is applied to each layer, there exists no physical interactions or mobility between each layer and that indefinite adsorption will occur onto the substrate.¹⁴

BET analysis was used to determine the surface areas of microsilica, nanosilica, Carbon Black (CB), Acetylene Black (ACB) and Carbon Nanotube (CNT) nanomaterials used in this work. For some of the modified nanomaterials, BET analysis was also used to assess changes to the measured surface area and micropores sizes.

2.5.1. Experimental

BET surface area analysis was performed at 195.9 °C by nitrogen sorption experiments using a micromeritics Tristar II PLUS surface area and pore size analyser. Before analysis samples (~0.8 g) were heated at 200 °C overnight using a micromeritics VacPrep 061 sample degas system. Where possible BET measurements have been repeated and the S.D. values are included as appropriate in the Results and Discussion Chapters.

2.6. Attenuated Total Reflectance-Infrared

Attenuated total reflectance-infrared Spectroscopy (ATR-IR) was used to identify the introduction of new surface groups following the performed functionalisation procedures to the nanomaterials. IR spectroscopy is a widely used technique, whereby chemical bonds and functional groups present in sample can be detected by the characteristic resonance frequencies at which they absorb in the infrared region. The addition of an attenuated total reflectance (ATR) attachment permits the advanced measurement of samples by the method of internal reflectance. By this technique, the sample is placed in contact with an internal reflectance component (IRE), which is of a high crystalline structure, for example germanium, silicon and diamond are frequently used. The IR beam is directed into the IRE at a set angle (according to the specific component), which permits total internal reflectance and the formation of an evanescent wave that enters the sample. Then, as the beam exits the sample it is detected and the output spectrum displays IR wavelengths as a function of absorbance or transmittance.¹⁵

2.6.1. Experimental

ATRIR was conducted using a Bio-Rad FTS-6000 Fourier Transform Infrared Spectrometer fitted with DuraSamplIR Diamond ATR accessory. Nanoparticle samples were clamped into position using the compression tip on the diamond accessory and the spectra collected with a resolution of 0.25 cm^{-1} from $6000\text{--}700\text{ cm}^{-1}$ by co-adding 256 scans.

2.7. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) measures the electronic transitions of molecules (ground state to excited state) when they are exposed to light in the visible and near-UV region of the electromagnetic spectrum. The basic set-up includes a light source, a diffraction grating in a monochromator (to separate the wavelengths), a sample and reference cell and a detector. This technique can be used to calculate the concentration of a UV-Vis active species through the intensity of the absorbance signal by applying the Beer-Lambert Law:

$$A = \log_{10} \left(\frac{I_0}{I} \right) = \epsilon \times [J] \times L \quad (\text{Equation 2.5})$$

Where A is the absorbance of a sample, I_0 is the incident intensity, I is the transmitted intensity, ϵ is the molar absorption coefficient (extinction coefficient), [J] is the molar concentration of the sample J and L is the length of the sample (cuvette width). Accordingly, for a fixed path length (L) and because ϵ is a constant, the absorption is proportional to the concentration.¹¹

2.7.1. Experimental

UV-Vis spectroscopy was used to evaluate the presence and concentration of UV-Vis active Triton X-100 surfactant in residual supernatant solutions from the modification procedure. The Triton X-100(aq) samples were analysed in quartz cuvettes using an Agilent Cary 4000 UV-Vis Spectrometer that has a wavelength range of 175-900 nm with ± 0.08 nm accuracy.

2.8. Electron Microscopy

Electron microscopy is an invaluable technique in nanomaterial technology, permitting the imaging at the nano-scale which would otherwise not be observed using traditional microscopes. Both techniques operate in vacuum conditions by striking sample with a beam of electrons focused by magnetic fields. TEM and SEM images typically have resolutions of ~ 2 nm and ~ 50 nm, respectively. In transmission electron microscopy (TEM) an ultra-thin sample is irradiated, and the electrons which are transmitted through the sample are focused and yield an image of the specimen. Alternatively, in scanning electron microscopy (SEM), as the electron beam is scanned across the sample, electrons are emitted and can be detected to produce an image of the sample, presenting information on the morphology of the sample.^{11, 16} TEM and SEM were used to characterise both the nanoparticles and PP nanocomposite samples, as detailed below.

2.8.1. TEM Experimental

CB nanoparticles and CB/PP nanocomposites were imaged by Dr Jonathan Moghal and Dr Kerstin Jurkschat, respectively. The nanoparticle samples were first dispersed in toluene, the TEM grid was then dipped in the solution and the prepared nanocomposite films (15 μm) embedded in epoxy before imaging – low to high magnification. A JEOL 2010 analytical TEM instrument was used with a LaB6 electron gun operable between 80 and 200 kV. The TEM has a resolution of 0.19 nm, an electron probe size down to 0.5 nm and a maximum specimen tilt of ± 10 degrees along both axes. It is equipped with an Oxford Instruments LZ5 windowless energy dispersive X-ray spectrometer (EDS) controlled by INCA. Before TEM analysis the morphology of the films samples was analysed using a Veho VMS-004 USB microscope at $\times 150$ optical zoom.

2.8.2. SEM Experimental

Scanning Electron Microscopy was also used to examine the CB nanoparticles and a pristine nanosilica/PP nanocomposite film (15 μm), and the measurements were performed by Dr. Jonathan Moghal. The CB nanomaterial (positioned on an aluminium stub with silver paint) and the nanocomposite film were both imaged using a JEOL 840F SEM instrument equipped with a cold cathode field emission gun and operates between 0.5 and 40 kV.

2.9. Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is a major thermal analysis technique that measures the mechanical properties by the response of a viscoelastic material to a periodic stress. As a result, DMA principally measures the E' – storage modulus (stored energy) and the E'' – loss modulus (dissipated energy) of the material. Additionally, the $\tan \delta$ – damping factor, can be calculated (E''/E'), and is related to the energy the material can absorb. This way, DMA can provide information on the crystalline relaxation processes, melting point (T_m) and glass transitions (T_g) of the material. Accordingly, it is a widely used technique to investigate the interfacial properties in polymer nanocomposites, as well as for general molecular structure analysis for a broad range of other materials, including biomaterials, thermoplastics and thermosets.

The principal investigation constitutes the application of a force at a certain magnitude and phase to a specimen of a known geometry held in place. The subsequent displacement phase and amplitude of the specimen, compared to the applied force, is then measured. In detail, for an elastic material this phase difference (between the applied and measured) would be 0° and equally for a viscous material it would be 90° . As such, viscoelastic materials exhibit a phase difference between these two extremes (0 - 90°). This result, combined with the amplitude difference of the phases, constitutes a DMA

measurement. Additionally, similar to the thermal analysis techniques presented above (TGA, DSC), various parameters can be altered. The force can be applied to the material at a number of geometries, such as the single or dual cantilever, tension, compression shear or three and four-point bending clamps. The temperature program can also either be isothermal or thermal scanning at different ramp rates. Equally, the applied frequency can be altered for frequency scanning experiments or step-isotherm experiments can also be used, combining the frequency and isothermal scanning programs. DMA is also a convenient material analysis method as it can be used for specimens of low mass and at a variety of sizes, from powder to films and fibres, amongst others.

2.9.1. Experimental

The DMA experiments of nanocomposite films were outsourced and performed using two DMA instruments, namely a PerkinElmer[®] DMA 8000 (Chapter 5 and 7) and a Mettler DMA 1 instrument (Chapter 6). The same parameters were used for the experiments for both instruments, in which tension mode was used and the static control was set at $1.5 \times$ dynamic to hold the samples in tension. The experiments measured rectangular nanocomposite samples ($\sim 5 \times 10$ mm) of two thicknesses (0.25 or 0.5 mm) under nitrogen at frequency of 1 Hz as a function of temperature from ~ -80 until the point at which the film could no longer be measured because it had become molten (~ 140 °C).

2.10. Electrical Conductivity

The conductive properties of polymer nanocomposites are most commonly calculated from the materials' electrical volume resistivity, measured in ohm-cm (Ωcm) or ohm-m (Ωm). The volume resistivity is a materials intrinsic resistance, i.e. irrespective of the sample size or shape and is related to the volume conductivity (measured in Scm^{-1}) by:

$$\sigma = \frac{1}{\rho} \quad (\text{Equation 2.6})$$

where σ is volume conductivity and ρ is the volume resistivity. More often, nanocomposite samples are prepared as conductive films or plaques in which case the measured sheet resistivity (Ωsq^{-1}) can be related to the volume resistance according to:

$$R = \rho \frac{L}{w.t} \quad (\text{Equation 2.7})$$

where ρ is the resistivity, R is the measured resistance and the L , w and t are the length, width and height of the measured sample.^{11, 17} Additionally, before the resistivity measurements, silver paste is often applied in order to minimize the contact resistance.¹⁸

2.10.1. Experimental

For DC electrical conductivity measurements, the CB/PP nanocomposite plaques were silver pasted on each pair of parallel sides,¹⁸ and the sheet resistance was measured at room temperature by the two-point probe method inside a shielding box using a Keithley Electrometer 617. For highly resistive samples ($R > 10^9$), a bias voltage (10 V) was applied and the resistance calculated from the voltage-current ratio:

$$R = V/I \quad (\text{Equation 2.8})$$

where R is the resistivity, V is the voltage and I is the current.

The volume conductivity of the plaque samples ($1 \times 1 \times \sim 0.1 \text{ cm}^3$) was calculated according the equations 2.6 and 2.7 presented above. The error of the conductivity

measurements across perpendicular sides of the nanocomposite plaque samples, and for the repeated control set of CB/PP of nanocomposites (at 10-30 wt. %), was calculated using:

$$Error = \frac{S.D.}{\sqrt{n}} = \frac{\sqrt{\frac{\sum(x - \bar{x})^2}{(n-1)}}}{\sqrt{n}} \quad (\text{Equation 2.9})$$

where n is the number of repeated measurements (2) and $\bar{x}$ the mean average of the sample set.

2.11. Dielectric Analysis

Dielectric analysis is a technique used to provide information on the molecular state of a material by measuring its response to an oscillating voltage. In this way, it is similar to DMA, for which an oscillating force is used. In dielectric analysis, the permittivity (polarising ability) of a material is measured, revealing the electrical characteristics of the material, namely the capacitance (capacity to store electrical charge) and the conductance (capacity to transfer electrical charge).^{19, 20}

For analysis, an alternative voltage signal is applied to the specimen (film, powder, pellets, liquid) which is in contact with a sensor. The materials' response can be tested at a range of frequencies (0.0001-100000 Hz), temperatures or as a function of time. The resulting current and the induced phase angle shift is then recorded, revealing the ϵ' – real permittivity (related to capacitance), and the ϵ'' – Imaginary permittivity (associated with the conductance) of the polymeric materials. The ϵ' is related to the degree of alignment of the molecular dipoles in accordance with the applied electrical field and the ϵ'' is associated with the energy required for this alignment change. The ϵ' dominates at temperatures below the glass transition (T_g) or the melting temperature (T_m), whilst the ϵ'' is the opposite.²⁰ The highly sensitive nature of this analysis technique means it can be used for materials with a low polymer percentage. Accordingly it is frequently used for

polymer nanocomposites, for which it can be highly informative, permitting evaluation of the microstructure, connectivity, and electrodynamics of the nanofillers dispersed in the polymer matrix.²¹⁻²⁴

2.11.1. Experimental

The dielectric analysis experiments were carried out by Fatma Shkal (Cardiff University) in collaboration with Dr Daniel Slocombe (Cardiff University, formerly ICL, Oxford University). The measurements were performed using a PNA-L Vector Network Analyzer N5232 and a flat coaxial reflectance probe with a 1.6 mm aperture. Prepared nanocomposite films (50 μm) were held in place using a PTFE stub to ensure good contact between the probe and samples. The diameter of the center conductor of the coaxial probe was 0.3 mm and the diameter of the outer conductor was 1.6 mm. The samples were each measured more than 50 times, at different positions of the film in the frequency range 10 MHz - 10 GHz at room temperature. The measurement error for each of the samples was calculated according to Equation 2.9.

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Part I:

Chemical Nanoparticle Modification Routes

3. Preliminary Study - Route A

3.1. Introduction

3.1.1. Background

The modification of a variety of surfaces, including polymers,^{1, 2} silica,³ SWCNTs⁴ and hydrogen-terminated diamond,⁵ using diarylcarbenes demonstrates potential for the broad application of this promising technology. Further, tailoring the functionality of the diarylcarbene complex has revealed that a comprehensive range of custom properties can be introduced to the selected material, such as colour,⁶ biocidal activity,⁷ biocompatibility⁸ and surface wettability control.⁹ As a result, this covalent modification approach presents an attractive approach for the tailored functionalisation of nanofillers for polymer nanocomposite applications. As a preliminary investigation, this chapter details the surface chemical modification of silica and CB powder using reactive diarylcarbenes and azo-coupling chemistry to introduce detectable nitrogen functionality to the nanomaterial surfaces.

The *bis*(dimethylamino)diaryl system used in this investigation has previously demonstrated the successful functionalisation of a number of polymers, establishing the reactive nature of this particular diazo compound. Functionalisation of ceramics, silica gel and alumina, was also performed (Figure 3.1).²

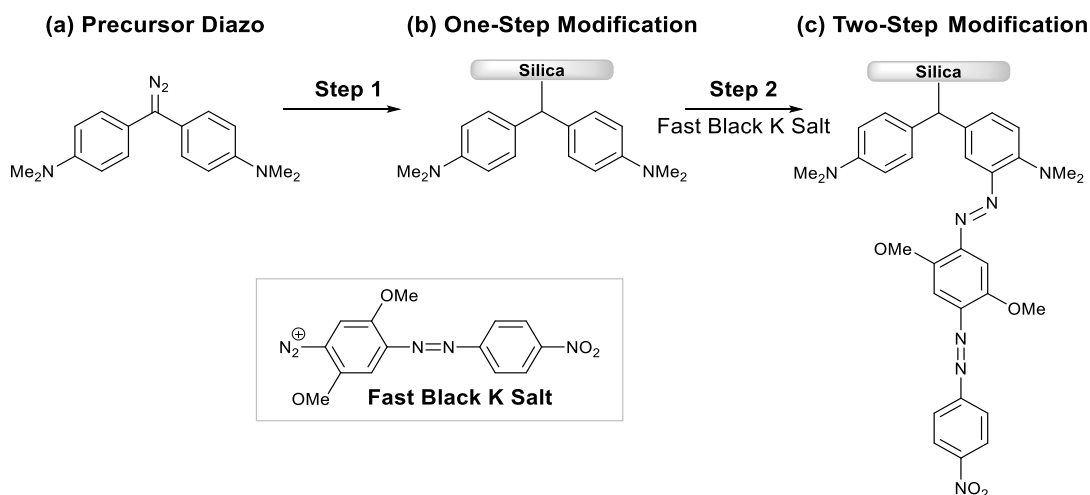


Figure 3.1: A scheme to show the modification of silica gel performed in a two-step approach by carbene modification followed by azo-coupling. The scheme was adapted with permission from John Wiley and Sons © 2014.²

In this work, characterisation of step one (i.e. the carbene insertion) proved difficult due to the low surface loadings of the functionalisation. Other than colour changes of various shades of yellow implying chemical modification (for example, silica (Figure 3.2(a)), more conclusive evidence was difficult to attain, and nitrogen could only be detected by XPS or CHN analysis on a few of the modified polymer substrates.

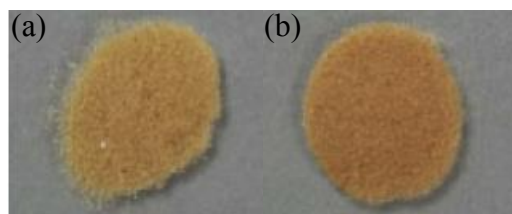


Figure 3.2: Modified silica gel after (a) step1 and (b) step 2. Photos used with permission from John Wiley and Sons © 2014.²

In Step 2, coupling reactions were performed to the carbene-modified substrates using a commercially available diazonium salt, Fast Black K Salt (Figure 3.1). The production of coloured product materials (for example modified silica (Figure 3.2(b))) affirmed the success of the modification, since the azo linkage formed in this dual modification procedure is a strong visible chromophore.³ Following this two-step surface modification, nitrogen content could be detected on some substrates by XPS, and for the high surface area polystyrene polymer substrate ($\sim 750 \text{ m}^2/\text{g}$) CHN analysis indicated a surface loading

in the range of 3.6×10^{12} to 3.3×10^{13} molecules/cm². Further, when the one-step and two-step modified materials were treated with hydrogen peroxide as an additional characterisation method, some exhibited bactericidal properties. For the silica gel, in addition to the yellow appearance after treatment (Figure 3.2), the success of the chemical surface modification could only be verified by the determined hydrogen peroxide loading of 2.4×10^{-6} mol g⁻¹.²

In this project, preparation of silica modified using the *bis*(dimethylamino)diaryl diazo aims to provide further insight into the density of the functionalisation by comprehensive surface analysis. Thermal analysis will be used to indicate the stability of the chemical functionalisation, an important consideration for viable use in polymer nanocomposites.

The same modification will also be used for CB nanoparticles (27 nm primary particle diameter), providing an interesting comparison of the modification on two nanoparticles types with different surface chemistries. The modification of CB using diarylcarbenes has not previously been reported. However, the graphitic nature of the CB means it can be expected to react in a similar way to SWCNTs, which have been modified by the same *bis*(dimethylamino)diaryl diazo – amongst other diaryldiazo derivatives.⁴ In this previous work, modification of the SWCNTs using the *bis*(dimethylamino)diaryl diazo was confirmed by a number of studies. TGA presented the degradation of organic moieties from the SWCNTs >250 °C at a weight loss of 84.6 % at 550 °C, compared to a weight loss of 96.4 % for unmodified SWCNTs. By ATR-IR analysis, C-H and C-N functional groups were detected at ν 1150 cm⁻¹ and at ν 1400 cm⁻¹, respectively, in addition to C=C, which was also detected on the pristine SWCNTs at ν 1600 cm⁻¹. Further, improved dispersability in THF compared to unmodified SWCNTs, along with Raman spectroscopic analysis, provided further evidence of functionalisation.⁴

An attractive feature of the *bis*(dimethylamino)diaryl unit, other than the advantage of the introduction of the N-label for surface characterisation, is its potential as an anchoring group for additional chemistry. The electron-donating effect from the dimethyl amino groups in the benzene rings allows for further manipulation of the pre-functionalised surface by azo-coupling reactions with diazonium salts. As such, in the pursuit of controlling the nanofiller surface chemistry in order to deter agglomeration, this two-step route can be employed as a method to insert hydrophobic, static stabilising hydrocarbon chains to the pre-modified surface. Silica and CB nanomaterials have both in fact been directly surface-functionalised by reaction with diazonium salts,^{3, 10} a procedure already in use commercially by Cabot Corporations for the production of speciality Carbon Blacks.¹¹ However, previous work has demonstrated the two-step modification approach, carbene insertion followed by diazonium coupling, is more efficient compared to diazonium coupling reactions directly to the substrate surface.^{12, 6} Accordingly, for this first investigation, carbene modification using the *bis*(dimethylamino)diaryl system, followed by second step azo-coupling reactions, appears an appropriate surface functionalisation approach in an effort to tailor the chemistry of the silica and CB nanoparticles.

3.1.2. Aims and Overview

This chapter presents the *bis*(dimethylamino)diaryl carbene and azo-coupling based modification routes and characterisation of silica and CB nanoparticles.

The major aims of this work include:

- To synthesise diazo and diazonium salt precursors for use in the surface modification of silica and CB nanoparticles;
- To identify whether the introduction of the N-label chemistry to the surface of the nanoparticles can be detected using any of XPS, thermal analysis, CHN, ATR-IR or

SSNMR surface characterisation techniques and then establish the extent of the modification;

- To determine if the introduction of hydrocarbon chains to the nanoparticle surfaces by the two-step modification is a viable synthetic route.

This preliminary study using carbene-based and azo-coupling technology will reveal if this approach can be developed for the tailored functionalisation of the nanoparticles for application in polymer nanocomposites.

3.2. Experiment Details

3.2.1. Materials

Commercial Monarch[®] CB (CB, M 430) was supplied from Cabot Corporation (Billerica, MA, USA). The CB possessed a primary particle size of 27 ± 10 nm diameter, density $1.1 - 1.9$ g/cm³ (manufacturer's data). All other reagents used were supplied from Alfa Aesar Chemicals Ltd., Sigma-Aldrich Chemicals and Lancaster Chemicals Ltd.

3.2.2. Nanoparticle Modification

3.2.2.1. Preparation of Carbene Precursor

The diaryldiazo compound **3**, *bis*-4,4'-*N,N*-dimethylaniline diazomethane, was prepared based on a two-step published synthetic procedure,² which uses the commercially available Michler's ketone **1**, (bis(4-(dimethylamino) phenyl) methanone, as the starting material (Figure 3.3).

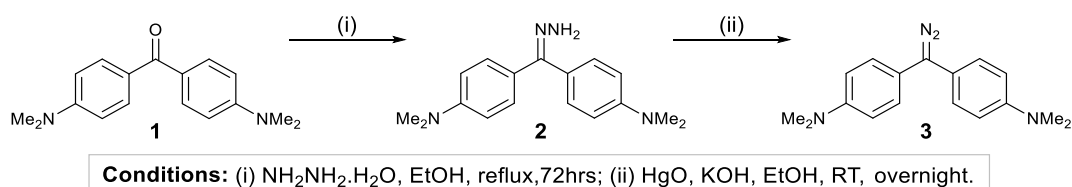


Figure 3.3: Scheme showing the synthesis of *bis*-4,4'-*N,N*-dimethylaniline diazomethane. Adapted with permission from the American Chemical Society © 2016.¹³

The synthetic procedure to produce the diaryldiazo **3** was repeated several times in an effort to improve the purity and yield, as summarised in Table 3.1.

Table 3.1: Reaction yield of repeat procedures for the synthesis of Diazo **3**.

Procedure	Hydrazone 2 Product Yield (%)	Diazo 3 Product Yield (%)
1	71	72
2	43 ^a	200 ^b
3	26 ^a	96
4	76	99
5	89	66
6	89	213 ^b

^a Low yields because the reaction was restarted after the first work up.

^b Solvent could not easily be removed *in vacuo* so the yield calculation is inaccurate. The amount of silica and CB nanoparticle added in the modification step was calculated according to the expected yield of diazo in the reaction.

The general method of the first step to produce hydrazone **2**, required treatment of the Michler's ketone reagent with hydrazine monohydrate in EtOH under reflux. Initially a 1:5 stoichiometric equivalence of Michler's ketone: Hydrazine monohydrate was attempted, employing the method of the published procedure.² Unfortunately, on the first attempt this reaction was unsuccessful and so for the second, the equivalence of hydrazine was increased to 1:10, and then 1:15 in subsequent repeat procedures. After 48 hrs under reflux, additional hydrazine monohydrate was added to the reaction, 2.5 equivalents in the first procedure and then 5 equivalents thereafter, and the temperature increased to aid the progress of the reaction. After mass spectroscopy identified the loss of the Michler's ketone starting material, typically after 72 hrs, the reaction was taken off reflux and cooled to allow the product to precipitate out of solution. The product was collected by filtration, washed with 2-propanol (5 mL) and dried *in vacuo* to yield a yellow solid product **2**, as a mixture of *syn-/anti*-diastereoisomers. The crude hydrazone product **2** cannot be purified by silica column chromatography because it is acid sensitive, which provides additional reasons to optimise reaction parameters to achieve the product directly in high final purity. In the work up of product **2** in procedures 2 and 3, the high loading of Michler's ketone starting material, as observed by NMR analysis, led to re-

treatment of the mixed crude product with hydrazine at 5 equivalents under reflux for a further 24 hrs.

After the eventual successful syntheses of the hydrazine product **2**, an oxidation reaction was performed with mercury (II) oxide (0.67 eq), sodium sulphate (1.39 eq) and saturated potassium hydroxide in EtOH (3 mL). After 18 hrs in the dark, the mixture was filtered through a pad of Celite™, and the filtrate collected and concentrated *in vacuo* to generate diazo **3** as a dark green oil. After the first procedure, the reactant equivalents of mercury (II) oxide and sodium sulphate were altered to 1.16 and 1.3 eq, respectively, again to improve the synthesis procedure. The reaction yields for the repeated procedures to produce diazo **3** are detailed in Table 3.1, above. The details of reaction procedure 7 have not been included, as the diazo was prepared by Dr Emily Parker.

3.2.2.2. Carbene Modification

The diazo compound **3**, bis-4,4'-*N,N*-dimethylaniline diazomethane, is particularly unstable, even in comparison with other substituted diaryldiazo systems, due the presence of the dimethylamine donating groups.¹⁴ The prepared diazo compound was therefore either used in the modification step immediately, or kept in the freezer overnight. For the modification of the nanofillers, the diazo compound was added to the silica and CB at low and high wt. addition loadings of 16 % and 66 %, respectively. Accordingly, diazo **3** was dissolved in THF for the first procedure, and subsequently in Et₂O thereafter, and sonicated, using a probe sonicator, for 30 min with the selected silica or CB nanoparticles. The choice of solvent was switched from THF to Et₂O for ease of removal on the rotary evaporator during the subsequent drying step, which was necessary to help avoid diazo decomposition during a prolonged synthesis procedure. The sonication step was included in the procedure in an effort to control an even diazo coating onto the nanoparticle surface through the effective dispersion of the nanoparticles in the solution.

Additionally, sonication allowed for the release of any trapped air that might be present in the nanoparticle structure. Subsequently, careful solvent evaporation *in vacuo* afforded the coloured diazo compound **3** physisorbed onto the nanoparticle surface, observable as a dark green coating for silica.

Thermal decomposition at 120 °C of the labile azo group present in the diazo precursor then generated the transient carbene and dinitrogen. The loss of the distinctive green colour of the diazo coated on the silica nanoparticles could be observed as the reaction progressed, indicative of the loss of diazo functionality. *In situ*, the carbene irreversibly modified the nanoparticle surface presumably by insertion reactions into C-H, O-H bonds and C=C addition reactions, forming new covalent linkages to silica and CB nanoparticles.^{3, 15} When the modified silica nanoparticles were removed from the heat, they displayed a range of yellow-orange-brown colours. The nanoparticles were washed in acetone to remove any impurities or unreacted starting materials, such as Michler's ketone **1** or hydrazone **2**, and dried *in vacuo* to give modified nanoparticles **Si_4** and **CB_5** as shown in Figure 3.4.

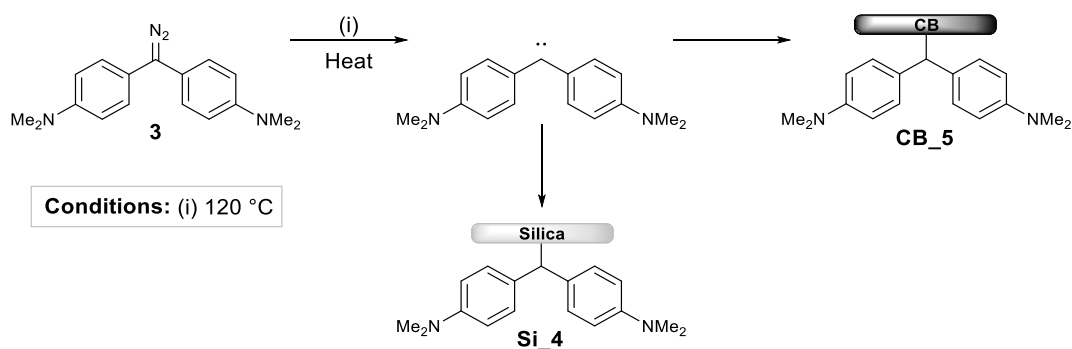


Figure 3.4: A scheme showing the modification of silica and CB nanoparticles with diazo **3**.

This modification was performed a number of times for both silica and CB nanoparticles due to the repeat procedures performed to prepare diazo **3**, as discussed above. Table 3.2 includes the details of the modified nanoparticles produced relative to the synthetic procedure used.

Table 3.2: Details of the silica and CB modified using diazo **3** made in repeat procedures.

Procedure	Diazo 3	Silica ^c		CB ^c	
	(C=N ₂) $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ (Transmittance %)	Code	Mass Modified (g)	Code	Mass Modified (g)
1	2018 (70 % - m ^d)	4.1	0.9	5.1	0.6
2	2013 (60 % - m)	4.2	2.0	5.2	0.4
3	2015 (80 % - w)	4.3	0.3	5.3	0.3
4	~2010 ^a (85 % - w)	-	-	5.4	1.2
5	2018 (50 % - s)	-	-	5.5	2.6
6	2011 (75 % - w)	4.6	5.8	-	-
7 ^b	2022 (80 % - w)	4.7a	0.5	-	-
		4.7b ^c	0.4		

^a The C=N₂ peak was estimated at ~2010 cm⁻¹.

^b This diazo compound was provided by Dr. Emily Parker.

^c Silica nanoparticles were prewashed in Na₂CO₃ before the modification reaction, to give modified silica 4.7b. Modified silica 4.7a was prepared using the diazo prepared in procedure 7 onto pristine silica in the same procedure as the other modified nanoparticles.

^d Description of the transmittance: s = strong, m = medium, w = weak.

^e Silica was modified at a 16 wt. % and CB at 66 wt. % diazo loading for all the repeated procedures.

The same characterised diazo compound **3** was used for each of the modification procedures, as confirmed by chemical analyses including the distinctive C=N=N sharp peak at ~2010-2025 cm⁻¹ region in the IR spectrum (included in the Appendix-Chapter 3). Nonetheless, the resulting functionalised silica nanoparticles exhibited observable variations in colour (yellow, orange, brown and blue/grey colour) even after vigorous washing in acetone, as displayed in Figure 3.5. Si_4.6 also had grainy/gummy texture compared to the other modified silica samples, all of which were dry powders.

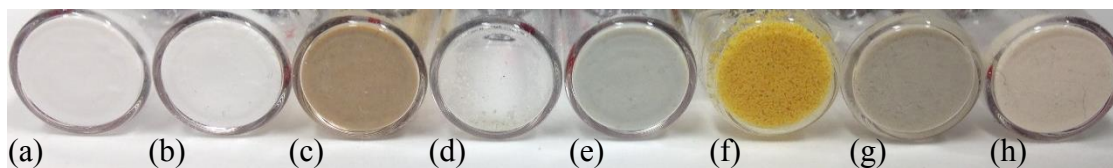


Figure 3.5: A photo displaying silica nanoparticles from left to right: (a) Si_Pristine, (b) Si_Processed (c) Si_4.1, (d) Si_4.2, (e) Si_4.3, (f) Si_4.6, (g) Si_4.7a, (h) Si_4.7b.

Modified CB, on the other hand, remained jet black, as would be expected for this nanoparticle type. It is supposed that any impurities that might remain chemisorbed onto the silica nanoparticles after modification would be readily soluble in acetone, and therefore removed during the vigorous washing step. Pristine silica is white and silica subjected to the modification procedure in the absence of the diazo modifier compound, termed processed silica, displays the same off white colour, confirming the change in

colour is due to surface modification with the diazo precursor. Previously modified polymer and silica substrates, using the same diazo **3** compound, demonstrated similar colour changes, as shown in Figure 3.2 for modified silica.² The colour variations of the modified silica nanoparticles is possibly due to differences in the surface loading of the modification. This is likely an indication of the purity of the diazo compound **3** in the repeated procedures, as the same 16 wt. % addition was used for all the samples.

Nonetheless, the high variation between the silica samples brought into question the nature of the diazo modification for this substrate. It is expected that the carbene will react with O-H silanol groups present on the surface of the silica nanoparticles, resulting in the formation of Si-O-C bonds. However, after attachment of the modifier, the nature of the electron-donating dimethyl amino group present on the surface might lend the modifier liable to cleavage, a mechanism that could also be further activated by adjacent silanol groups. This proposed cleavage mechanism is shown in Figure 3.6, in which the powerful electron donating effect of the dimethylamino groups initiates the loss of the labile group diaryl complex.

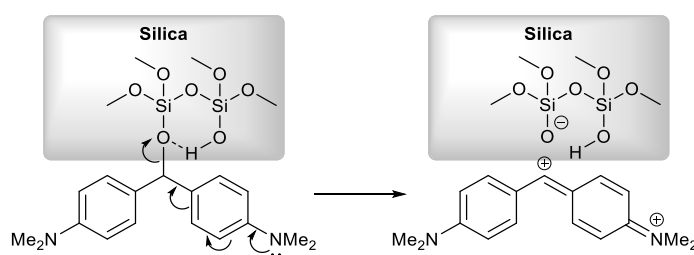


Figure 3.6: Scheme displaying potential cleavage mechanism of pre-functionalised silica under the acidic conditions of the diazonium coupling step.

For silica modified by a less reactive diaryldiazo system, in which the ring substituents were methoxy groups instead of dimethyl amino groups, the Si-O-C bond formed was found to be highly labile when subjected to acid reaction conditions, with some lability even observed at pH 7.³ Therefore, for the final silica functionalisation using the diaryl amino diazo **3** (procedure 7), an extra step was used in an attempt to reduce the

concentration of silanol surface groups in order to at least partially prevent further activation for the cleavage of the labile modification. Accordingly, some of the diazo **3** was used to modify a pre-treated silica – previously subjected to 30 min in a Na_2CO_3 (aq) (10 %) solution before filtering and drying overnight (80 °C) – producing sample **Si_4.7b**. The rest of the diazo **3** from procedure 7 was also used to modify silica nanoparticles (0.5 g) by the normal procedure to give a control sample, **Si_4.7a**.

3.2.2.3. CB Diazonium Coupling Modification

The nature of the diaryldiazo modifier allows for further manipulation of the pre-functionalised nanoparticle surface by diazonium coupling reactions, as detailed in the Introduction. However, acidic conditions are used for the procedure, and considering the concerns of the hydrolytic sensitivity of the Si-O-C bond formed in the modified **Si_4** nanoparticles, second step azo-coupling reactions were therefore not performed. Nonetheless, for pre-functionalised **CB_5**, two hydrocarbon terminated diazonium salts **9a-b** were prepared, as shown in the scheme in Figure 3.7.

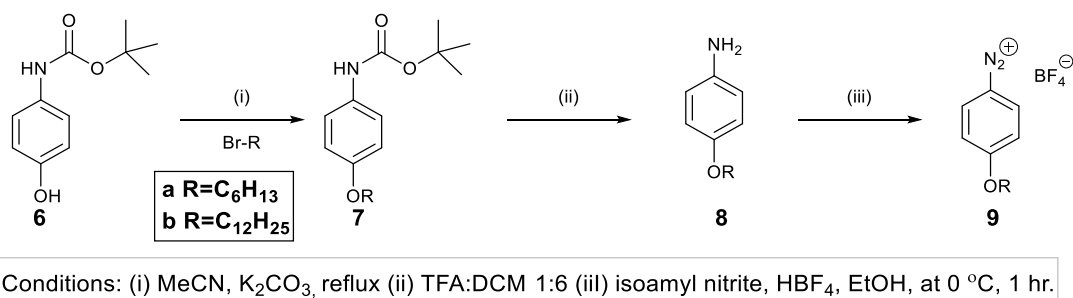


Figure 3.7: Scheme of the preparation of hydrocarbon terminated diazonium salts. Adapted with permission from the American Chemical Society © 2016.¹³

First, the *tert*-butyl-(4-(hexyloxy)phenyl)carbamate compound **6** was reacted with the required alkyl bromide, giving white solid compounds **11a-b** (57 % and 68 %, respectively), terminating in hexyl and dodecyl chains. Following BOC removal reactions, the required aniline products **12a-b** (68 % and 99 %, respectively) were generated. Reaction with isoamyl nitrite in tetrafluoroboric acid produced the

corresponding diazonium salts **9a-b** and their presence was confirmed using the H-acid test: conversion of the solution colour from light brown to dark pink/purple indicated that diazonium functionally was present.¹ In view of the improvements made to the diazo compound procedure, the final repeat CB modification, which gave **CB_5.5**, was selected for the azo-coupling procedure. Procedure 5, in which this diazo was prepared, gave the purest hydrazine product as well as the strongest diazo peak by IR spectroscopy. Accordingly, **CB_5.5** was added to the *in situ* generated diazonium salts solutions **9a-b** and left overnight (Figure 3.8).

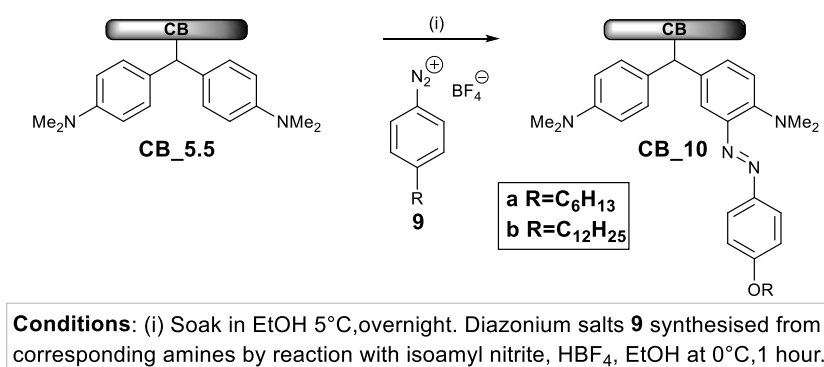


Figure 3.8: Scheme of the second modification of **CB_5.5** to produced **CB_10a-b**. Adapted with permission from the American Chemical Society © 2016.¹³

The two-step modified CB was washed with acetone, again to ensure the removal of any impurities, and dried *in vacuo*, to give functionalised **CB_10a** and **CB_10b**, possessing an ether linker terminated in hexyl and dodecyl hydrocarbon chain, respectively. This azo linkage onto **CB_5.5** is expected to generate a highly coloured chromophore on the substrate, usually providing additional visual evidence of surface functionalisation.⁶ Unfortunately, as would be expected, this will not be visible for the modified CB nanoparticles.

In summary, the modified nanoparticles produced in this section of work include variants of **Si_4** and **CB_5** whereby the nanoparticle surfaces were modified with a diaryl amino complex, permitting the introduction of a nitrogen label. Additionally, secondary

modification by azo-coupling reactions to **CB_5.5** yielded **CB_10a** and **CB_10b**, for which additional nitrogen and terminal hexyl and dodecyl groups, respectively, were inserted to the nanomaterial surface. The introduction of nitrogen to the nanoparticle surfaces will form a large part of the discussion in determining the success of these functionalisation routes.

3.3. Results and Discussion

The modified silica and CB nanoparticles have been analysed by a number of surface characterisation techniques to evaluate the success of the functionalisation. The results are presented below, in separate sections for the silica and CB nanoparticles due their different surface types.

3.3.1. Silica Nanoparticle Characterisation

The carbene modified and as received silica nanoparticles were analysed by BET, XPS, Thermal analysis, CHN and SSNMR, as presented below.

3.3.1.1. BET

Nitrogen surface area analysis was performed on the as-received silica, Si_Pristine, nanoparticles (the adsorption and desorption isotherms are included in the Appendix.) The BET surface area was found as 168.7 m²/g, which includes the total surface area as well as the surface area of internal open pores. The average pore size diameter was found to be 250.2 Å, with a t-plot micropore volume of 0.01 cm³/g and a t-plot micropore area of 29.0 m²/g, revealing the t-plot external surface area to be 139.7 m²/g.

3.3.1.2. XPS

X-ray photoelectron spectroscopy (XPS) of pristine and modified silica was used to assess the changed surface composition after the performed carbene functionalisation, and most importantly, the detection of the nitrogen label now introduced at the surface.

Accordingly, survey and high resolution scans of silicon, oxygen, carbon and nitrogen were performed on all the silica samples to determine the elemental percentage composition, the derived data is included in Table 3.3.

Table 3.3: The relative chemical percentage composition of the carbon, oxygen, silicon and nitrogen content and elemental N/C ratio by XPS analysis.

Sample	XPS (%)				N/C ^a
	C	O	Si	N	
Si_Pristine	6.4	65.9	27.7	n.d. ^b	
Si_Processed	3.4	62.9	33.6	n.d.	
Si_4.1	9.6	59.4	30.5	0.6	0.188
Si_4.2	24.7	52.7	21.8	0.7	0.038
Si_4.3	9.0	59.4	31.4	0.3	0.115
Si_4.6	64.8	27.1	4.4	3.7	0.063
Si_4.7a	10.0	59.9	29.8	0.3	0.083
Si_4.7b	13.5	58.0	28.3	0.2	0.028

^a Ratios calculated from the detected increased in C and N found on the modified silica nanoparticles compared to pristine silica by XPS analysis.

^b n.d. = Not detected.

The XPS results immediately indicate the introduction of nitrogen to the silica surfaces following carbene treatment in the repeated procedures. In detail, the main features of the unmodified silica samples, Si_Pristine and Si_Processed, are the core levels of SiO₂ by Si 2p and Si 2s photoemission peaks at ~103 eV and ~149 eV binding energies, and an O 1s peak at ~532 eV (Figure 3.9). Additionally, a C 1s component was detected for both unmodified silica samples at a binding energy of ~284.5 eV, presumably from contamination. All the samples were charge-corrected to this peak.

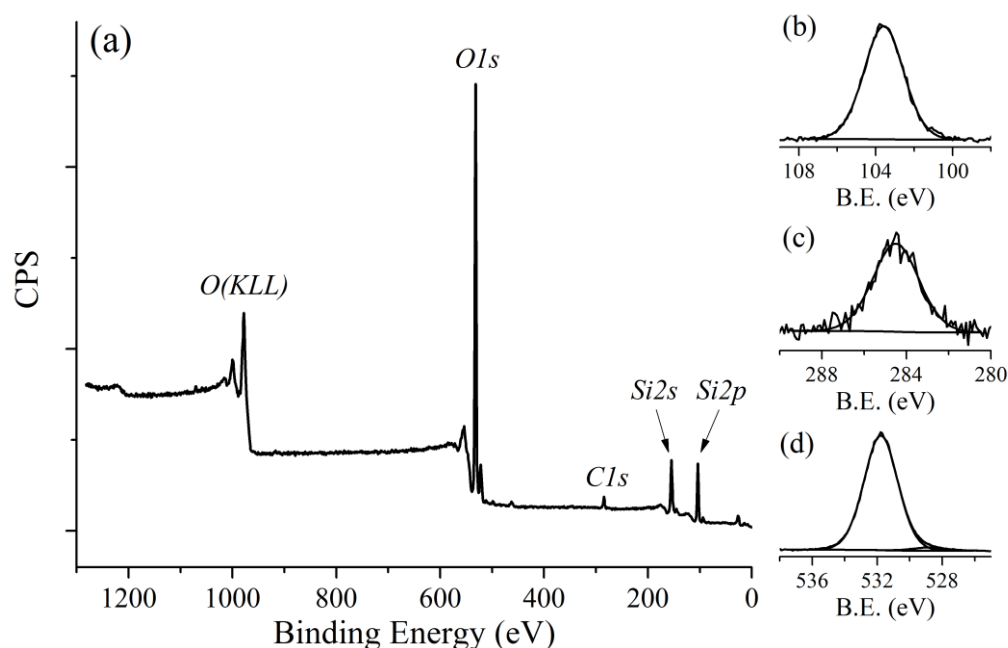


Figure 3.9: XPS spectra of Si_Pristine displaying (a) the wide scan and high resolution scans of the (b) Si 2p region (c) C 1s region and (d) O 1s region. The XPS spectra for Si_Processed is also presented in the Appendix.

For the modified silica samples, the C 1s, O 1s and N 1s high resolution XPS spectra is displayed in Figure 3.10. The Si 2p peaks have not been included in the figure as they were not deconvoluted into separate peaks and are generally similar to the unmodified silica XPS spectra, but are included in the Appendix for reference purposes. Additional information on the deconvoluted peaks from the high resolution scans (including the binding energies, charging and the FWHM of the main peaks) can also be found in the Appendix. A number of contaminants could be observed in the survey spectra of several of the modified silica nanoparticles. For example, Na 1s, K 2p and Cl 2p peaks were detected at binding energies of ~ 1070 eV, ~ 294 eV and ~ 200 eV, respectively. These are likely due to contamination during the modification, for example from residual KOH and Na_2SO_4 from the hydrazone to diazo step, and are potentially also stabilised by chelation to the modified silica surface.

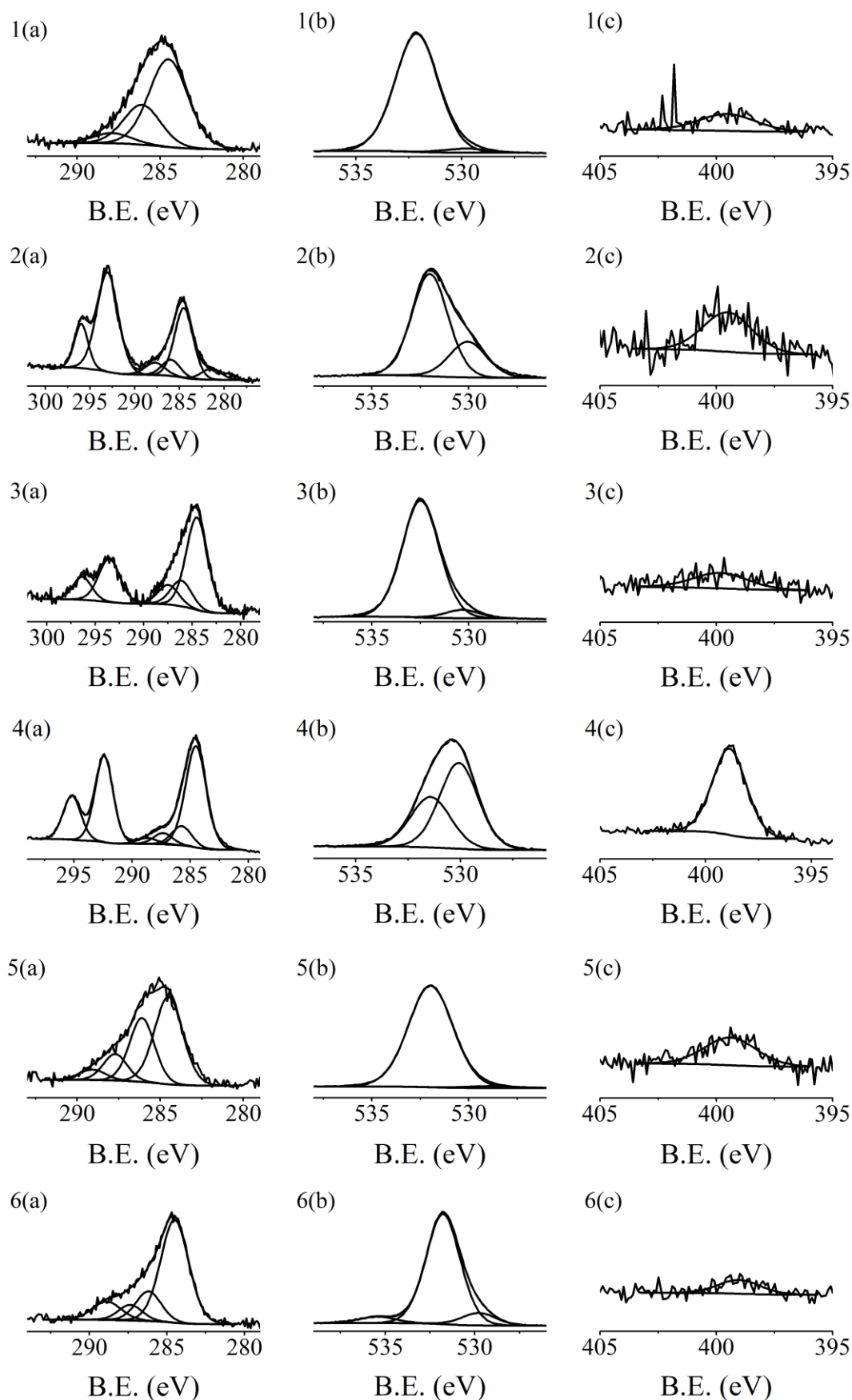


Figure 3.10: High resolution scans of (a) C 1s (b) O 1s and (c) N1s of modified silica nanoparticles 1. Si_4.1; 2. Si_4.2; 3. Si_4.3; 4. Si_4.6; 5. Si_4.7a and 6. Si_4.7b.

After modification, small N 1s photoelectron features detected at ~ 399 eV at 0.2-3.7 % content establishes the success of the carbene functionalisation, due to the detection of the NMe₂ group present on the precursor diazo **3** now on the silica surfaces. It can be observed that the low loadings detected for modified sample Si_4.3 and Si_4.7b are close to the detection limit of the XPS and peak fitting was only just achieved with a high level of noise present in the spectra (Figure 3.10 3(c) and 6(c)). The calculated N/C values (Table 3.3) can be compared to the expected N/C ratio for the introduced modifier to silica of 0.12, indicating a strong correlation with Si_4.3, which displayed the closest N/C ratio of the modified silica samples of 0.115, despite the low level of detection. It can be observed that in particular Si_4.6 (Figure 3.10 4(c)) displays a high loading of nitrogen at 3.7 %, compared to the other modified silica samples.

In addition to the confirmed presence of nitrogen, the increase of carbon content following surface functionalisation can be observed, compared to the pristine and processed silica nanoparticles, providing further evidence of the organic surface modification. High resolution C 1s spectra of the modified silica nanoparticles could be deconvolved into several peaks due to contributions from different chemical environments: the first is ascribed to adventitious carbon and hydrocarbon (C-C, C-H) at 284.5 eV, the second has contributions from carbon atoms with single bonds to oxygen and nitrogen (C-O, C-N) at $\sim 286.0 \pm 0.1$ eV and carbonyl (C=O) at ~ 287.6 eV ± 0.2 eV. Silica samples Si_4.6 and Si_4.7a-b additionally each showed a fourth C 1s deconvolved peak attributed to carboxyl contribution (COOH) at ~ 289.0 eV, ± 0.2 eV binding energy. Contaminated samples Si_4.2, Si_4.3 and Si_4.6 display K 2p peaks at ~ 293 and ~ 296 in the C 1s regions, which have also been peak fitted to increase the accuracy of the C 1s peak areas due to the close proximity of the peaks. The majority of the modified silica nanoparticles display a similar carbon content of ~ 10 % except Si_4.2 and Si_4.6, both indicating a

substantially higher content at 25 % and 65 %, respectively. Si_4.2 also displayed an extra C 1s peak compared to the rest of the samples at 281.4 eV, which possibly suggests the presence of a Si-C bond, previously reported at 282.6 eV binding energy.^{16, 17}

The O 1s high resolution spectra of all the samples were devolved into two peaks. The major peak at $\sim 532.2 \pm 0.5$ eV is from oxygen species present in the Si-O-Si bonds^{18, 19} and Si-O-H bonds, which are typically located at 232 eV and 233 eV,²⁰ but could not be devolved easily into separate peaks. A second, generally weak contribution, was detected at $\sim 530.0 \pm 0.6$ eV for pristine and modified silica, likely due to C=O (carbonyl and carboxyl) oxygen species, usually reported at ~ 530.6 eV binding energy.²¹ This is presumably as a result of general contamination, and corresponds to peaks found in the C 1s high resolution scans. However, Si_4.2 and Si_4.6 samples differ from the general trend, by larger contributions at ~ 530 eV binding energy. This change could be explained by the presence of Si-O-C bonds, which have previously been reported at 531.9 eV,¹⁶ consistent with the performed surface modification. A shoulder peak can also be seen in sample Si_4.7b at 535.4 eV (Figure 3.10 6(a)), which can be attributed to a sodium auger peak (Na KLL). Contamination by sodium was present for many of the modified samples, as mentioned above, however due to the high content present in this sample as observed from the survey scan, a high resolution scan of the Na 1s region was also performed. The elemental concentration was found to be 10 %, strongly suggesting that there is residual Na₂CO₃ present on Si_4.7b from the pre-modification treatment of this silica sample.

The Si 2p spectra was generally unremarkable for the majority of the samples with XPS binding energies at ~ 103.4 eV ± 0.3 eV, attributed to SiO₂ (103.5 eV),²² at a general content of ~ 29.8 %, which was between the detected content of pristine and processed silica, at 27.7 % and 33.6 %, respectively. Alternatively, Si_4.2 and Si_4.6 however exhibited lowered Si content of 21.8 % and 4.4 %, in contrast to the increased nitrogen

and carbon content, as presented above. Additionally, a small shift to lower binding energies of 102.5 eV and 102.6 eV for Si_4.2 and Si_4.6, respectively, was observed. This could be explained by the formation of Si-alkyl bonds (102.9 eV),²² whereby electron donation from the attached modification is altering the peak position.²³ These results correlate to the degree of the surface modification in accordance with the detected N 1s and C 1s content, indicating that in particular Si_4.6 has a high level of surface modification.²⁴

3.3.1.3. Thermal Analysis

Simultaneous Thermal Analysis (STA) experiments of the pristine and modified silica nanoparticles indicates the thermal stability of the modification. Further, this analysis affords the opportunity to directly estimate the surface loading from the determined mass losses of the modified silica, in comparison to the unmodified samples. The Thermogravimetric Analysis (TGA) thermograms, displaying mass loss (%) of the unmodified and modified silica nanoparticles samples upon heating (20-800 °C) are shown in Figure 3.11 and a summary of the weight loss data is included in (Table 3.4)

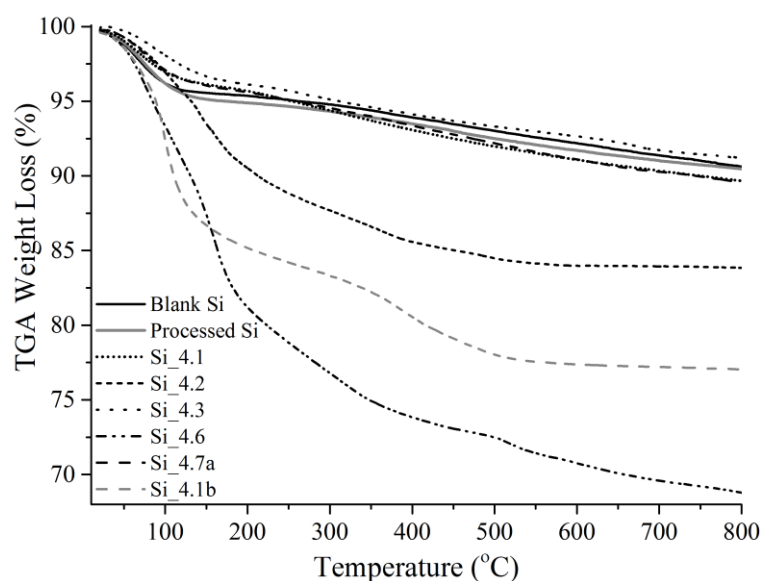


Figure 3.11: TGA thermogram of pristine and modified silica nanoparticles under nitrogen flow.

Table 3.4: Thermogravimetric analysis weight loss data of pristine and modified silica.

Sample	TGA Weight Loss (%)					
	30-200 °C		200-500 °C		500-800 °C	
	%	(S.D)	%	(S.D)	%	(S.D)
Si_Pristine ^a	4.3	(0.1)	2.2	(0.2)	2.1	(0.3)
Si_Processed ^a	4.5	(0.2)	2.4	(0.1)	2.1	(0.0)
Si_4.1 ^b	3.9	(0.1)	4.1	(0.5)	2.6	(0.4)
Si_4.2 ^b	9.2	-	6.0	-	0.7	-
Si_4.3 ^c	4.2	(0.5)	2.4	(0.5)	1.5	(0.9)
Si_4.6 ^b	15.7	(3.6)	8.6	(0.1)	3.2	(0.7)
Si_4.7a ^b	4.4	(0.4)	3.0	(0.5)	2.3	(0.5)
Si_4.7b ^b	13.5	(1.0)	7.1	(0.0)	1.7	(1.1)

^a Average 3 runs.

^b Average 2 runs.

^c Result of 1 STA experiment. The repeat experiment was tested by a different STA Program (30-700 °C at a rate of 20 °C min⁻¹) and so an average has not been included.

Pristine silica displays a weight loss of 4.3 % up to 200 °C which can be attributed to the loss of physically adsorbed water or other solvent residues.²⁵ This is to be expected considering the large contact surface area of the 10-20 nm silica nanoparticles used. After this, a weight loss of 4.3 % is observed up to the end of the program (~850 °C). A small TGA weight loss step can be observed with an onset at ~268 °C, attributed to the loss of vicinal silanols from the silica surface.^{26, 27} Processed silica, as expected, displayed similar weight loss results. The TGA curves of the modified silica nanoparticles display the weight loss profiles, revealing the thermal decomposition of the carbene surface modification. Si_4.1, Si_4.3 and Si_4.7a display similar weight loss profiles, ~10 %, compared to Si_4.2, Si_4.6 and Si_4.7b samples, which demonstrate a large variation of weights losses up to ~30 %, under the same experimental conditions. The major weight difference between the two sets of modified silica samples is in the 30-200 °C temperature range. This might suggest that different loadings of the modification alter the degree of water sorption or solvent contamination. However, in fact the organic nature of the modification is expected to reduce the degree of water adsorption compared to pristine silica, as observed elsewhere.²⁶

Fortunately, more data can be extracted for the STA experiments, to help understand the TGA results. The first derivative of the TGA curves, DTG curves, indicates the rate of changes of mass, and so can be used to highlight mass loss steps.²⁸ Additionally, DTA (differential thermal analysis) was simultaneously measured and converted to DSC-type curve, and indicates the energy changes of the sample upon heating, enabling changes to the sample not accompanied by mass changes, for example melting and crystallisation, to also be detected. Mass losses detected by TGA can also lead to endothermic DSC peaks due to the work of expansion on the formation of the volatile reaction product during the decomposition process. Therefore, thermal events can in some cases be detected in all three, TGA, DTG and DSC-type curves.²⁹ To analyse the differences of the modified silica nanoparticles by the same carbene precursor further, Figure 3.12 displays the TGA, DTG and DSC curves of pristine, processed and the modified silica nanoparticles and Table 3.5 includes the key extracted thermal analysis data.

Table 3.5: Extracted TGA, DTG and DSC peak data from thermal analysis runs (20-800 °C) of silica nanoparticles. The thermal events for each sample are labelled by a numbered superscript, with the same numbers when the same thermal event was observed by the different analyses. The same TGA and DTG thermal events observed in multiple samples are organised in the same columns, and the major DTG peak corresponding with the loss of the modifier is in bold.

Sample	TGA Onset (°C)				DTG Peak (°C)				DSC (°C)		
	T _o ^a	T _o	T _o	T _o	T _p ^b	T _p	T _p	T _p	T _p	T _o	T _p
	Impurity	Silanol groups	Modification	Water/Solvent	Imp.	Modification	Water/Solvent	Impurity			
Si Pristine		267.0 ²			74.3 ¹						
Si Processed		287.0 ²			67.4 ¹						
Si 4.1			201.6 ²		69.2 ¹	239.5²		82.4 ¹			
Si 4.2	137.8 ²		331.0 ³		101.2 ¹	147.2 ²	370.4³	488.5 ⁴	101.9 ¹	62.5 ²	145.6 ²
Si 4.3 ⁴			238.4 ²		87.0 ¹	293.1²		119.2 ¹			
Si 4.6	141.5 ²		278.3 ³	500.9 ⁴	82.2 ¹	159.3 ²	323.9³	522.2 ⁴	84.5 ¹	129.9 ²	166.2 ²
Si 4.7a			246.0 ²		77.4 ¹	327.6²		88.5 ¹			
Si 4.7b	85.0 ¹		347.7 ²			100.5 ¹	391.7²	495.2 ³		79.1 ¹	105.9 ¹

^a T_o, onset temperature.

^b T_p, peak temperature.

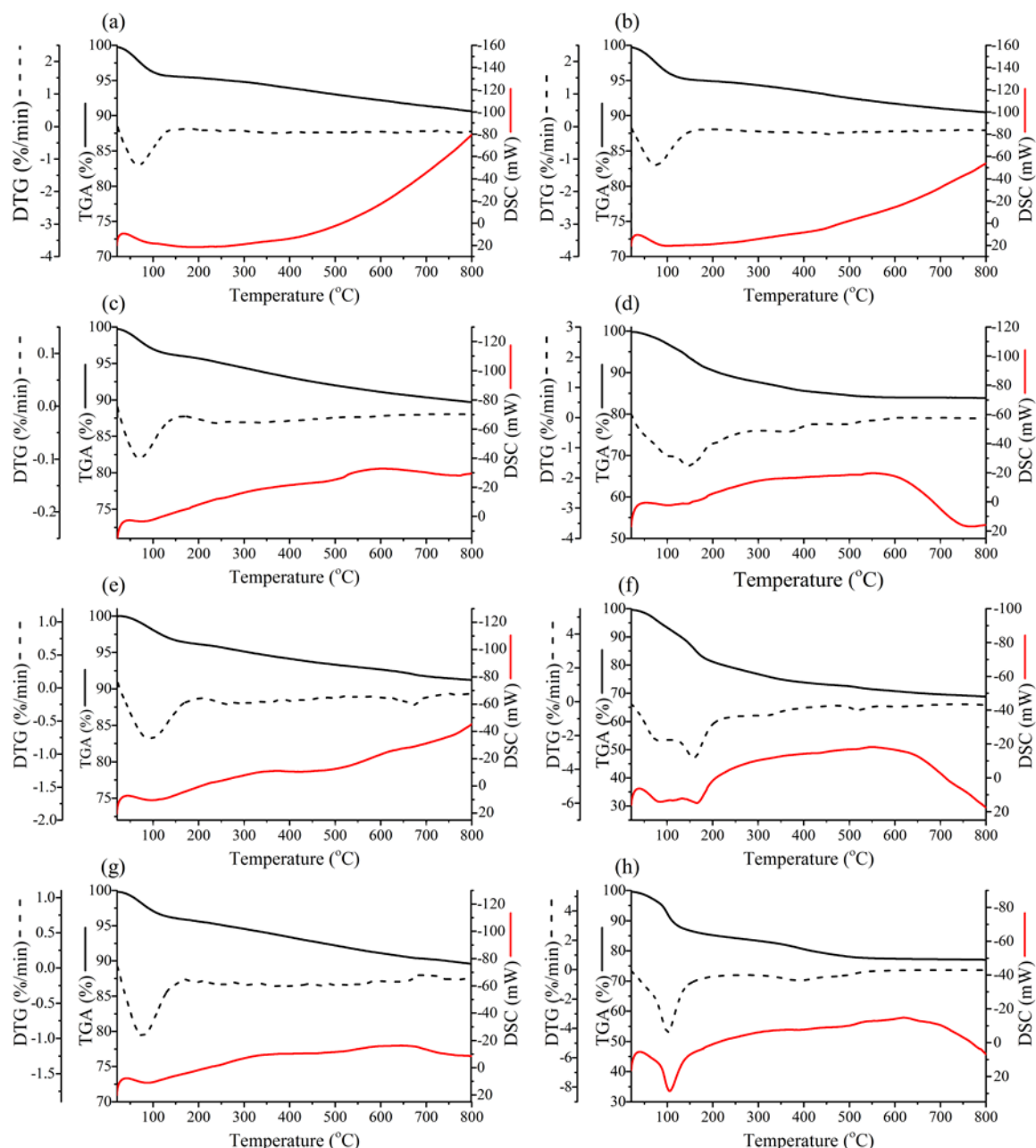


Figure 3.12: Thermal Analysis data displaying TGA, DTG and DSC curves (heat flow endo down) of (a) Si_Pristine (b) Si_Processed (c) Si_4.1 (d) Si_4.2 (e) Si_4.3 (f) Si_4.6 (g) Si_4.7a and (h) Si_4.7b silica nanoparticles.

Pristine and processed silica display the decomposition of the water at the beginning of the thermal run, as discussed above, and this is paralleled by DTG peaks at 74.3 °C and 67.4 °C (Table 3.5), respectively. DSC peaks were unobserved in these samples runs. However, in other repeat unmodified silica thermal runs some parallel small, broad endothermic DSC peaks ~89-95 °C were detected.³⁰

Comparing first samples Si_4.1, Si_4.3 and Si_4.7a, with similar TGA weight loss profiles, all three samples exhibited the loss of water at the beginning of the thermal program, observable by DTG peak at ~69-87 °C and small, broad DSC peaks at ~82-119 °C. The decomposition of the modification for Si_4.1, Si_4.3 and Si_4.7a is established by small TGA onsets detected at 201.6-246.0 °C, coupled by small DTG peaks at 239.5-327.6 °C, in the temperature range that would be expected for the decomposition of a covalent modification.³¹

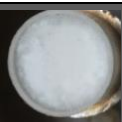
The thermograms for Si_4.2 and Si_4.6 demonstrated more complex patterns. The loss of water, observed for both samples by DTG and DSC maxima, intersects the removal of another surface component by the detection of TGA onsets at 137.8 °C and 141.5 °C, DTG peaks at 147.2 °C and 159.3 °C and broad DSC peaks at 145.6 °C and 166.2 °C for each Si_4.2 and Si_4.6, respectively. This large weight loss of 9 % and 16 % for Si_4.2 and Si_4.6 at the beginning of the thermal run is unlikely to be the cleavage of surface functionalisation in this temperature range (30-200 °C),³¹ but rather the presence of physisorbed surface contaminants. A third weight loss step can be observed at TGA onsets of 331.0 °C and 278.3 °C and prominent DTG peaks at 370.4 °C and 323.9 °C, respectively, in line with the results from the rest of the modified silica nanoparticles. Finally, for Si_4.6 an extra weight loss step can be observed by a TGA weight loss onset at 500.9 °C, undetected for Si_4.2, but DTG maxima at 488.5 °C and 522.2 °C could be detected for both modified silica samples, Si_4.2 and Si_4.6 respectively. It is likely the higher degree of modification is revealing a more detailed weight loss pattern, as decomposition mechanisms can be highly complex.²⁸

Si_4.7b displayed a similar modification decomposition weight loss step at a TGA onset of 347.7 °C coupled with a broad DTG peak at 391.7 °C and a secondary DTG peak at 495.2 °C, while the prominent weight loss step for this sample is observed at the

beginning of the thermal run. The TGA onset at 85.0 °C, with DTG maximum at 100.5 °C and DSC peak at 105.9 °C, suggests the presence of unwashed Na₂CO₃, from the pre-modification treatment to the silica, which has a literature DTG and DSC value of 100 ± 1 °C.³²

Further, the silica nanoparticles after analysis in the STA instrument revealed additional visual information, Table 3.6.

Table 3.6: Photos of unmodified and modified silica nanoparticles (~12 mg) in the crucible pans before and after STA analysis.

	Silica Samples							
	Si_Pristine	Si_Processed	Si_4.1	Si_4.2 ^a	Si_4.3	Si_4.6	Si_4.7a	Si_4.7b
Before TGA								
After TGA								

^a Only ~3 mg of Si_4.2 could be tested for this experiment.

Pristine and processed silica indicate no colour changes post STA analysis. However, it is noticeable that all the nanoparticle samples, except Si_4.3, demonstrate a degree of charring concomitant with the incomplete combustion of the organic matter on the sample, which is to be expected for a thermal program in nitrogen.³³ This result strongly denotes the success of the modification procedure. Alternatively, Si_4.3 exhibited a white silica residue similar to the unmodified silica after analysis. Taking into account the low determined TGA weight loss of this sample, this result could simply indicate that the markedly low surface loading may have permitted complete volatilisation of the modification during the thermal program. Equally, sample Si_4.7a indicates the second least charred silica sample, implying the modification was almost totally removed, and corresponds to the modified sample with the second lowest average TGA weight loss (5.3 % in the 200-800 °C range). An additional observation for Si_4.7b is that the silica

sample reduced in size during the analysis, unlike any of the other modified silica samples, probably by result of the decomposition of the residual Na_2CO_3 from the pre-modification treatment, as indicated in the thermograms for this sample.

To further investigate whether the modification is successfully removed during the STA analysis XPS analysis was performed to some of the modified silica nanoparticles retrieved after TGA analysis in order confirm the loss of nitrogen, previously introduced to the surface by the modification. The elemental composition is displayed in Table 3.7 and as an example Figure 3.13 shows the loss of the nitrogen species observed for Si_4.2.

Table 3.7: Chemical percentage of carbon, oxygen, silicon and nitrogen composition by XPS analysis of pristine and selected modified silica nanoparticles after thermal treatment (30-800 °C).

Sample	XPS (%)			
	C	O	Si	N
Si_Pristine	2.5	65.7	31.8	n.d.
Si_4.1	10.3	60.5	29.2	n.d.
Si_4.3	12.6	60.0	27.5	n.d.
Si_4.7a	5.3	64.1	30.6	n.d.
Si_4.7b	28.3	53.1	18.6	n.d.

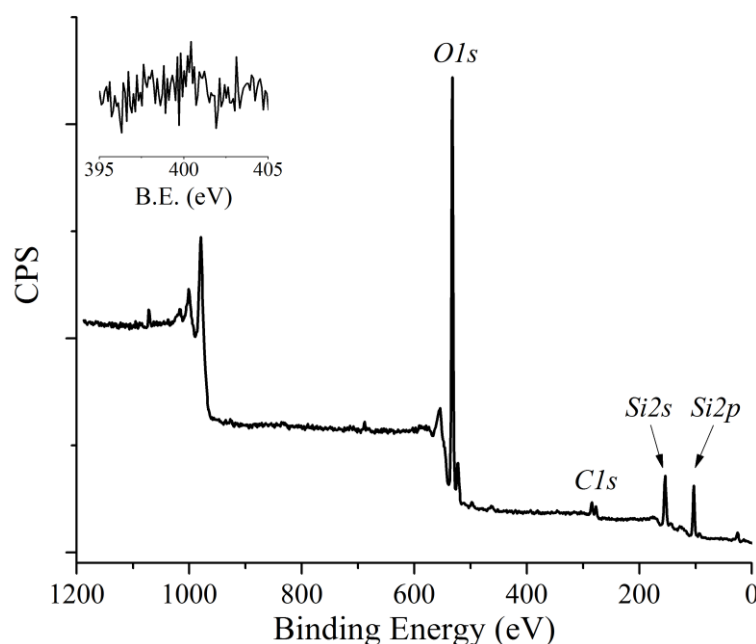


Figure 3.13: XPS survey scan of modified Si_4.1 following treatment by thermal analysis (insert shows the high resolution scan of the N 1s region).

Indeed, nitrogen could not be detected for any of the pristine and modified silica samples after thermal treatment (Table 3.7). Compared to the blank, a higher carbon content for the modified silica was still observed, a similar result to samples analysed by XPS without STA thermal treatment. This is a likely a result of the observed charring of the samples (Table 3.6). Further, Na 1s photoelectron peaks could also be observed for Si_4.7b, suggesting residual Na₂CO₃ is still present after thermal analysis. There remains a possibility that there is some modification still present on the silica nanoparticles after STA analysis, at a level below the sensitivity of the XPS instrument used. However, the observed loss of nitrogen, together with the high temperature program the samples are subjected to, along with the weight loss patterns of the presented thermograms together suggest the modifier has been removed. As such, the weight loss percentage of the modified silica can be compared to pristine silica during the major decomposition of the surface modification during the thermal program (30-800 °C). Furthermore, an estimate of the number of molecules per unit area present on silica can be made (Table 3.8) by taking into account the known surface modifier present and the experimental BET surface area of silica (168.7 m²/g).

Table 3.8: Surface loadings of modified silica nanoparticles, as calculated from the determined mass losses by thermal analysis experiments.

Sample	Decomposition		Surface Loading ^a	
	Sample Wt. Loss due to Modification (g)	Theoretical Wt. Loss Expected due to Modification on Sample in STA (g)	Moles/g	Molecules /cm ²
Si_4.1	2.4×10^{-4}	1.5×10^{-3}	5.8×10^{-5}	2.9×10^{13}
Si_4.2	5.3×10^{-4}	9.1×10^{-4}	3.2×10^{-4}	1.1×10^{14}
Si_4.3 ^a	3.0×10^{-5}	1.6×10^{-3}	9.4×10^{-6}	3.4×10^{12}
Si_4.6	2.5×10^{-3}	1.6×10^{-3}	9.4×10^{-4}	3.4×10^{14}
Si_4.7a	1.5×10^{-4}	1.6×10^{-3}	4.9×10^{-5}	1.8×10^{13}
Si_4.7b	1.8×10^{-3}	1.6×10^{-3}	6.4×10^{-4}	2.3×10^{14}

^a Only one of the two modified Si_4.3 samples tested exhibited a greater mass loss than the average mass loss of silica, in the 30-800 °C temperature range. The surface loading included in the table has therefore only been calculated from this one sample.

The diaryldiazo was added to the silica at 16 wt. % in the modification step, and therefore in the event of maximum conversion of the precursor diazo to the reactive carbene compound and 100 % modification of the surface of the silica, the theoretical surface modification loading would be 14.4 wt. %, that is 5.7×10^{-4} moles/g and with the known BET surface area, this result in 2.0×10^{14} molecules/cm². Accordingly, the theoretical estimates, based on this assumption, for each of the tested silica samples of known mass, are included in Table 3.8. Additionally, the Limiting Area of the carbene modifier can be calculated at 8.7×10^{-15} cm², using Chemicalize predictive software,³⁴ indicating a maximum loading for a monolayer surface coverage estimation at 2.1×10^{14} molecules/cm². The estimated surface coverage for Si_4.3 and Si_4.7a samples by TGA analysis was 3.4×10^{12} and 1.8×10^{13} molecules/cm², which displayed the lowest surface coverage, a result which is consistent with the observed reduced charring of these samples. The rest of the modified samples demonstrate loadings in the range of 2.9×10^{13} - 3.4×10^{14} molecules/cm², a comparable result to the previous work using diaryldiazo modifications.³ Si_4.6 and Si_4.7b samples loading estimates are larger than the expected loading for 100 % carbene modification, albeit at the same order of magnitude. This is unsurprising for Si_4.7b as the additional decomposition of residual Na₂CO₃ will have compromised the surface loading calculations. For Si_4.6, although the XPS results indicated a high degree of modification, the TGA surface loading is however likely to be an over-estimation due sample contamination, evident from the thermograms but equally XPS analysis identified the largest elemental percentage of potassium at 12 %, compared to the rest of the modified silica.

3.3.1.4. Combustion Analysis (CHN)

Qualitative evidence by CHN confirms the presence of nitrogen following surface modification for three of the six modified silica nanoparticles (Table 3.9).

Table 3.9: CHN elemental analysis of pristine and modified silica nanoparticles.

Sample	CHN Raw Data (%)			N/C Ratio ^a	Surface Loading	
	C	H	N		Moles /g ^b	Molecules /cm ² ^c
Si_Pristine	0.42	1.46	0.00			
Si_Processed	0.37	1.08	0.00			
Si_4.1	2.98	1.34	0.37	0.124	1.3×10^{-4}	1.1×10^{14}
Si_4.2	2.66	1.59	0.00			
Si_4.3	0.67	0.78	0.00			
Si_4.6	4.42	2.08	0.37	0.083	1.3×10^{-4}	1.1×10^{14}
Si_4.7a	1.70	1.37	0.25	0.147	8.9×10^{-5}	7.4×10^{13}
Si_4.7b	2.56	1.57	0.00			

^a Calculated from the detected increased in C and N for the modified silica nanoparticles by CHN analysis.

^b CHN surface loading calculated from the detected nitrogen content on the modified silica nanoparticles.

^c Assumes a monolayer surface coverage of the determined BET silica surface area, 168.7 m²/g.

Nitrogen was not detected for modified silica samples Si_4.2, Si_4.3 and Si_4.7b. For Si_4.3, it is unsurprising that nitrogen content was undetected, which was amongst the lowest nitrogen loading detected by XPS (0.3 %) and gave the lowest loading estimate by TGA, and as such, the modification is likely to be below the detection limit of the CHN instrument. Similarly, only a low Si_4.7b nitrogen content was detected by XPS (0.2 %) and the considerable TGA mass loss observed has been largely attributed to Na₂CO₃ contamination. Alternatively, Si_4.2 demonstrated a comparatively larger nitrogen loading by XPS (0.7 %) and TGA surface loading (1.1×10^{14} molecules/cm²), compared to for example 4.7a, which had a lower TGA surface loading (1.8×10^{13} molecules/cm²) and nitrogen loading detected by XPS (0.3 %), but nitrogen content was detected by CHN (0.25 %). This highlights that the modification loading is at the edge of the CHN detection limit and as such, the absence of nitrogen detection does not invalidate successful modification, but neither does it conclusively prove successful modification. It could also indicate uneven modification on the silica surface.

For silica samples Si_4.1, Si_4.6 and Si_4.7a, further confirmation of the presence of nitrogen, comparable to the XPS results, which was undetected on pristine or processed silica, is consistent with the N-label functionality introduced by the carbene modification. The N/C ratio can be calculated from the added carbon and nitrogen content following the

modification procedure, as shown in Table 3.9, giving 0.14, 0.09 and 0.19 for Si_4.1, Si_4.6 and Si_4.7a modified silica nanoparticles, respectively, and presents a relatively close comparison to the expected N/C ratio of 0.12 for the modification introduced to the surface. Additionally, the ratio of the detected elemental abundance of carbon, hydrogen and nitrogen, compared to processed silica, can be used to determine the molecular formula and compared to that of the modifier ($C_{17}H_{21}N_2$) introduced to the silica surface. Considering the crudeness of this calculation, the molecular formulas were found to be $C_{16}H_{20}N_2$ for Si_4.1, $C_{26}H_{75}N_2$ for Si_4.6 and $C_{12}H_{35}N_2$ for Si_4.7a, demonstrating a close correlation with the modification.

Furthermore, surface coverage estimates extracted from the CHN results provide quantitative data in a similar method to the TGA analysis, assuming a monolayer surface coverage of the experimentally determined silica BET surface area ($168.7 \text{ m}^2/\text{g}$). As displayed in Table 3.9, the estimate modification surface loading on silica is estimated to be $1.1 \times 10^{14} \text{ molecules/cm}^2$ for Si_4.2 and Si_4.6 and $7.4 \times 10^{13} \text{ molecules/cm}^2$ for Si_4.7a silica nanoparticles, which is consistent with the TGA and theoretical estimate surface loadings.

3.3.1.5. SSNMR

Solid-State NMR (SSNMR) permitted further analysis of the surface chemistry of the silica following treatment with the carbene modifier (Figure 3.14 and Figure 3.15).

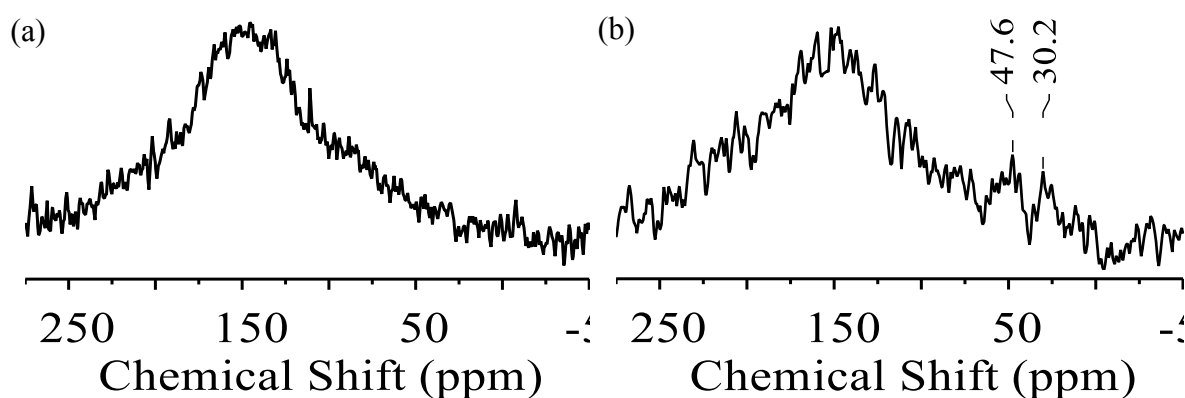


Figure 3.14: ^{13}C CP MAS SSNMR of unmodified silica (a) Si_Pristine and (b) Si_Processed.

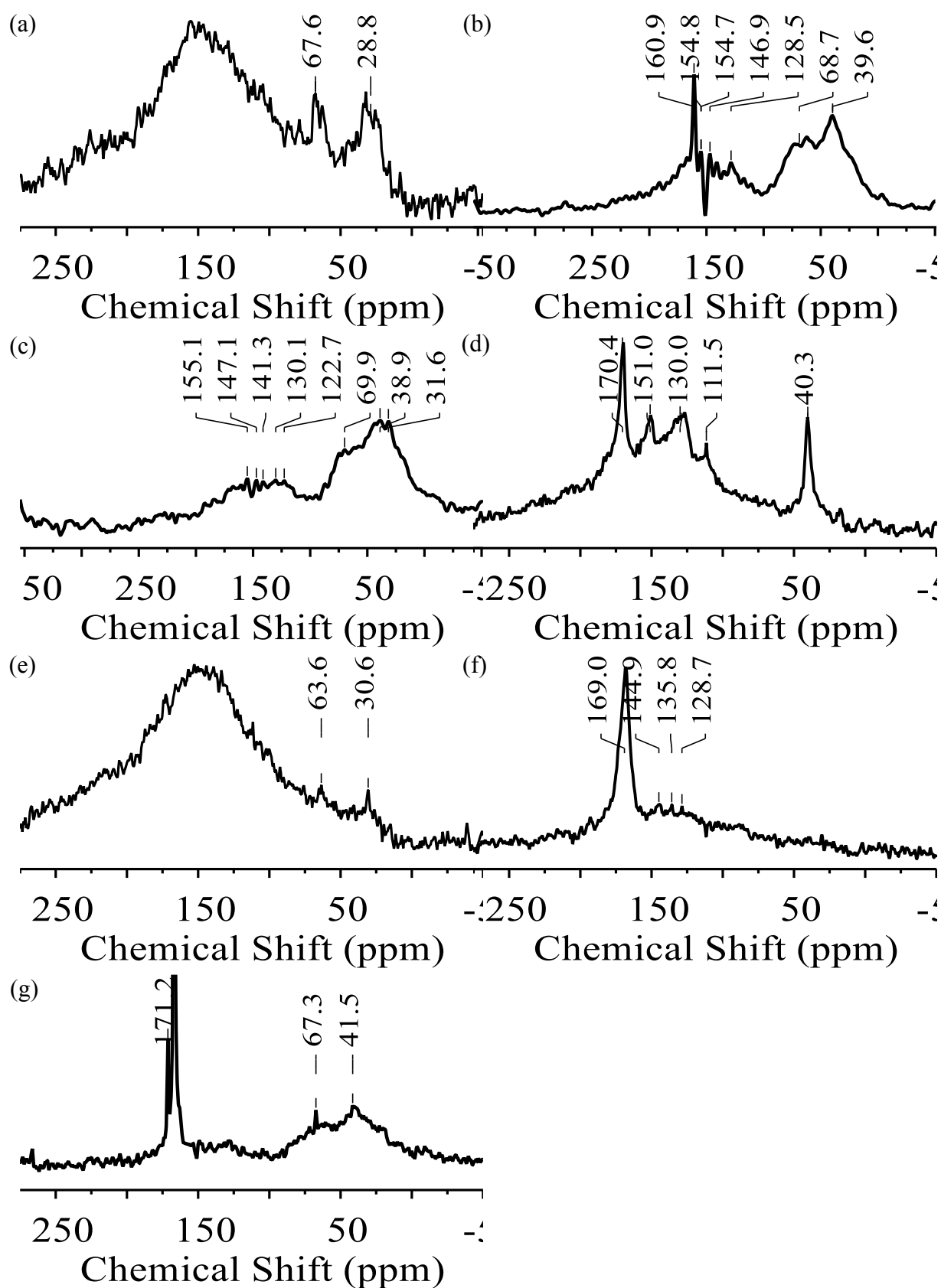


Figure 3.15: ^{13}C CP MAS SSNMR of (a) Si_{4.1} (b) Si_{4.2} (c) Si_{4.3} (d) Si_{4.6} (e) Si_{4.7a} and (f) and (g) both display Si_{4.7b} modified silica.

Figure 3.14 and Figure 3.15 display the ^{13}C CP MAS, cross-polarisation magic-angle spinning, spectra of the unmodified and modified silica nanoparticles. The spectrum of Si_4.6, which has until now demonstrated the highest degree of functionalisation to silica, indicates the presence of the modifier by the assignment of the benzene rings at $\sim 112\text{--}151$ ppm and the dimethyl amino groups at ~ 40 ppm. An unassigned peak can also be observed at ~ 170 ppm, presumably as a result of contamination. These peaks are unobserved on pristine silica, which displays a spectrum of only broad background noise. The spectrum for processed silica also shows broad background noise peaks, but additionally two small peaks at 48 ppm and 30 ppm can be detected, presumably as result of solvent residues from the modification procedure. Acetone, for example, used to wash the silica nanoparticles after the modification, is expected at ~ 31 ppm, $(\text{CH}_3)_2\text{CO}$, and ~ 206 , $(\text{CH}_3)_2\text{CO}$.³⁵ Methanol is reported at ~ 48 ppm,³⁵ however this solvent was not used in the modification procedure and so it is a bit surprising for it to be present on the processed silica samples. For reference, the solvents used in the modification procedures were THF for Si_4.1 and Et_2O for processed silica and the rest of the modified samples. Peaks at ~ 25 ppm and ~ 68 ppm for THF, and at ~ 15 ppm and ~ 66 ppm for Et_2O ,³⁵ would be anticipated if these residual solvents from the modification step remained on the samples.

The spectrum for Si_4.2 also denotes the presence of the modifier, however an extra peak can be observed at ~ 69 ppm. This peak could be assigned to a Si-O-C bond, reported at 66 ppm,³⁶ which would affirm covalent attachment of the modifier. It could also be assigned to residual Et_2O , however this cannot be easily established due to the broad nature of the spectrum in the region of the expected second peak for this solvent. Si_4.3, which by XPS, TGA and CHN has displayed very low loadings of modification, however

indicates largely the same peaks as Si_4.2, with an added acetone contaminant peak at ~32 ppm.

The first spectrum of Si_4.7b, Figure 3.15.(h), is dominated by a peak at 169 ppm, however the presence of the benzene rings, at 129-145 ppm, can also be detected. The experiment was therefore rerun to see if peaks at lower chemical shifts could be identified. Figure 3.15.(i) indeed confirms modification by the detection of a peak at ~42 ppm, for the dimethyl amino functionality, and also a peak at ~67 ppm, for the Si-O-C linkage (or Et₂O). The peak at ~169 ppm can be attributed to Na₂CO₃ which has been reported at 168.9 ppm.³⁵ This however, does not explain the presence of the peak in the same region at ~170 ppm, on sample Si_4.6. This is presumably due to sample contamination, peaks in this region are expected to be from carbonyl groups present in acids or esters. It was considered that this might be the result of physisorbed benzophenone impurities, as this could explain the weight loss below 200 °C observed by TGA and the carbonyl contribution detected by XPS. However, a ketone carbonyl would be expected more downfield than the detected peak by SSNMR at ~170 ppm.

The spectra of the remaining two modified silica samples are less distinct with a high degree of background noise in both, presumably as a result of lower loadings of the modification. Si_4.1 and Si_4.7a each display peaks at ~29 ppm and ~31 ppm, respectively, which can be assigned to residual acetone, and peaks at ~68 ppm and ~64 ppm, respectively, which could again be assigned to residual solvents or tentatively to the Si-O-C bonds.

The general low density of the surface functionalisation performed and the presumed modification mechanism (O-H bond insertion) means that the ²⁹Si SSNMR spectra of the unmodified and modified silica are not expected to present significant results. Nonetheless, a few silicon NMR experiments, ²⁹Si CP MAS and ²⁹Si DP MAS (direct-

polarisation) were performed and are included in the Appendix. Indeed, the spectra demonstrated no major shifts in the contribution of silicon sites present in the modified silica. However, these results do demonstrate the failure of the extra pre-modification procedure of the $\text{Na}_2\text{CO}_3(\text{aq})$ treatment for Si_4.7b, undertaken with the aim of reducing the presence of Si-OH surface groups.

3.3.2. CB Nanoparticle Characterisation

Surface analysis, by XPS, thermal analysis, CHN and ATRIR, was performed to evaluate the success of the chemical functionalisation routes used to modify the CB. Samples prepared include variants of CB_5.1-5 modified by carbene insertion through treatment with diazo compound **3** prepared in repeated synthetic procedures. Modified CB_5.5 was further functionalised by azo-coupling of diazonium salts terminated with hexyl and dodecyl groups to give CB_10a and CB_10b, respectively. For the second modification step, the diazonium salts were added at an estimate of 2 equivalents to the modifier present on CB_5.5. Therefore, for two-step modified CB_10a-b, it is likely that there will be some variation of functionality that can be introduced as a monolayer coverage to the surface, as shown in Figure 3.16 below.

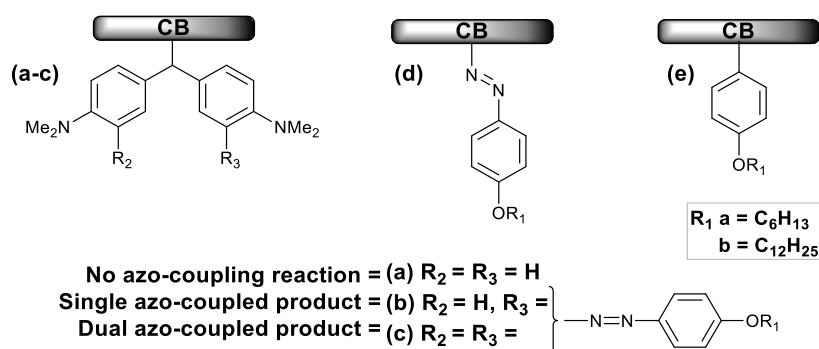


Figure 3.16: Potential functionalised surface CB_10a-b following the two-step carbene insertion and diazonium coupling reactions: (a) unsuccessful diazonium coupling (same surface as CB_5.5) (b) single azo-coupling to single aromatic ring on CB_5.5 surface (c) dual azo-coupling to both aromatic rings on CB_5.5 (d) azo-coupling directly to the CB surface (e) C-C linkage to CB surface. Adapted with permission from the American Chemical Society © 2016.¹³

Some areas of the CB surface may remain unchanged following exposure to the diazonium salt solution, retaining the surface of CB_5.5 (Figure 3.16(a)), or the unmodified CB surface. Otherwise, the diazonium coupling step is expected to occur at one or both of the rings on CB_5.5, due to the electron donating effect from each of the NMe₂ groups present, to give single or dual insertion products (Figure 3.16(b-c)). Additionally, direct azo-coupling to CB (Figure 3.16(d)), by reaction directed from the phenolic groups present on the graphitic surface, has been reported,¹⁰ as well as C-C linkage (Figure 3.16(e)) initiated by the reduction of diazonium cations by the graphitic surface.^{37, 11} However, in both instances, as the reaction with the diazonium salt is the second step onto pre-functionalised CB_5.5, it is expected that any direct linkages to the CB surface to be minimal.

3.3.2.1. BET

Nitrogen surface area analysis was performed on the as-received pristine CB nanoparticles and the adsorption and desorption isotherms can be found included in the Appendix. The average BET surface area was found to be 72.5 m²/g. The average pore diameter is 360.5 Å with a t-plot micropore volume of 0.004 cm³/g and a t-plot micropore surface area of 10.1 m²/g, revealing the t-plot external surface area to be 62.5 m²/g.

3.3.2.2. SEM and TEM Analysis

CB_Processed was produced as a control sample, in which the CB was subjected to the modification procedure in absence of the diazo precursor modifier, similar to Si_processed. One important consideration during the modification procedure is the sonication step, used to aid an even coating of the modifier onto the nanoparticles. It is widely reported that sonication damages carbon nanotubes, but the general consensus is that it does not affect CB.^{38, 39} Consequently, pristine and processed CB were sent for SEM (Figure 3.17) and TEM (Figure 3.18) analysis to test this hypothesis.

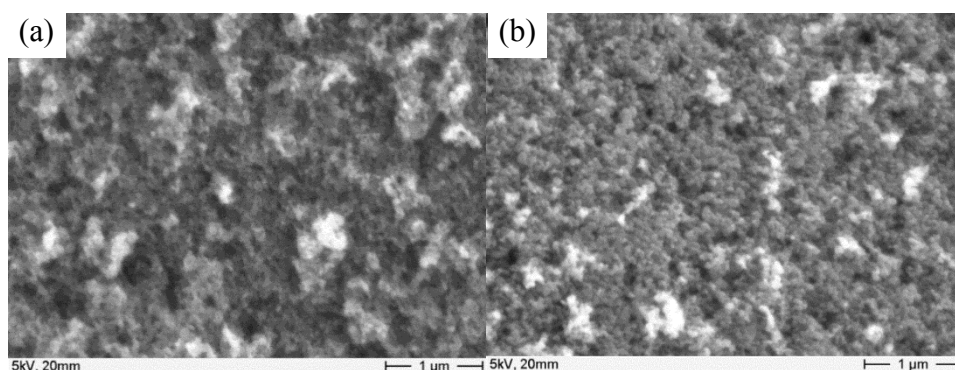


Figure 3.17: SEM images of (a) Pristine and (b) Processed CB nanoparticles at 1 μm resolution.

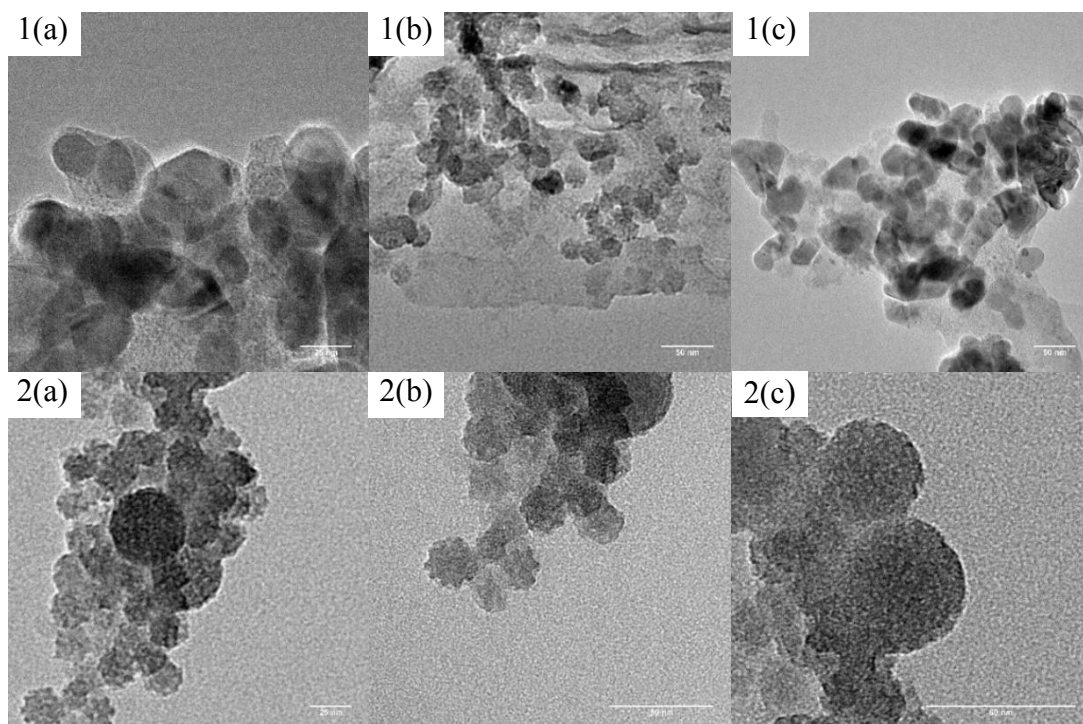


Figure 3.18: TEM images of 1. CB_Pristine at (a) 25 nm, (b-c) at 50 nm and 2. CB_Processed at (a) 25 nm and (b) 50 nm and (c) 60 nm resolution. The CB was dispersed in a solution of toluene for the TEM measurement.

It is evident from the SEM images (Figure 3.17) that the CB is quite agglomerated for both the pristine and processed CB, but the individual particles can still be seen for both samples and indeed the particles are the same size after sonication (30-40 nm). The TEM images, taken with the CB in toluene, suggest on the other hand that in solution the CB agglomerates have been broken during the sonication step. Nonetheless, the TEM images also indicate that the particle size has remained unchanged, which is an important result if the nanoparticles are to be used after modification for nanocomposite applications.

3.3.2.3. XPS

The elemental composition and graphitic character of the CB was assessed by X-ray photoelectron spectroscopy (XPS) to provide further evidence of successful functionalisation by carbene insertion reactions.⁴⁰ The main features on the wide spectrum of pristine and processed CB include a dominant C 1s photoemission peak at ~285 eV binding energy and a small O 1s peak at ~532 eV binding energy, as shown in Figure 3.19.

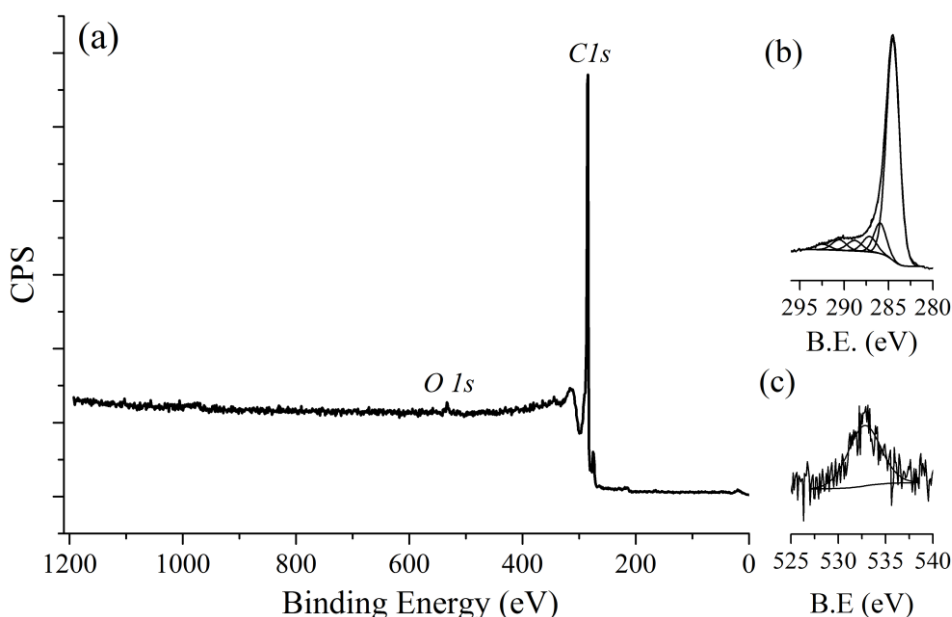


Figure 3.19: XPS spectra of CB_Pristine including (a) a survey scan and high resolution scans of the (b) C 1s region and (c) O 1s region.

Oxygen functionalities are a characteristic surface component of many types of CB and carboxylic, lactonic and phenolic groups are reported to be present on the CB used.⁴¹ On this basis, reaction at the surface with diarylcarbenes might be expected to lead to the formation of benzhydryl esters and ethers along with C-C and C-H insertion products.

Accordingly, the determined relative elemental abundance by XPS analysis of carbon, oxygen and nitrogen for pristine, processed and modified CB are included in Table 3.10. Further information, including the peak binding energy, charging and FWHM are included in the Appendix.

Table 3.10: Chemical Percentage of the carbon, oxygen and nitrogen composition of pristine, processed and modified CB by XPS analysis. Adapted with permission from the American Chemical Society © 2016.¹³

Sample	XPS (%)			N/C
	C	O	N	
CB_Pristine	98.4	1.6	n.d. ^a	
CB_Processed	97.2	2.8	n.d.	
CB_5.1	92.1	5.4	2.5	0.027
CB_5.2	87.4	12.0	0.6	0.007
CB_5.3	94.5	4.6	0.9	0.009
CB_5.4	82.3	15.2	2.6	0.031
CB_5.5	96.5	2.1	1.4	0.015
CB_10a	92.7	6.9	0.4	0.004
CB_10b	91.8	7.1	1.1	0.012

^a n.d., not detected.

The major XPS result is established by the detection of the nitrogen species introduced at 0.4-2.6 % to the CB surface following the carbene and azo-coupling functionalisation procedures (Table 3.10). Analogous to the silica XPS results, all variants of the modified CB_5.1-5 displayed notable features in the N 1s region at ~400 eV binding energy, owing to the NMe₂ group inserted onto the CB surface. Additionally, the high resolution scans of N 1s components (Figure 3.20) present an improved peak to noise ratio compared to the modified silica XPS results (Figure 3.10).

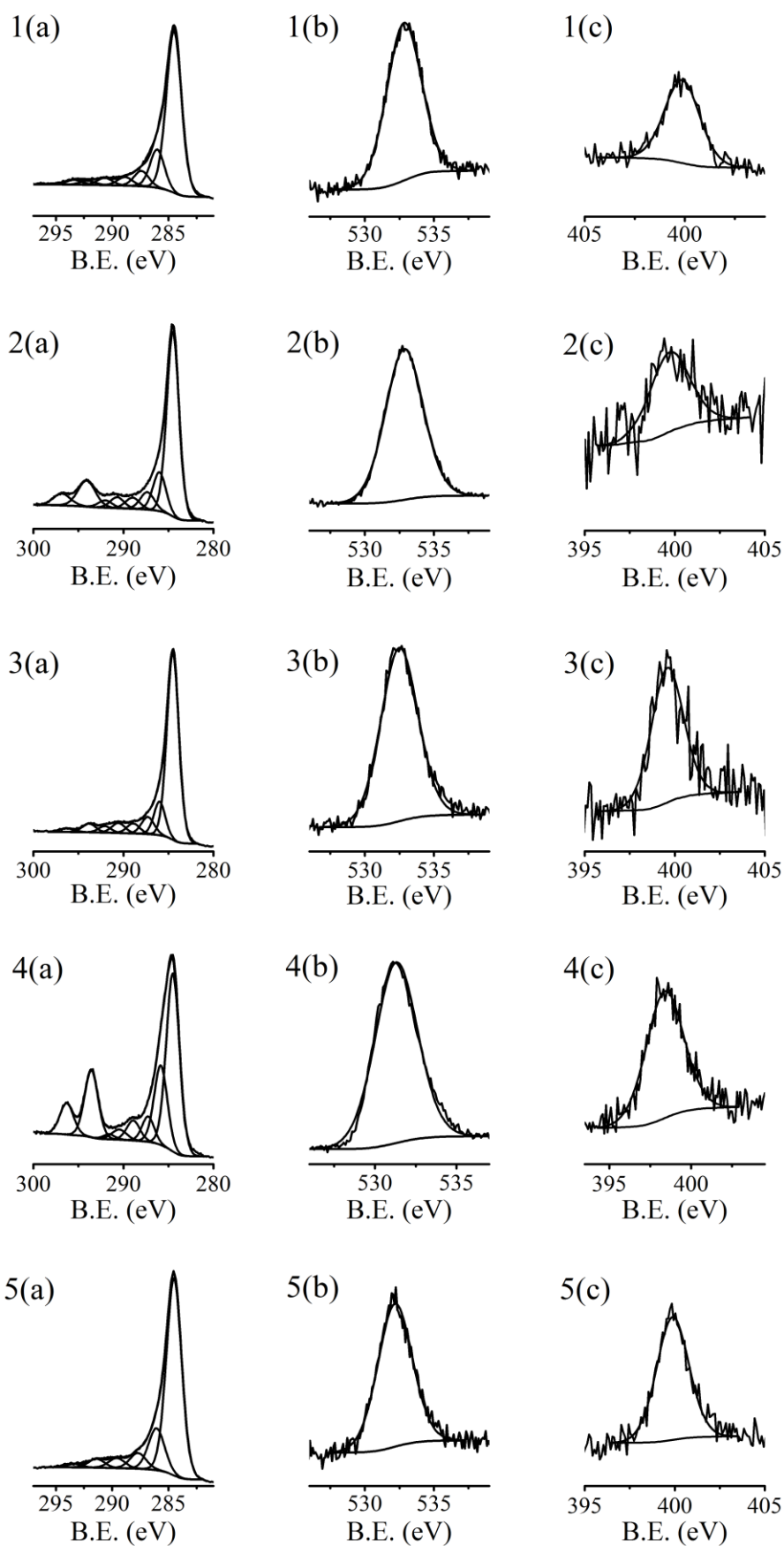


Figure 3.20: High resolution scans of (a) C 1s (b) O 1s and (c) N 1s of modified CB nanoparticles 1. CB_5.1; 2. CB_5.2; 3. CB_5.3; 4. CB_5.4; 5. CB_5.5.

Two-step modified CB_10a-b each display a N 1s peak at 400.0 eV and 400.6 eV binding energies, respectively, as shown in Figure 3.21, below. This can be attributed to the NMe₂ and additional N=N functionality present on the modified surface, consistent with detected azo linkage reported elsewhere.³

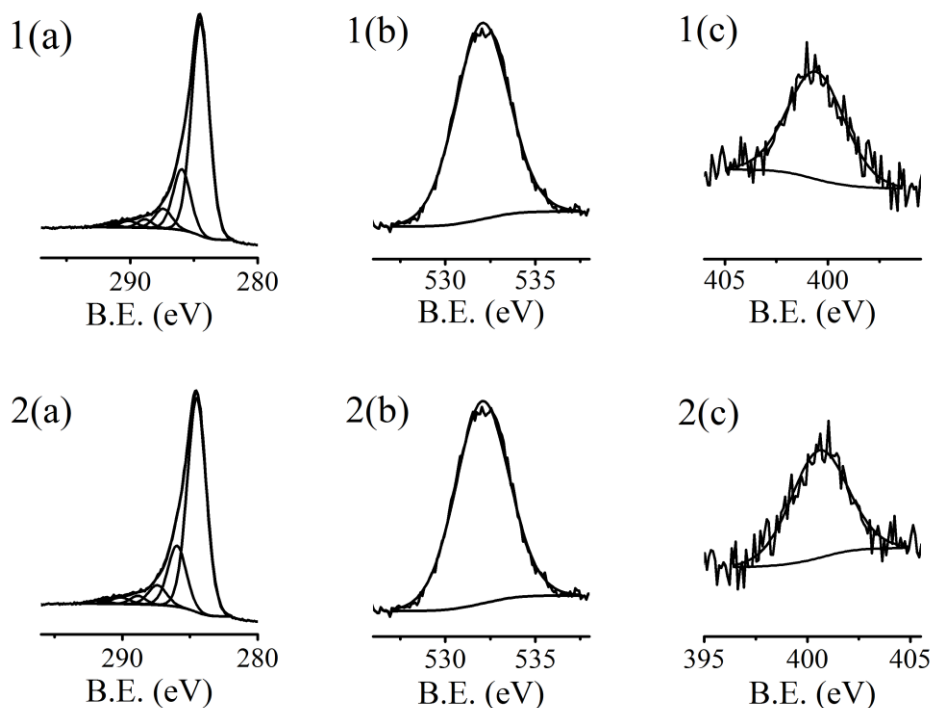


Figure 3.21: High resolution scans of (a) C 1s (b) O 1s and (c) N 1s of two-step modified carbene and azo-coupled CB nanoparticles 1. CB_10a and 2. CB_10b.

High resolution spectra of the C 1s region allows devolution into 6 photoelectron peaks of different chemical environments, including a first asymmetric peak at a binding energy of ~ 284.5 eV (C-C, C-H), to which the spectra were all charge-corrected to.¹⁰ This dominant devolved peak identifying the aliphatic contribution is typical for graphitic surfaces like CB.⁴² Further contributions are present from carbon coordinated to oxygen and nitrogen, with peaks at ~ 286.0 eV (C-O, C-N, ± 0.1 eV), ~ 287.4 eV (C=O, ± 0.3 eV) and ~ 289.1 eV (COOH, ± 0.3 eV) binding energies. Finally, weaker π - π^* features can be observed at ~ 290.9 eV (π - π^* , ± 0.3 eV) and ~ 292.3 eV (π - π^* , ± 0.5 eV). These 6 peaks are all present on pristine CB, Figure 3.19, as well as the modified CBs, Figure 3.20 and Figure 3.21.

The relative peak areas of the devolved C 1s peaks before and after modification, as well as the expected changed surface contribution, can be compared as shown in Table 3.11.

Table 3.11: Relative peak areas of devolved C 1s peaks in the high resolution spectra. Adapted with permission from the American Chemical Society © 2016.¹³

Sample	C-C/C-H (284.5)		C-N/C-O (285.9)		C=O COOH (287.3) (289.0)		π - π^* (290.6)	π - π^* (292.2)
	Found	(Expected)	Found	(Expected)	Found	Found	Found	(Expected)
CB_Pristine	74.4		9.8		5.5	4.2	4.0	2.2
CB_Processed	74.8		11.0		5.9	3.6	3.1	1.6
CB_5.1	69.8	(66.7)	15.5	(11.1)	6.4	3.6	3.1	1.7 (22.2)
CB_5.2	66.2	(66.7)	14.7	(11.1)	7.1	4.6	4.4	3.0 (22.2)
CB_5.3	70.4	(66.7)	12.0	(11.1)	6.8	4.1	4.2	2.6 (22.2)
CB_5.4	56.3	(66.7)	25.1	(11.1)	7.3	6.3	3.6	1.4 (22.2)
CB_5.5	70.1	(66.7)	15.8	(11.1)	6.0	3.8	3.2	1.2 (22.2)
CB_10a	64.2	(76.7)	17.5	(3.3)	9.0	4.5	3.4	1.5 (20.0)
CB_10b	69.4	(82.0)	19.2	(2.6)	6.1	2.2	2.0	1.0 (15.4)

It is evident that after the performed carbene and diazonium coupling modifications, there is a general decreased C-C, C-H contribution and an increased C-N, C-O contribution, compared to pristine and processed CB, which is consistent with the functionality introduced to the surface. Comparing the one-step carbene modified, CB_5.1-5, and the resulting two-step azo-coupled products, CB_10a-b, the C-C and C-H contribution is expected to increase, due to the introduction of terminal hexyl and dodecyl hydrocarbon chains, coupled with a reduction to the C-N and C-O contributions. However, this is not noticeably evident, which is likely due to the sensitivity of the XPS as well as the added complication of the irregular pristine CB surface. The peak areas from C=O and COOH functionality range from 5.5-9.0 % and 2.0-4.4 %, respectively, across the modified and unmodified samples. It is not expected for this functionality to differ between the pristine and modified CB considering the performed surface modifications. It is therefore presumed that the variation of this contribution is a reflection of the irregularity of the original pristine CB surface. The π - π^* peak areas can provide information on the changes of the graphitic nature of the CB surface.⁴⁰ The relative peak areas of the π - π^* contribution in Table 3.11 range from 2.7-3.9 % and 1.0-2.2 %, respectively from each

π - π^* contribution, across the modified and unmodified samples. It should be expected that a monolayer surface coverage of the diaryldiazo and azo-coupling modification might not significantly alter the existing π - π^* contribution from the CB substrate at the surface and near surface region analysed by XPS. As such, no correlation between the found and expected π - π^* peak areas for the modified CB samples was observed.

Pristine CB showed a small elemental percentage of oxygen, 1.6 %, at ~532 eV, attributed to C-O and C=O functionality present on the original CB surface. The modified CB samples all displayed an increase in the detected oxygen content. The increased oxygen content of processed CB and modified CB samples of 2.1-15.2 % is attributed to moisture or contaminants physisorbed during the modification procedure and storage, as no oxygen functionality was added in the carbene functionalisation route. For two-step modified CB_10a-b, the detected oxygen content of 6.9 % and 7.1 %, compared to 2.1 % for the pre-azo coupled CB_5.5, is consistent with the introduced ether linker functionality in the modification procedure. It is however, worth noting that this oxygen increase, could also be a result of CB oxidation side-reactions in the acidic conditions of the azo-coupling reactions to CB_5.5.

3.3.2.4. *Thermal Analysis*

TGA analysis of the functionalised CB nanoparticles indicates a large variation of weight loss profiles in a similar result to the modified silica (Figure 3.22, Table 3.4). The pristine, processed and modified CB samples CB_5.1, CB_5.5 and CB_10b showed a similar weight loss, 0.5-1.0 %, in the temperature range 30-200 °C, due to degassing and volatilisation of water or residual solvents.¹¹ Samples CB_5.2-4 alternatively displayed defined step weight losses ~5 % in this temperature range, which is likely to be due to physisorbed contaminants. In the 200-800 °C temperature range, Figure 3.22, shows the significant weight loss for the functionalised CB samples compared to pristine CB and

this is attributed to the thermal decomposition, or cleavage, of the covalent modifications, which is in agreement with the reported thermal stability of similar covalent bound moieties on carbon-based substrates.^{4, 43}

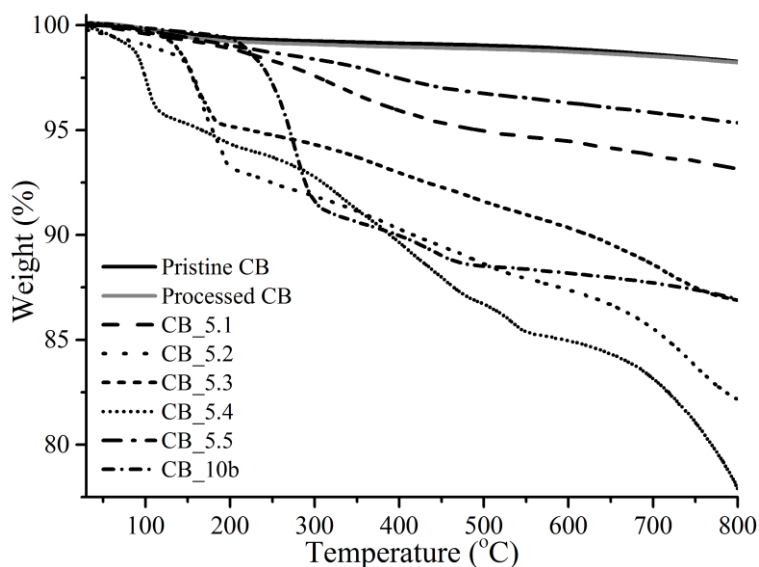


Figure 3.22: TGA thermogram of pristine and modified CB nanoparticles under nitrogen flow. Adapted with permission from the American Chemical Society © 2016.¹³

Table 3.12: Thermogravimetric analysis of pristine and modified CB nanoparticles. Adapted with permission from the American Chemical Society © 2016.¹³

Sample	TGA Weight Loss (%)					
	30-200 °C		200-500 °C		500-800 °C	
	%	(S.D)	%	(S.D)	%	(S.D)
CB_Pristine ^a	0.5	(0.0)	0.3	(0.0)	0.8	(0.0)
CB_Processed ^a	0.7	(0.1)	0.4	(0.0)	0.7	(0.1)
CB_5.1 ^b	1.0	(0.1)	5.5	(2.1)	1.8	(0.0)
CB_5.2 ^b	5.9	(0.1)	4.3	(0.1)	6.3	(0.0)
CB_5.3 ^b	4.8	(0.0)	3.6	(0.0)	4.7	(0.0)
CB_5.4 ^b	5.7	(0.3)	6.0	(2.0)	7.6	(1.6)
CB_5.5 ^b	1.0	(0.0)	2.3	(0.0)	1.4	(0.0)
CB_10b ^c	0.7	-	10.9	-	1.6	-

^a Results are an average of 3 repeat runs by TGA.

^b Results are an average of 2 repeat runs by TGA.

^c Results from 1 TGA experiment.

For pristine and processed CB, above 500 °C to the end of the TGA run, ~850 °C, a small similar weight loss can be observed and generally this can be ascribed to the loss of appreciable non-graphitic fractions present on the CB.⁴⁴ CB_5.1, CB_5.5 and CB_10b samples again display a similar weight loss to the unmodified CB in this temperature region, suggesting the removal of the majority of the organic modification, if not all.⁴

To further determine the difference between the modified CB nanoparticles by the same carbene precursor, Figure 3.23 below, displays the separate TGA, DTG and DSC curves of pristine, processed and the modified CB nanoparticles and Table 3.13, includes a summary of the extracted data from the simultaneous thermal analysis.

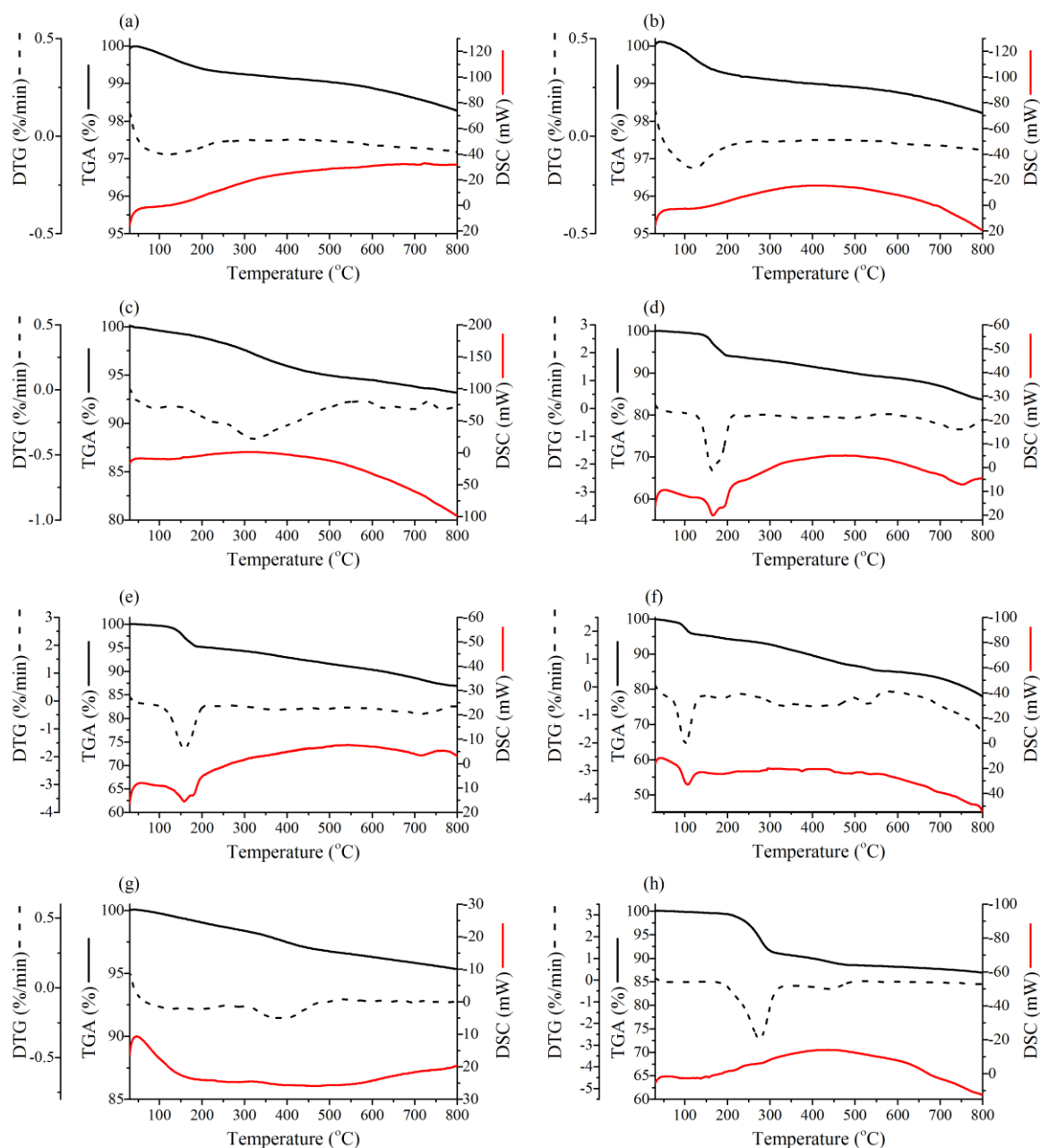


Figure 3.23: Thermal analysis data displaying TGA, DTG and DSC curves of (a) CB_Pristine (b) CB_Processed (c) CB_5.1 (d) CB_5.2 (e) CB_5.3 (f) CB_5.4 (g) CB_5.5 and (h) CB_10b CB nanoparticles. Note STA analysis was not performed for CB_10a.

Table 3.13: Extracted TGA, DTG and DSC peak data from thermal analysis runs (30-800 °C) of unmodified and modified CB nanoparticles. The thermal events for each sample are labelled, denoted with a numbered superscript, with the same numbers when the same thermal event was observed by the different analysis techniques. The same TGA and DTG thermal events observed in multiple samples are organised in the same columns, and the major DTG peak corresponding with the loss of the modifier is in bold.

Sample	TGA Onset (°C)							DTG Peak (°C)					DSC (°C)				
	T _o ^a	T _o	T _o	T _o	T _o	T _o	T _o	T _p ^b	T _p	T _p	T _p	T _p	T _p	T _p	T _o	T _p	T _p
	Impurity	Modification	Imp. ^c	Water/ Solvent	Impurity	Imp./ Mod. ^d	Modification	Imp.	Impurity								
CB_Pristine				119.3 ¹													
CB_Processed				119.1 ¹													
CB_5.1		241.6 ²				215.1 ¹	323.0 ²										
CB_5.2	148.5 ¹	348.5 ³	672.6 ⁵		164.6 ¹ 184.2 ¹		242.1 ² 380.6 ³ 487.1 ⁴	749.6 ⁵ 138.6 ¹ 164.9 ¹ 182.1 ¹ 753.0 ⁵									
CB_5.3	134.6 ¹	323.8 ²	657.4 ⁴		157.2 ¹		369.1 ² 490.1 ³	719.0 ⁴ 119.2 ¹ 158.7 ¹ 178.7 ¹ 716.2 ⁴									
CB_5.4	88.0 ¹	162.5 ²	288.0 ³ 514.0 ⁴ 760.3 ⁵		101.0 ¹	185.3 ²	328.2 ³ 532.4 ⁴	86.2 ¹ 105.2 ¹									
CB_5.5		335.2 ¹					388.2 ¹										
CB_10b		237.1 ¹ 403.5 ²					217.3 ¹ 439.2 ² 275.4 ¹										

^a T_o, onset temperature.
^b T_p, peak temperature.
^c Imp. = impurity.
^d Mod. = modification.

The STA results of pristine and processed CB display, as discussed above, the decomposition of the water and volatiles at the beginning of the thermal run, paralleled by DTG peaks for both samples at 119 °C. First, discussing the modified CB nanoparticles that displayed the more similar TGA weight loss profiles: CB_5.1, CB_5.5 and CB_10b. CB_5.1 show a small TGA one-step weight loss with an onset decomposition temperature of 241.6 °C, results mirrored by a broad DTG peak at 323.0 °C. A second small DTG maximum at 215.1 °C was observed, which could be the result of the complex decomposition of the modifier or the presence of contaminants. Sample CB_5.5 also displayed a TGA one-step weight loss with an onset decomposition temperature of 335.2 °C, with a DTG peak at 388.2 °C. Two-step modified CB_10b presents a two-step weight loss, with onset temperatures of 237.1 °C and 403.5 °C, respectively. Corresponding DTG peaks were observed at 275.4 °C, with a shoulder at 217.3 °C and a second peak maximum at 439.2 °C. The peak areas of the DTG peaks can be integrated to determine the specific mass in the weight loss step, giving 0.57 mg and 0.06 mg for each of the peaks, respectively. The mass of the second weight loss step of CB_10b is comparable to the mass loss calculated in the DTG peak observed at 388.2 °C for CB_5.5 of 0.05 mg. This strongly indicates that the second weight loss step in CB_10b can be attributed to the decomposition process, or part of it, of the carbene modification, which demonstrates a higher thermal stability on CB_10b of ~50 °C compared to CB_5.5 due to the presence of the second azo-modification. The first more prominent weight loss step for sample CB_10b is therefore likely due to the cleavage of the azo-coupling step. This result strongly indicates the success of the two-step reaction following the procedure with diazonium salts.

The other 3 modified CB samples CB_5.2-4 display quite different weight loss patterns, with additional peaks observed in the DSC curves as well. First CB_5.2 and CB_5.3 both

display large TGA onsets at 148.5 °C and 134.6 °C, with DTG peaks at 164.6-184.2 °C and 157.2 °C and endothermic DSC curves with onset temperatures of 138.6 °C and 119.2 °C. In this temperature range (30-200 °C), this thermal event is unlikely to be the cleavage of surface functionalisation, but rather the presence of physisorbed surface impurities. Second, they each show complex weight loss patterns, evident by the number of DTG peaks. Nevertheless, it is worth highlighting for each of the samples, CB_5.1 and CB_5.5, the similarity of the TGA onset peaks at 348.5 °C and 323.8 °C, and subsequent DTG peaks at 380.6 °C and 369.1 °C, respectively, which is likely due to the removal of the modification. Last, at the end of the thermal program DTG peaks at 749.6 °C and 719.0 °C and endothermic DSC peaks at 753.0 °C and 716.2 °C, indicate the decomposition of an extra surface component, in line with the high mass of loss 6.3 % and 4.7 %, compared to samples CB_5.1, CB_5.5 and CB_5.10b, which displayed mass losses in the range of 1.4-1.8 % close to unmodified CB, 0.7-0.8 %. These peaks are likely to be the result of contaminants rather than due to the performed modification as both CB_5.2 and CB_5.3 revealed a lower surface nitrogen content compared to CB_5.1 and CB_5.5 by XPS.

Sample CB_5.4 also demonstrates a complicated mass loss pattern, with a prominent weight loss step at the beginning of the thermogram. The TGA onset of 88.0 °C and subsequent DTG peak at 101.0 °C and endothermic DSC peak at 105.2 °C. Together they suggest a different surface contaminant to the modified CB_5.2 and CB_5.3 samples. Other peaks observable in the TGA curve at 162.5 °C and at 760.3 °C at the end of the run suggest further surface contamination. However, the comparable TGA onset peak at 288.0 °C, and DTG peak at 328.2 °C on CB_5.4 to the other functionalised CB can be attributed to the loss of the modification.

Unfortunately, the black appearance of unmodified, modified and STA tested CB means visual evidence of charring cannot be determined, as it was for the silica nanoparticles.

Therefore, to find out if the modification was removed following thermal treatment, XPS analysis was performed to CB_5.1 and CB_5.5 retrieved after TGA analysis. Figure 3.24 indicates the loss of the nitrogen species by the survey scan of CB_5.5, however it is not fully lost as 0.9 % relative elemental abundance remains on the CB surface, as established by the small N 1s peak in the high resolution XPS scan, Figure 3.24 (insert). Indeed, CB_5.1 also indicated that some of the surface modification survives the thermal treatment (Table 3.14).

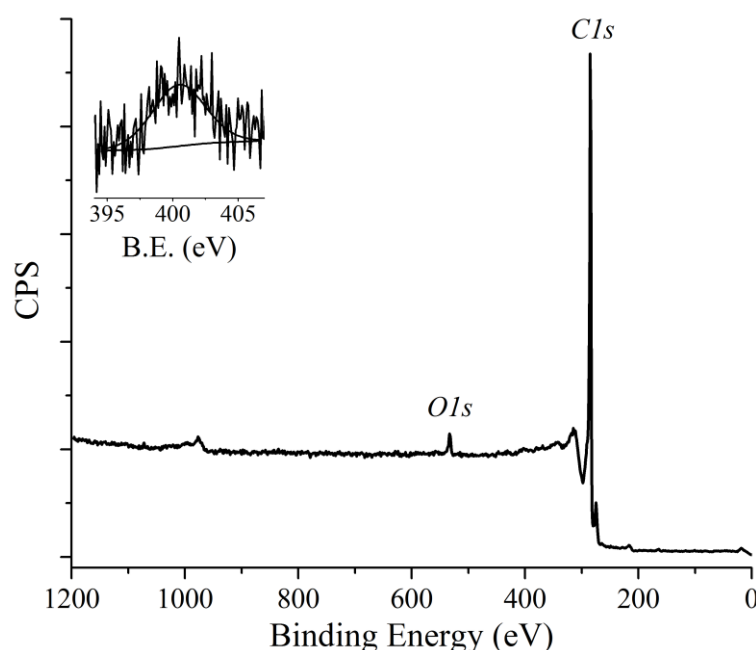


Figure 3.24: XPS Survey scan of modified Si_5.5 following treatment by thermal analysis (insert shows the high resolution scan of the N 1s region).

Table 3.14: The chemical percentage of carbon, oxygen and nitrogen composition of pristine and modified CB_5.1 and CB_5.5 nanoparticles after thermal treatment (30-800 °C) by XPS analysis.

Sample	XPS (%)			N/C
	C	O	N	
CB_Pristine	98.7	1.3	n.d.	
CB_5.1	95.8	3.2	1.0	0.010
CB_5.5	96.8	2.3	0.9	0.009

Nevertheless, the TGA thermograms still demonstrate the loss of the majority of the covalent modification. Accordingly, the percentage weight loss of the modified CB can be compared to pristine CB during the major decomposition of the surface modification,

as observed by TGA in the 200-800 °C temperature range, to calculate the number of molecules present on CB (Table 3.15). The theoretical surface modification loading would be 2.3×10^{-3} moles/g, which is 1.9×10^{15} molecules/cm², in the event of maximum carbene insertion at 59.9 % by weight addition to the CB substrates. The theoretical estimates by this assumption for each of the tested CB samples are included in Table 3.15. Additionally, the limiting area of the carbene modifier, as calculated using Chemicalize predictive software,³⁴ indicates the maximum loading for a monolayer surface coverage is estimated at 2.1×10^{14} molecules/cm².

Table 3.15: Calculated surface modification loadings of modified CB nanoparticles as calculated for the determined mass losses by thermal analysis experiments. Adapted with permission from the American Chemical Society © 2016.¹³

Sample	TGA Weight Loss (%)		Surface Loading ^a	
	Sample Wt. Loss due to Modification (g)	Theoretical Wt. Added due to Carbene Modification (g)	Moles Surface Modification /g CB	Molecules /cm ²
CB_5.1	6.5×10^{-4}	4.7×10^{-3}	2.1×10^{-4}	1.8×10^{14}
CB_5.2	1.8×10^{-3}	4.6×10^{-3}	6.9×10^{-4}	5.7×10^{14}
CB_5.3	1.5×10^{-3}	4.8×10^{-3}	5.1×10^{-4}	4.3×10^{14}
CB_5.4	2.2×10^{-3}	4.6×10^{-3}	8.6×10^{-4}	7.1×10^{14}
CB_5.5	3.9×10^{-4}	4.7×10^{-3}	1.3×10^{-4}	1.0×10^{14}
CB_10b ^b	8.7×10^{-4}	4.5×10^{-4}	2.4×10^{-4}	2.0×10^{14}
CB_10b ^c		6.9×10^{-4}	1.6×10^{-4}	1.3×10^{14}

^a Assumes a monolayer surface coverage of the experimentally determined BET CB surface area, 72.5 m²/g.

^b The estimated number of modifier molecules/cm² calculation assumes single azo-coupling reactions of the diazonium salt to pre-modified CB_5.5, as shown in Figure 3.16(b).

^c The estimated number of modifier molecules/cm² calculation assumes dual azo-coupling reactions of the diazonium salt to pre-modified CB_5.5, as shown in scheme Figure 3.16(c).

TGA analysis estimates the surface loading to be in the range of 2.4×10^{13} to 1.3×10^{14} molecules/cm², successfully in the region of the estimated monolayer surface coverage and a comparable result to the previous work using diaryldiazo modifications.³ The TGA data from CB_10b can be used to assess whether single or dual azo-coupling, or direct insertion to the CB surface, to the pre-modified CB_5.5 is taking place (Figure 3.16(a-e)). According to the performed functionalisation, the modification loading would be expected to be 7.2×10^{-3} moles/g corresponding to complete conversion of the carbene

modification and azo-coupling reaction to the CB_10b sample. For a more accurate estimation, from the calculated surface loading by TGA of 1.0×10^{14} molecules/cm² for CB_5.5, the expected weight loss of CB_10b can be estimated at 4.5×10^{-4} g and 6.9×10^{-4} g for single or dual insertion products, respectively. The measured weight loss of CB_10b by TGA was found to be 8.7×10^{-4} g, suggesting that the dual insertion modification mechanism pre-dominates for the pre-functionalised CB_5.5.

3.3.2.5. CHN

Further qualitative evidence by CHN confirmed the presence of nitrogen following surface modification for all the modified CB samples except CB_5.2 and CB_5.3, consistent with the low nitrogen content found by XPS (Table 3.16).

Table 3.16: Combustion analysis of pristine and modified CB nanoparticles and calculated surface modification loadings. Adapted with permission from the American Chemical Society © 2016.¹³

Sample	CHN Data (%)			N/C Ratio	No. of N Atoms /Molecule of Surface Modification	Surface Loading	
	C	H	N			Moles /g	Molecules /cm ²
CB_Pristine	96.46	1.15	0.00		0		
CB_Processed	96.82	0.91	0.00		0		
CB_5.1	93.37	0.77	0.76	0.008	2	2.7×10^{-4}	2.3×10^{14}
CB_5.2	78.31	0.72	0.00		2		
CB_5.3	82.16	0.69	0.00		2		
CB_5.4	56.34	1.33	0.69	0.012	2	2.5×10^{-4}	2.1×10^{14}
CB_5.5	95.24	1.19	0.77	0.008	2	2.8×10^{-4}	2.3×10^{14}
CB_5.5	94.85	0.63	0.54	0.006	2	1.9×10^{-4}	1.6×10^{14}
CB_10a	95.19	0.91	0.40	0.004	4 ^d	7.1×10^{-5}	5.9×10^{13}
					6 ^e	4.8×10^{-5}	4.0×10^{13}
CB_10b	91.81	1.63	0.91	0.010	4 ^d	1.6×10^{-4}	1.4×10^{14}
					6 ^e	1.1×10^{-4}	9.0×10^{13}

^a Ratios calculated from the detected C and N found on the modified CB nanoparticles by CHN analysis. The measurable detection limit of CHN is <0.1%.

^b CHN surface loading calculated from the detected nitrogen content present on the modified CB nanoparticles and the known number of nitrogen atoms present in the modifier introduced to the surface during the functionalisation routes.

^c Assumes a monolayer surface coverage of the experimentally determined BET CB surface area, 72.5 m²/g.

^d Estimation for single azo-coupling reaction (Figure 3.16(b)).

^e Estimation for dual azo-coupling reaction to pre-modified CB_5.5 (Figure 3.16(c)).

The detected nitrogen content was used to estimate the surface loading (Table 3.16), again assuming a monolayer surface coverage of the experimentally determined CB BET surface area (72.5 m²/g). CHN estimates the surface loadings on CB to be in the range of

4.0×10^{13} to 1.9×10^{14} molecules/cm², which is in good agreement with the TGA estimated surface coverage, within the same order of magnitude.

3.3.2.6. ATR-IR

ATR-IR analysis of the two-step modified CB_10b, with the highest surface modification, further established the introduction of new functionality (Figure 3.25).

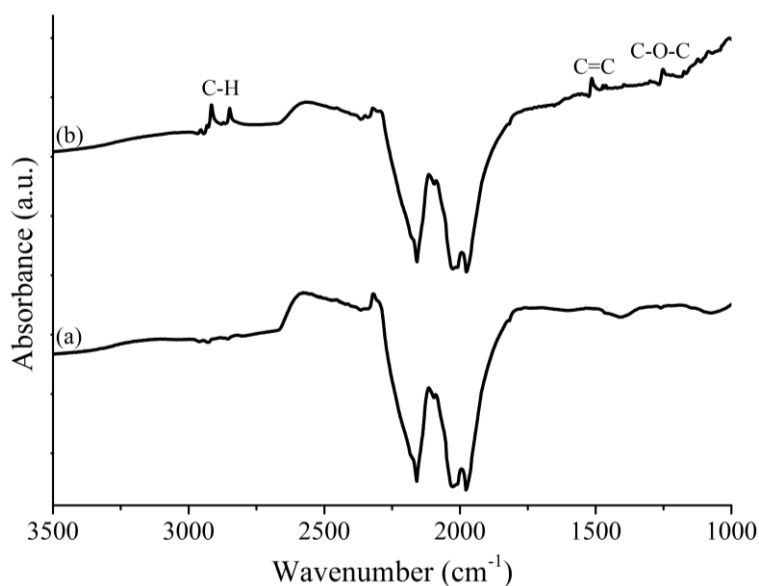


Figure 3.25: ATR-IR spectra of (a) CB_Prisitine and (b) modified CB_10b. Adapted with permission from the American Chemical Society © 2016.¹³

Characteristic C-H symmetric and asymmetry bending bands were identified at ν 2916 cm⁻¹ and ν 2849 cm⁻¹ respectively, presumably from the introduction of the dodecyl hydrocarbon chain added in the diazonium coupling step. Further, a stretching band at ν 1514 cm⁻¹ corresponded to aromatic C=C and can be attributed to the benzene rings, and an aryl alkyl asymmetric stretch can be observed at ν 1251 cm⁻¹ from the introduced C-O-C functionality in the diazonium coupling reaction, all of which are not observed for pristine CB. Unfortunately, the *trans* azo N=N stretching vibration in the 1400-1500 cm⁻¹ region is typically rendered inactive on the IR spectrum⁴⁵ and therefore, as expected, was not observed. The presence of functional groups for the other modified one-step and two-step CB samples could not be detected, presumably a result of being below the sensitivity

limit for the ATR-IR instrument. In addition, CB as a substrate is known to be difficult for ATR-IR spectroscopy, as it is an effective absorber and its high refractive index is also close to that of the diamond accessory.⁴⁶

3.4. Concluding Remarks

In summary, silica and CB nanoparticles were modified using the precursor diazo compound, 4,4-*bis-N,N*-dimethylaminophenyldiazomethane, in repeated synthesis procedures. A secondary azo-coupling step was performed to one of the pre-modified CB samples using diazonium salts terminated by ether linkers with hexyl and dodecyl hydrocarbon chains. The degree of functionalisation to the nanoparticles was characterised by XPS, TGA, CHN, SSNMR and ATR-IR measurements. This preliminary investigation into nanoparticle modification has led to a number of conclusions:

- The large variation of the modified silica and CB nanoparticles is not directly correlated to changes made to the diazo synthesis procedure, for example CB_5.1 and CB_5.5 displayed very similar TGA and XPS data. The reactive nature of the diazo compound meant the synthesis procedure was difficult, but also the reaction of the silica and CB substrates was changeable. For example, Si_4.2 and CB_5.2 were both modified by the same synthesised diazo compound in procedure 2, but whereas Si_4.2 demonstrated a relatively high surface loading compared to the other modified silica nanoparticles, CB_5.2 was the opposite.
- The nanoparticle characterisation highlights contamination from the modification synthesis as detected in XPS, SSNMR and thermal analysis. This might be a result of chelation to the NMe₂ functionalisation present on the modified nanoparticle surfaces. However, for further work with diaryl carbene modifications, a more vigorous washing procedure with acetone might be necessary to help reduce the level of surface contamination.

- The N-label functionality of the modifier enabled direct evidence of the introduction of nitrogen to the silica and CB nanoparticle surfaces, confirmed by XPS and supported by CHN analysis results.
- SSNMR and XPS analysis presented evidence of the covalent linkage of the modification by the detection of Si-O-C and Si-C bonds for the functionalised silica nanoparticles. The degree of modification, characterised foremost by XPS and TGA, but also supported by CHN and SSNMR measurements, was Si_4.6>Si_4.2>Si_4.1>Si_4.7a>Si_4.3. For Si_4.7b, it is evident that the surface was functionalised, as confirmed by SSNMR analysis. However, the modification was not enhanced by the pre-modification step by treatment with Na₂CO₃(aq), which remained on the silica as confirmed in the thermal analysis measurements.
- The degree of modification for the CB nanoparticles, established predominately from the XPS and CHN results, and supported by the thermal analysis, was found to be: CB_5.4>CB_5.1>CB_5.5>CB_5.2 and CB_5.3. The thermal analysis results of CB_5.2 and CB_5.3 indicate a high degree of contamination, by the large weight loss steps observed towards the beginning and end of the thermal runs. CB_5.4, also displayed a prominent weight loss step at the start of the thermal program due to another surface contaminant, however the relatively high nitrogen content found by XPS and CHN nevertheless indicates a high degree of functionalisation at the surface.
- The labile nature of the Si-O-C bond in the carbene reaction to the silica nanoparticles meant secondary diazonium coupling reactions were not performed. On the other hand, the success of the second step modification of CB_5.5 by azo-coupling to CB_10a-b, was established by XPS analysis thanks to the changed nitrogen content and increased oxygen content following the treatment with the

prepared diazonium salts. Analysis of CB_10b by thermal analysis and ATRIR, further confirmed the two-step modification, establishing the higher degree of functionalisation compared to the carbene-only modified samples. TGA weight loss profiles also indicated the improved thermal stability of the carbene modification. This two-step modification therefore presents a viable route for the introduction of hydrophobic groups to the surface of CB.

The performed characterisation of the modified silica and CB nanoparticles demonstrates the changed surface chemistry following functionalisation procedures using carbene and diazonium salts. This study therefore demonstrates the potential for this strategy in the pursuit of tailored nanoparticle surfaces for nanocomposite applications.

3.5. References

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4. Tailored Carbene Functionalisation - Route B

4.1. Introduction

This chapter further explores covalent nanoparticle functionalisation routes in the pursuit of controlling their surface chemistry, to improve compatibilisation in polymer nanocomposites. Chapter 3 demonstrated the potential for reactive carbene insertion chemistry and diazonium coupling reactions for the tailored functionalisation of silica and CB nanoparticles. In this work, an alternative carbene synthesis strategy has been adopted with the aim of introducing extended hydrocarbon chains directly to the particle surfaces in a one-step approach, eliminating the need for secondary diazonium coupling reactions. Additionally, the modification approach has been expanded to a number of substrate types, namely microsilica (MP), acetylene black (ACB) and multi-walled carbon nanotube (MWCNT) as well as nanosilica (NP) and Carbon Black (CB), as used in Chapter 3.

Expanding the silica modification to microparticles presents an opportunity to test the versatility of this modification process as a general method for the introduction of hydrophobic properties to hydrophilic surfaces. Additionally, silica microparticles might be expected to be easier to functionalise for application in polymer composites because the agglomerates tend to be less tightly bound, associated with the general lowered surface energy, compared to nanosilica.¹ This study therefore presents an opportunity to compare the different silica types following the preliminary investigation in the previous chapter.

The work in Chapter 3 successfully demonstrated the potential for carbene functionalisation for carbon black (CB) and it is a key aim to develop this work further here-in, along with the modification of acetylene black (ACB) and multi-walled carbon

nanotubes (CNTs). Carbon Blacks, such as ACB and CB, present a distinct advantage over many other prevalent carbon nanomaterials, including CNTs, graphene and nano-onions, as they are substantially more economical to produce in bulk quantities.² Additionally, CBs demonstrate valuable properties, typical for carbon-based nanomaterials, such as high surface areas and promising electrical conductivity.³ The specific surface properties of the CBs, including the surface functionalities, surface area and structure types, are primarily governed by the manufacture method which is employed.⁴ The CB in this work (and previously used in Chapter 3) is a furnace CB, a common CB type produced by the incomplete combustion of hydrocarbon before quenching by water and is known to be of low structure.⁵ ACB on the other hand, prepared by the decomposition of acetylene gas, is of a high structure type and exhibits a high degree of crystallinity.^{6, 7} Using ACB in this work therefore presents an opportunity to functionalise the highest quality subtype of Carbon Black. The differences between the CB subtypes will likely have direct consequences on the resulting polymers nanocomposites, it is therefore desirable to also assess the versatility of the carbene surface modification of these nanomaterials.

Nevertheless, due to their exceptional function as a filler in polymer nanocomposites, CNTs have attracted an enormous research into their superior electronic, structural, mechanical and thermal properties – that are associated with their high aspect ratio – compared to conventional carbon-based nanofillers, such as CB.⁸ However, as with CB, the promise of CNTs is inhibited by their tendency to exist in bundles due to strong intermolecular forces, dramatically reducing the usability of this high quality carbon nanomaterial.⁹ Accordingly, functionalisation methods to manipulate the advantageous surface and bulk properties of CNTs are an expanding area of research.¹⁰ However, many covalent functionalisation routes that have been shown to create defects in the nanotube walls, which can dramatically reduce their valuable conductive properties.^{11, 12} This is an

important consideration for nanocomposites for electrical conductivity applications, however the extent of the damage is highly dependent upon type and magnitude of the employed modification approach. The low surface reactivity of CNTs, due to the curved graphene-like arrangement of the hexagon rings, has challenged research efforts in the pursuit of less aggressive side-wall functionalisation methods.¹³ SWCNTs have previously been modified by diaryldiazo chemistry, as discussed in the introduction of Chapter 3.¹⁴ The low surface loadings (10^{12} - 10^{14} molecules/cm²)¹⁵ of this type of functionalisation approach is expected to negate the usual disadvantages of covalent modifications, presenting a promising approach for the surface modification of CNT.

4.1.1. Aims of the Project

A second route, Route B, was developed to tailor the surface chemistry of selected silica and carbon-based nanomaterials for nanocomposite applications. This approach entails the introduction of sterically stabilising alkyl chains in a four-step synthesis to functionalise the nanoparticles, using a more direct route by a single diazo modification step.

The principal aims for this section of research include:

- To synthesise diarylcarbene derivatives terminated in hydrocarbon chains which are variable in length, for the surface modification of a range of nanomaterials;
- To evaluate the success of the surface functionalisation, without the aid of an element marker inserted onto the surface, using any of BET, thermal analysis, SSNMR, XPS, CHN and ATR-IR analysis techniques;
- To determine if this approach presents an opportunity for tailored surface functionalisation on nanomaterials for use in nanocomposite technology.

4.2. Experimental Details

4.2.1. Materials

Microsilica (Si_MP) was purchased as Merck Geduran Si 60 silica gel (40-63 μm) and nanosilica (Si_NP, 10-20 nm, density 2.2-2.6 g/mL) from Sigma-Aldrich. Commercial Monarch[®] Carbon Black (CB, M 430, 27 ± 10 nm, density 1.1 - 1.9 g/cm³) was supplied by Cabot Corporation (Billerica, MA, USA) and acetylene black (ACB, AB50P) was provided by IRPC Ltd., Thailand. Multi-walled carbon nanotube powder (CNT, diameter 80-85 nm, length 10-15 μm) was sourced from Graphene Supermarket. All other reagents used were supplied from Alfa Aesar Chemicals Ltd., Sigma-Aldrich Chemicals and Lancaster Chemicals Ltd.

4.2.2. Preparation of Organic Compounds for Nanoparticle Functionalisation

The diaryldiazo compound **14a-b**, terminated by alkyl chains, was prepared in a four-step procedure (Figure 4.1), Route B.

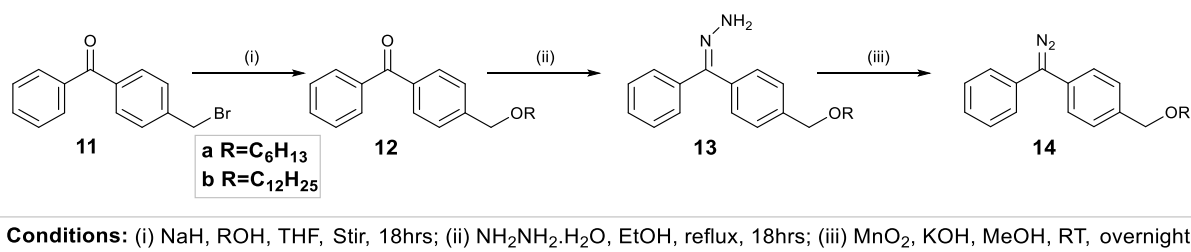


Figure 4.1: Synthetic scheme of the preparation of Route B modification. Adapted with permission from the American Chemical Society © 2016.¹⁶

4-Bromomethyl benzophenone, **11**, was for the most part provided by Oxford Advanced Surfaces Ltd. but was otherwise prepared using the literature procedure, by the reaction of 4-methyl benzophenone with recrystallized NBS in chloroform under overnight reflux in the presence of a light bulb.¹⁷ A Williamson ether reaction with 4-bromomethylbenzophenone and hexanol or dodecanol generated hydrocarbon-terminated

diaryl ketocompounds **12a-b**, as yellow oils. Purification by silica chromatography was challenging due to the non-polar nature of the product and impurities, but nonetheless gave **12a** and **12b** as a colourless oil and light yellow oil, respectively, in reliably good yields in repeat procedures (50-56 %). Treatment with hydrazine monohydrate under reflux overnight afforded the hydrazone derivatives as a mixture of *syn-/anti*-diastereoisomers, **13a-b**, which were both yellow oils. The crude hydrazone products **13a-b** are not acid stable and therefore could not be purified by column chromatography. Unfortunately, in some cases it was evident by NMR analysis that small amounts of an alcohol by-product were formed. This has previously been observed in other similar works,¹⁸ and it is attributed to the oxidation of aging hydrazine monohydrate to the presence of diimide (HN=NH), which is known to reduce ketones to alcohol products.¹⁹ Finally, oxidation of the hydrazone products with manganese dioxide led to the target diazo compounds **14a-b** as characteristic dark pink oils (93-98 %).

4.2.3. Carbene Modification

The Route B hydrocarbon terminated diaryldiazo compound **14** is less reactive than the *bis*(dimethylamino)diaryl diazo **3** that was presented in Chapter 3. Nonetheless, the general reactive nature of diazo compounds means there is opportunity for azine interconversion. The modification reaction was therefore performed either immediately after preparation of the diazo compound or the diazo was stored in the freezer. Nanoparticles were modified by the same procedure as detailed in Chapter 3: addition of the diazo compound **14a-b** and the selected nanoparticles in Et₂O, 30 min sonication, and solvent removal *in vacuo* to give the diazo coated substrates. Finally, thermal decomposition of the labile precursor diazo *in situ* generates dinitrogen and the reactive carbene, which irreversibly surface modifies the nanoparticles. As the reaction progressed in the oil bath, the loss of the distinctive pink colour of the coated silica could be

observed, indicative of the decomposition of the diazo compound. The modification reaction procedure was the same for the different substrates, except the CNTs, which were sonicated for only 10 min. The alteration was made because it has been widely reported that sonication damages this nanomaterial type.²⁰

A summary of the performed modification reactions using hexyl and dodecyl-terminated diaryldiazo modifiers **14a-b** are detailed in Figure 4.2 and Table 4.1, indicating the codes of the as-produced functionalised nanomaterials. The modification reactions of the nanomaterials were performed at high and low diazo loadings (Table 4.1). In particular, microsilica terminated in a hexyl hydrocarbon chain, Si_MP_15a, was modified at the two different surface loadings of 5 % and 20 % by weight diazo addition and the samples are therefore labelled as Si_MP_15a_5 and Si_MP_15a_20, respectively. Otherwise, the samples will be labelled only according to the nanomaterial (Si_MP-microsilica, Si_NP-nanosilica, CB-Carbon Black, ACB-acetylene black and CNTs-multi-walled carbon nanotubes), and modification types (15a-hexyl and 15b-dodecyl terminated diaryl complexes).

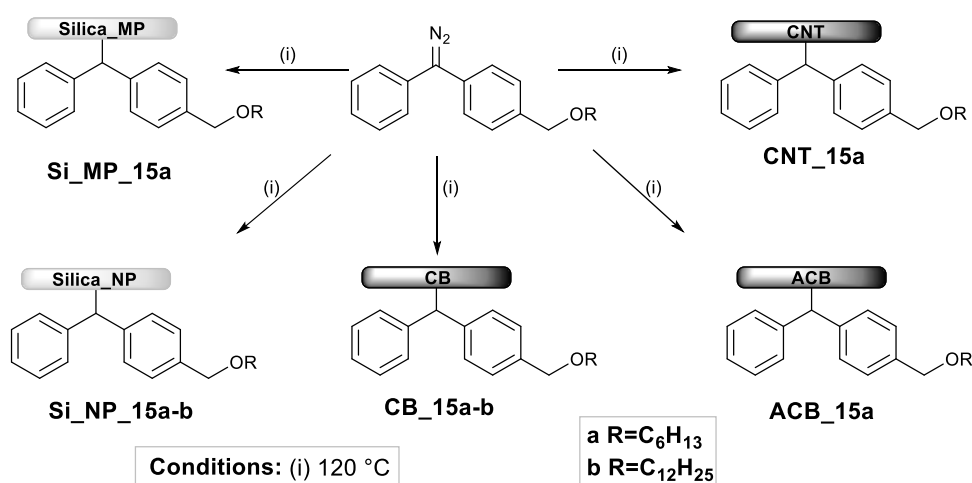


Figure 4.2: Scheme to show the performed modifications of microsilica (Si_MP), nanosilica (Si_NP), Carbon Black (CB), acetylene black (ACB) and multi-walled nanotube (CNT), and the codes that will be used to refer to these modified substrates.

Table 4.1: Details of the performed modifications of hexyl and dodecyl terminated diaryldiazo compounds (**14a-b**) to silica and carbon-based particles.

Diazo Precursor	Percentage Addition of Diazo Modification (Wt. %)				
	Microsilica Si_MP_15a	Nanosilica Si_NP_15a-b	Carbon Black CB_15a-b	Acetylene Black ACB_15a	Multi-Walled Carbon Nanotubes CNT_15a
Hexyl-terminated 14a	5, 20	16	66	10	5
Dodecyl-terminated 14b	-	16	66	-	-

4.3. Results and Discussion

The modified silica and carbon-based nanomaterials were analysed using the same surface analysis techniques as presented in Chapter 3 in order to determine to the success of the carbene modification. The modifiers used in this chapter, however, present a challenging investigation because the inserted chemistry does not include a nitrogen label, which was previously a useful element marker in the characterisation of the modified nanofillers in Chapter 3.

4.3.1. Silica Nanoparticle Surface Characterisation

Modified Silica microparticles and nanoparticles, including hexyl terminated Si_MP_15a_5 and Si_MP_15a_20, and hexyl and dodecyl modified Si_NP_15a-b, were analysed by BET, STA, XPS, CHN and SSNMR techniques, as detailed in this section.

4.3.1.1. BET

Nitrogen surface area analysis was performed on the as-received, pristine silica microparticles, and both hexyl modified Si_MP_15a samples, modified at loadings of 5 % and 20 %, and the adsorption and desorption isotherms are included in the Appendix. Pristine microsilica presents a high BET surface area of 450.4 m²/g, and the hysteresis indicates a mesoporous material with an average pore diameter of 64.6 Å, as included with additional information in Table 4.2.

Table 4.2: BET summary data of pristine microsilica, hexyl modified microsilica (Si_MP_15a), pristine nanosilica and dodecyl modified nanosilica (Si_NP_15b).

Sample	BET Surface Area (m ² /g)	t-Plot External Surface Area (m ² /g)	BJH Adsorption Average Pore Diameter (Å)	BJH Desorption Average Pore Diameter (Å)	BET Adsorption Average Pore Diameter (Å)
Si_MP_Pristine	450.4	482.8	62.4	57.4	64.6
Si_MP_15a_5	393.5	394.9	67.8	60.9	73.1
Si_MP_15a_20	396.8	406.9	67.6	60.3	72.4
Si_NP_Pristine	168.7	139.7	242.8	257.6	-
Si_NP_15b	146.5	149.6	296.8	319.7	-

Comparing the BET results of the unmodified and modified microsilica particles it can be observed that following the treatment with the carbene modifier, the silica microparticles display a reduced surface area and an increased average pore diameter. This result suggests that the surface modification caps the micropores, preventing nitrogen adsorption in these regions of the silica, thereby reducing the detected BET surface area and altering the average pore size of the detected pores.²¹⁻²³ In terms of the effect of loading at 5 % or 20 % for the modified silica, the BET results indicate no substantial trend between the two modified samples.

Additionally, BET analysis was performed on the modified nanosilica Si_NP_15b, terminated by the dodecyl hydrocarbon chain (Table 4.2), adsorption and desorption isotherms can also be found in the Appendix. Equally, a reduction in the BET surface area and augmentation in the pore diameter can be observed for the modified nanosilica, presumably for the same reasons discussed for the microsilica.

4.3.1.2. Thermal analysis

Thermal analysis of the silica before and after treatment afforded the opportunity to determine the success of the functionalisation procedure, as well as important associated information including the thermal stability and degree of surface loading. In the previous chapter the visible charring of the silica nanoparticles after thermal analysis gave an immediate indication as to the presence and success of the surface modification. Once

more, Table 4.3 presents the photos of the silica samples in the alumina crucibles before and after the performed thermal analysis measurements in the STA instrument.

Table 4.3: Photos of unmodified and modified microsilica and nanosilica (~12 mg) in the crucible pans before and after STA analysis.

	Silica Samples							
	Si_MP_Pristine	Si_MP_Processed	Si_MP_15a_5	Si_MP_15a_20	Si_NP_Pristine	Si_NP_Processed	Si_NP_15a	Si_NP_15b
Before TGA								
After TGA^a								

^a The photos of all the samples, except Si_NP_15a, were taken from saved samples post thermal analysis.

The visible charring for two of the modified silica samples, Si_MP_15a_20 and Si_NP_15a, strongly suggests the success of the modification procedure, consistent with the incomplete combustion of the organic matter on the sample.²⁴ On the other hand, Si_MP_15a_5 and Si_NP_15b modified silica samples after the thermal program display the same white silica residue as the unmodified samples. This could suggest the surface modification was unsuccessful, but rather results from Chapter 3 indicated that the degree of charring was concomitant with the degree of surface modification, therefore it could mean that these latter samples had a lower surface loading, low enough to enable total volatilisation of the modification during the STA analysis.

The TGA, DTG and DSC thermal analysis results of pristine, processed and modified silica microparticles, Si_MP_15a_5 and Si_MP_15a_20, are displayed in Figure 4.3, and extracted key data in Table 4.4. Processed microsilica refers to the control sample of pristine microsilica, which has been subjected to the modification procedure without the addition of the precursor diazo modifier.

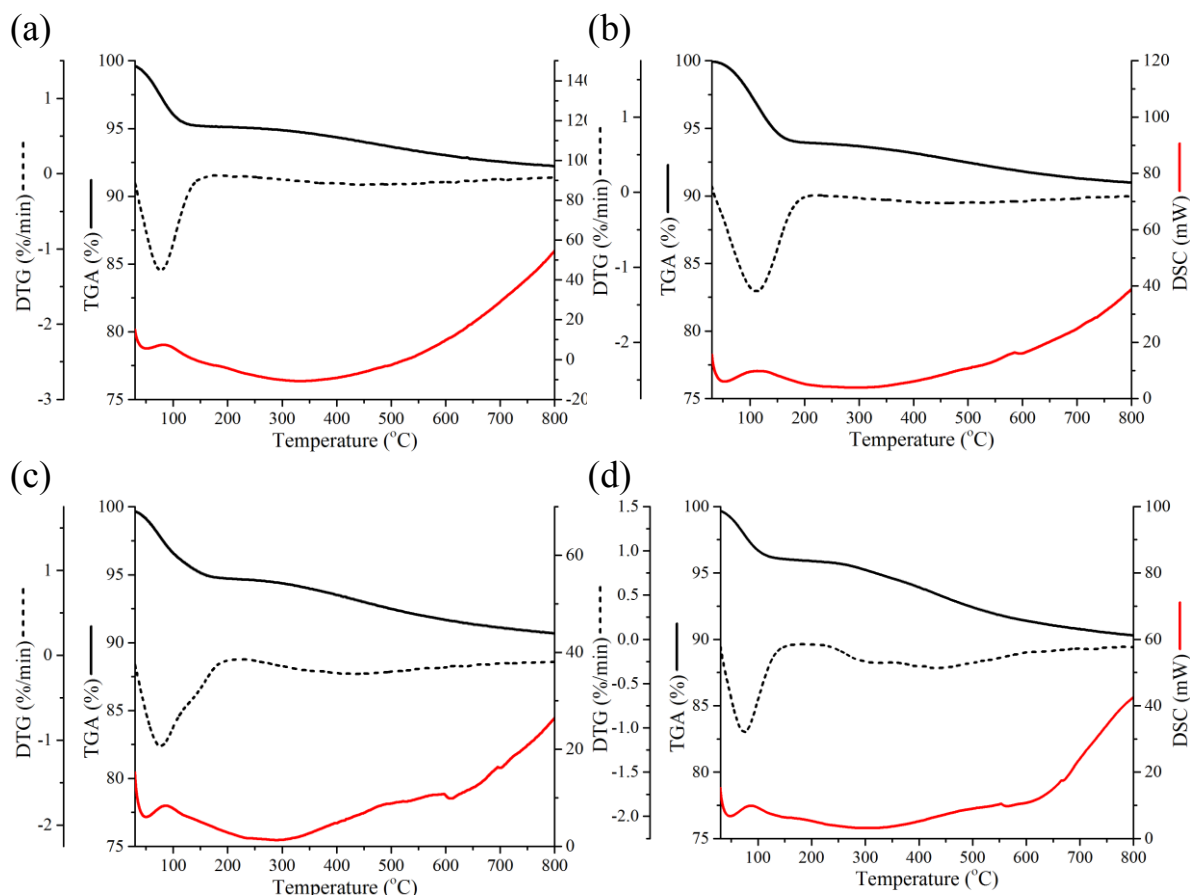


Figure 4.3: Thermal analysis data displaying TGA, DTG and DSC curves (heat flow endo down) of (a) Si_MP_Pristine (b) Si_MP_Processed (c) Si_MP_15a_5 and (d) Si_MP_15a_20 silica microparticles.

Table 4.4: Extracted TGA, DTG and DSC peak data from thermal analysis runs (30–800 °C) of microsilica and nanosilica. The thermal events for each sample are labelled with a numbered superscript, with the same numbers when the same thermal event was observed by the different thermal analysis techniques. The same TGA, DTG, DSC thermal events observed in multiple samples are organised in the same columns, and the major DTG peak corresponding with the loss of the modifier is in bold.

Sample	TGA Onset (°C)		DTG Peak (°C)								DSC (°C)	
	T _o ^a	T _o	T _p ^b	T _p	T _p	T _p	T _p	T _p	T _p	T _p	T _p	T _p
	Silanol Groups	Mod. ^c	N ₂	Water/Solvent	Impurity	Modification					Water/Solvent	Mod.
Si_MP_Pristine	299.7 ²			76.8 ¹							89.5 ¹	
Si_MP_Processed	329.8 ²			110.9 ¹							116.5 ¹	
Si_MP_15a_5		308.5 ³		77.9 ¹	140.9 ²		345.1 ³	434.3³	526.0 ³	588.0 ³	85.6 ¹	
Si_MP_15a_20		262.9 ²		75.1 ¹		294.2 ²	396.4 ²	436.4²	538.2 ²		87.6 ¹	
Si_NP_Pristine	267.0 ²			74.3 ¹								
Si_NP_Processed	287.0 ²			67.4 ¹								
Si_NP_15a_Mod			58.4 ¹									
Si_NP_15a		282.9 ²		81.0 ¹		280.1 ²	331.6 ²	374.2 ²	429.5²	522.3 ²	563.7 ²	
Si_NP_15b		312.5 ²		79.28 ¹		278.5 ²	333.5 ²	443.5²	499.7 ²	536.4 ²	87.6 ¹	483.4 ³

^a T_o, onset temperature.

^b T_p, peak temperature.

^c Mod., modification.

Pristine and processed microsilica display relatively similar thermograms, and therefore indicate that any observed altered thermal property changes for the modified microparticles can be attributed to the performed diazo treatment. In detail, pristine microsilica displays the decomposition of physically absorbed water at the beginning of the thermal programs by the TGA weight loss step, paralleled by a DTG peak at 76.8 °C and a DSC peak at 89.5 °C.²⁵ Processed microsilica displayed a slightly larger TGA weight loss step and shifted DTG and DSC peaks to 110.9 °C and 116.5 °C, likely a result of the removal of absorbed solvent residues as well as water.²⁶ Both pristine and processed microsilica display broad TGA weight loss steps at 299.7 °C and 329.8 °C, respectively, which can be attributed to the dihydroxylation of the silanol groups present on the silica.²⁷

Alternatively, the hexyl terminated modified silica microparticles at different loadings, Si_MP_15a_5 and Si_MP_15a_20, display additional peaks, indicative of the presence of the introduced organic moieties. Si_MP_15a_5, indicates the loss of adsorbed water and solvent residues by the TGA weight loss step and corresponding DTG and DSC peaks at 77.9 °C and 85.6 °C. A shoulder on the DTG peak at 140.9 °C suggests the decomposition of physisorbed surface contaminants at this temperature, perhaps due to residual unreacted starting materials unremoved during the washing procedure following the modification. However, above 200 °C, in the same temperature range that silanol dihydroxylation occurs, extra features can be observed in the broad TGA weight loss step by the observation of an altered onset at 308.5 °C, accompanied by a series of DTG peaks of which the principal is found at 434.3 °C. These additional features are attributed to the decomposition of the surface modification. Further, this result can be supported by the thermal analysis results of Si_MP_15a_20, modified at the higher loading of 20 wt. %, in

which the prominent TGA weight loss step at an onset of 262.9 °C is coupled with a number of DTG peaks, with the major peak maxima observed at 436.4 °C.

Thermal analysis measurements were also performed on the modified nanosilica, terminated with hexyl and dodecyl hydrocarbon chains, (Figure 4.4) and the derived data is also included in Table 4.5, above. Processed silica has not been presented here, but for reference the data has been included in Table 4.5 and the corresponding figures can be found in Chapter 3.

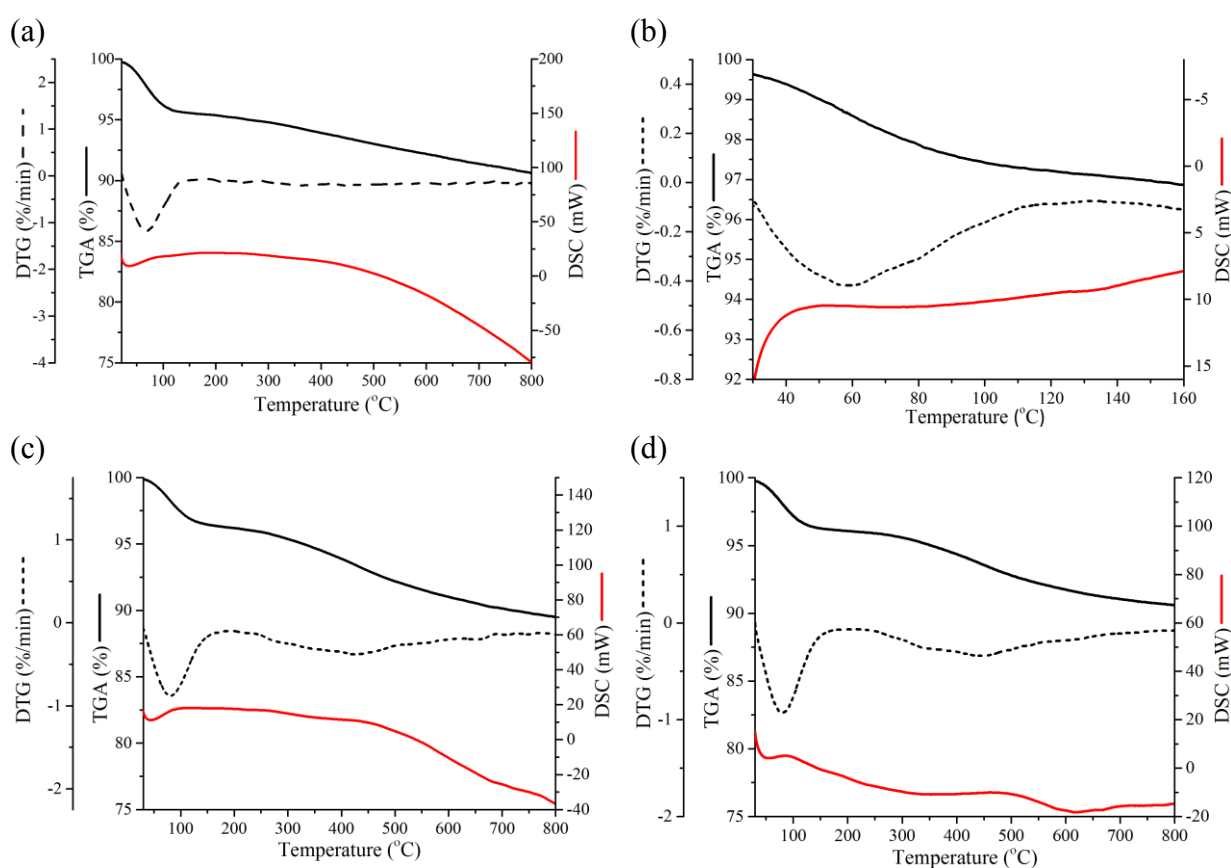


Figure 4.4: Thermal analysis data displaying TGA, DTG and DSC curves (heat flow endo down) of (a) Si_NP_Pristine (b) Si_NP_15a_Mod, in which the surface modification reaction was performed in the STA instrument of nanosilica coated in the diazo precursor **14a** (c) Si_NP_15a and (d) Si_NP_15b modified silica.

Pristine nanosilica, as presented in detail in Chapter 3, displays similar thermal analysis results as pristine microsilica. In addition to the analysis of the modified nanosilica samples, it was also of interest to see whether the carbene functionalisation reaction at the silica surface could also be observed by thermal analysis. Accordingly, a small sample of

nanosilica coated with diazo **14a**, with the hexyl termination, was subjected to a thermal program in the STA from 30 to 280 °C at a ramp rate of 10 °C min⁻¹. Unfortunately, the thermogram (Figure 4.4(b)) does not exhibit the insertion reaction, which is expected ~120 °C, and only a broad weight loss feature evident by the TGA and DTG patterns indicates the removal of water and residual solvents, as has otherwise been observed by pristine and modified nanoparticles. It may be that the tested ~6 mg of diazo coated silica nanoparticles was too low a sample mass for the reaction to be observed by the performed thermal analysis. Alternatively, the thermal analysis data of the modified nanosilicas denotes the success of the modification in similar results to modified microsilica. Si_NP_15a displays a broadened and larger TGA weight loss step with onset temperatures of 282.9 °C, corresponding to a number of DTG peaks with the main peak observed at 429.5 °C. This result is further paralleled by the dodecyl modified Si_NP_15b, in which the TGA onset from the modification decomposition is observed at 312.5 °C, reflected by a principal DTG peak at 443.5 °C.

Comparison of the TGA weight loss profiles between the unmodified and modified silica during the thermal program, 30-800 °C, indicates the percentage weight loss of the tested samples which can be attributed to the modification present on the silica. Further, the number of molecules per unit area can be estimated, taking into account the known surface modifier in each case, and the experimentally determined BET surface areas of microsilica (393.5 m²/g) and nanosilica (168.7 m²/g). Accordingly, the TGA weight loss data and calculated surface loading of the modified silica are presented in Table 4.5.

Table 4.5: Thermogravimetric analysis weight loss data and calculated surface modification loadings of microsilica and nanosilica.

Sample	TGA Weight Loss (%)					Surface Loading ^b		
	30-200 °C	200-500 °C	500-800 °C	Wt. Attributed to Modification (g)	Theoretical Wt. Added due to Carbene Modification (g)	Efficiency (%)	Moles Surface Modification /g CB	Molecules /cm ²
Si_MP_Prisine	4.5	1.5	1.2					
Si_MP_Processed	6.0	1.5	1.5					
Si_MP_15a_5	5.0	2.2	1.8	2.0×10^{-4}	5.4×10^{-4}	37	4.5×10^{-5}	6.8×10^{12}
Si_MP_15a_20	3.8	3.5	2.1	2.5×10^{-4}	1.9×10^{-3}	13	5.6×10^{-5}	8.6×10^{12}
Si_NP_Pristine ^a	4.3	2.2	2.1					
Si_NP_Processed ^a	4.5	2.4	2.1					
Si_NP_15a	3.7	4.0	2.7	2.3×10^{-4}	1.6×10^{-3}	15	6.7×10^{-5}	2.4×10^{13}
Si_NP_15b	3.7	3.3	2.2	8.0×10^{-5}	1.6×10^{-3}	5	1.8×10^{-5}	6.4×10^{12}

^a Results are an average of 3 repeat experiments. The rest of the measurements are from single thermal experiments.

^b Assumes monolayer surface coverage of the experimentally determined BET surface areas of Si_MP_Pristine (393.5 m²/g) and Si_NP_Pristine (168.7 m²/g).

It should be noted that the results in Chapter 3 indicated the continued presence of the modification for some CB samples after heating using same thermal program. It is therefore expected that the thermal program might not fully remove the modification of these analysed samples, and so the loading estimations should be considered as a lower bound estimation. Further, it can be observed for Si_NP_15a after thermal analysis (Table 4.3) that the charring is greatest at the centre of the sample in the crucible pan, demonstrating the thermal gradient experienced by the sample during the heating program and accordingly the strong likelihood that the modification has not been fully removed. This considered, the results of the modified silica indicate lower bound surface loadings in the range of 6.8×10^{12} - 2.4×10^{13} molecules/cm², a highly comparable result to diaryldiazo work literature and as reported in Chapter 3.¹⁵ It can also be observed that a small loading increase of 6.8×10^{12} to 8.6×10^{12} is evident for the micro-modified silica, likely associated with the diazo loading increase from 5 % to 20 % during the modification procedure. Additionally, at this point it is worth comparing the surface loadings to the observed charring of the silica samples following thermal analysis (Table 4.3), and indeed the lower loadings found for Si_MP_15a_5 and Si_NP_15b is consistent

with the two modified samples which were found to be uncharred after the heating program.

The efficiency calculation included in Table 4.5 provides the opportunity to compare the addition of the carbene modifier added to the silica surface and the resulting degree of modification as detected by TGA, determining a range in efficiency from 5 - 37 %. This variation is likely to be affected by the range of diazo additions used in the functionalisation procedures, 5 %, 16 % and 20 %, but will also be a result of the reactive nature of the carbene and precursor diazo compounds. The loading estimations of the number of molecules/cm² can otherwise be compared to theoretical estimations of the surface loadings that can be expected based upon the size of the modifiers, as determined by Chemicalize predictive software.²⁸ The limitation of these estimations is however also associated with the appropriate choice of the calculated projection area of the modifier compounds (Figure 4.5).

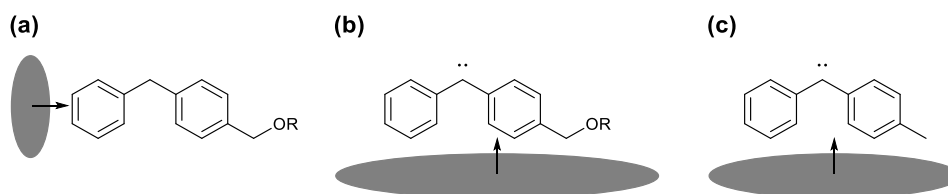


Figure 4.5: Potential projection areas for the carbene modifiers generated from the diazo **14a-b** precursor compounds.

Based on the carbene insertion mechanism to the substrates surfaces, it is evident that the minimal projection areas, as indicated in Figure 4.5(a), will provide inadequate information for these calculations. For the maximal projection areas, however, assessing whether the terminated hydrocarbon chains should be included in the calculations presents a challenge. It may be that steric hindrance from the hydrocarbon chains might mean that the entire modifier (Figure 4.5(b)) will influence the alignment of the modifier compounds or perhaps only the core diaryl section (Figure 4.5(c)) should be considered in

the calculation. To consider both possibilities, both assumptions are included in Table 4.6, below, for the theoretical estimations of the surface loadings of the modifications performed using **14a-b**.

Table 4.6: Theoretical calculations of the maximum number of molecules/cm² for the carbene modifier generated from the precursor diazo **14a-b**.

	Diazo Precursor 14a	Diazo Precursor 14b	Diaryl Core
	Figure 4.5 (b)	Figure 4.5 (b)	Figure 4.5 (c)
Maximal Projection area (Å ²)	96.4	128.8	63.9
Theoretical no. of molecules/cm ²	1.0×10^{14}	7.8×10^{13}	1.6×10^{14}

Despite the various parameters from which the theoretical loading estimations can be calculated, it is evident the difference is relatively small and most importantly both theoretical predictions are consistent with the calculated loadings by TGA. From this, the surface coverage can be estimated at 7 % or 4 % for Si_MP_15a_5, or 8 % or 5 % for Si_MP_15a_20, according to the theoretical estimation calculated using first the modifier (Figure 4.5(b)) or second the core diaryl complex (Figure 4.5(c)), respectively. For the silica nanoparticles, the surface coverages can be calculated at 23 % or 15 % for Si_NP_15a, or 8 % and 4 % for Si_NP_15b, by the same estimation conditions. Additionally, it is worth noting here that that π - π stacking interactions between aligned modifiers might encourage a horizontal formation to the substrate rather than the assumed vertical structure (Figure 4.6), as discussed in previous work on diaryldiazo surface modifications.¹⁸

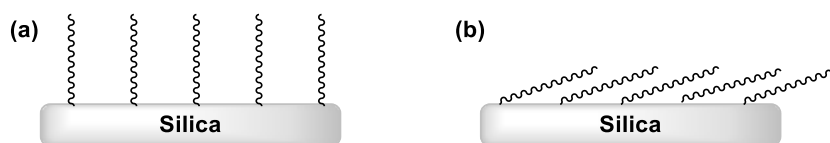


Figure 4.6: Depiction of the silica particle surface if the modification is aligned by (a) a vertical or (b) a horizontal structure. Adapted from reference.¹⁸

The interactions between the modifiers in this simple figure exposes the crudeness of the Chemicalize calculation parameters, but at the same time signifies the effect the packing of the surface modification will likely have upon the modification loading and as well as

the ultimate effect of the modification upon the surface chemistry. This said, the horizontal structure (Figure 4.5 (b)) is more unlikely to be promoted by the silica surface, compared to, for example, the graphitic surface of CB, in which case π interactions would also exist between the substrate and surface modification.

4.3.1.3. XPS

X-ray photoelectron spectroscopy (XPS) of pristine and modified silica was used to assess the changed surface composition after carbene surface functionalisation. Unfortunately, as no element markers have been added to the surface in this modification approach, XPS can only be used to expose an altered surface composition of the same detected elements (silicon, oxygen and carbon) present on the silica samples. Accordingly, high resolution scans of these regions were performed from analysis of the devolved peaks areas, which were used to determine the elemental compositions of the silica samples (Table 4.7).

Table 4.7: Relative chemical percentage composition of the carbon, oxygen and silicon content by XPS analysis.

Sample	XPS (%)		
	C	O	Si
Si_MP_Prisine	9.3	61.4	29.4
Si_MP_Processed	7.5	64.7	27.8
Si_MP_15a 5	8.0	64.2	27.8
Si_MP_15a 20	10.1	62.2	27.7
Si_NP_Pristine	6.4	65.9	27.7
Si_NP_Processed	3.4	62.9	33.6
Si_NP_15a	12.8	59.0	28.2
Si_NP_15b	9.6	60.1	29.6

Minor variations in the oxygen and carbon content can be observed between the unmodified and modified microsilica samples, however they are not significant enough to provide clear evidence of the success of the carbene modification. That said, the increased carbon content of ~13 % and ~10 % of the hexyl and dodecyl modified nanosilica

compared to the detected ~6 % and ~3 % from pristine and processed nanosilica is highly suggestive that the silica surface has indeed been functionalised.

In detail, the spectra are displayed in Figure 4.7 and Figure 4.8 below, and further information of the devolved peaks including the binding energies, the charging values and the FWHM of the analysed peaks are included in the Appendix. Additionally, the Si 2p peaks can also be found in the Appendix and have not been included in the figures here because the peaks demonstrate little change before and after modification.

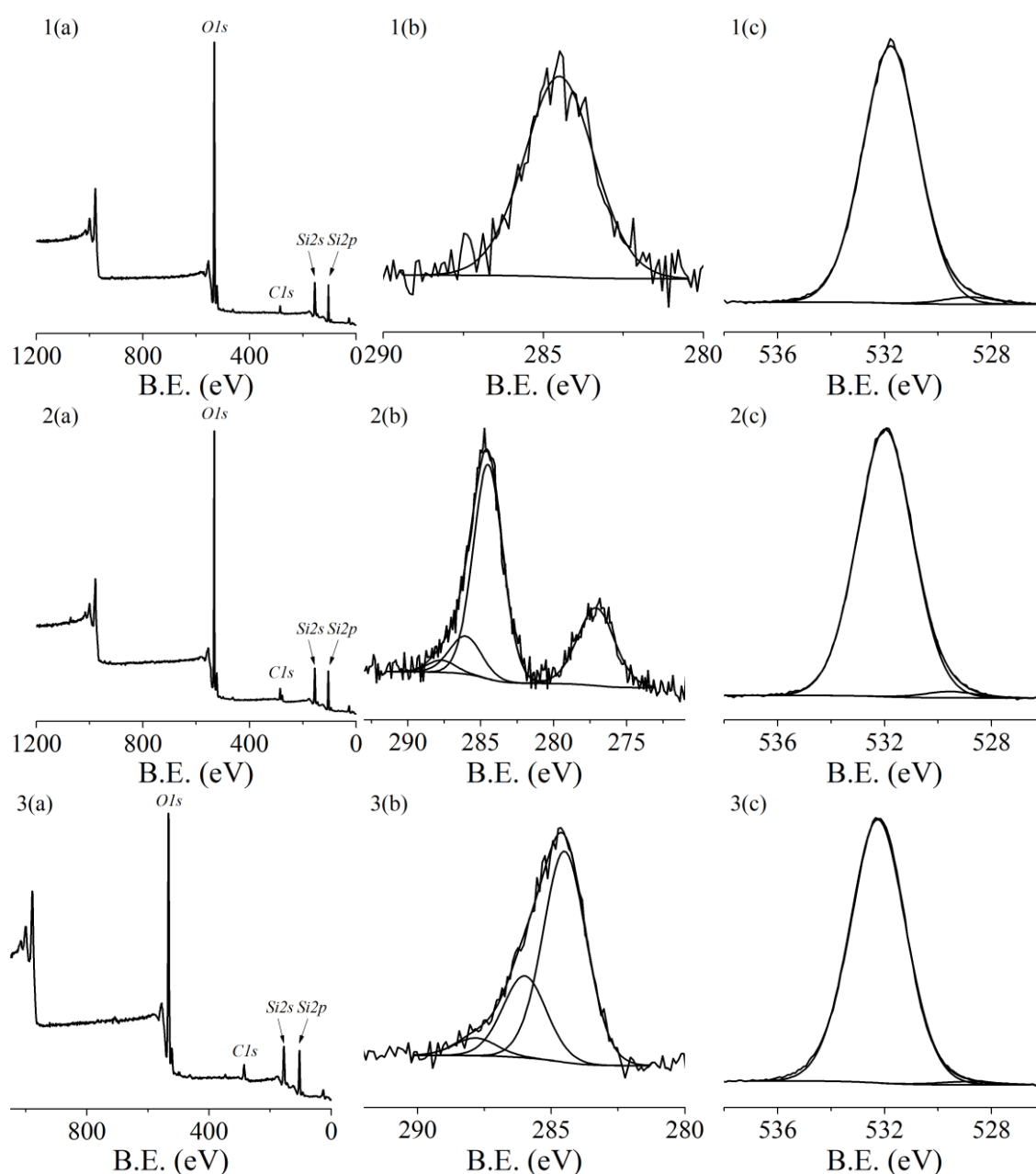


Figure 4.7: XPS spectra displaying (a) the wide scan and high resolution (b) C 1s and (c) O 1s scans of (1) Si_NP_Pristine (2) Si_NP_15a (3) Si_NP_15b.

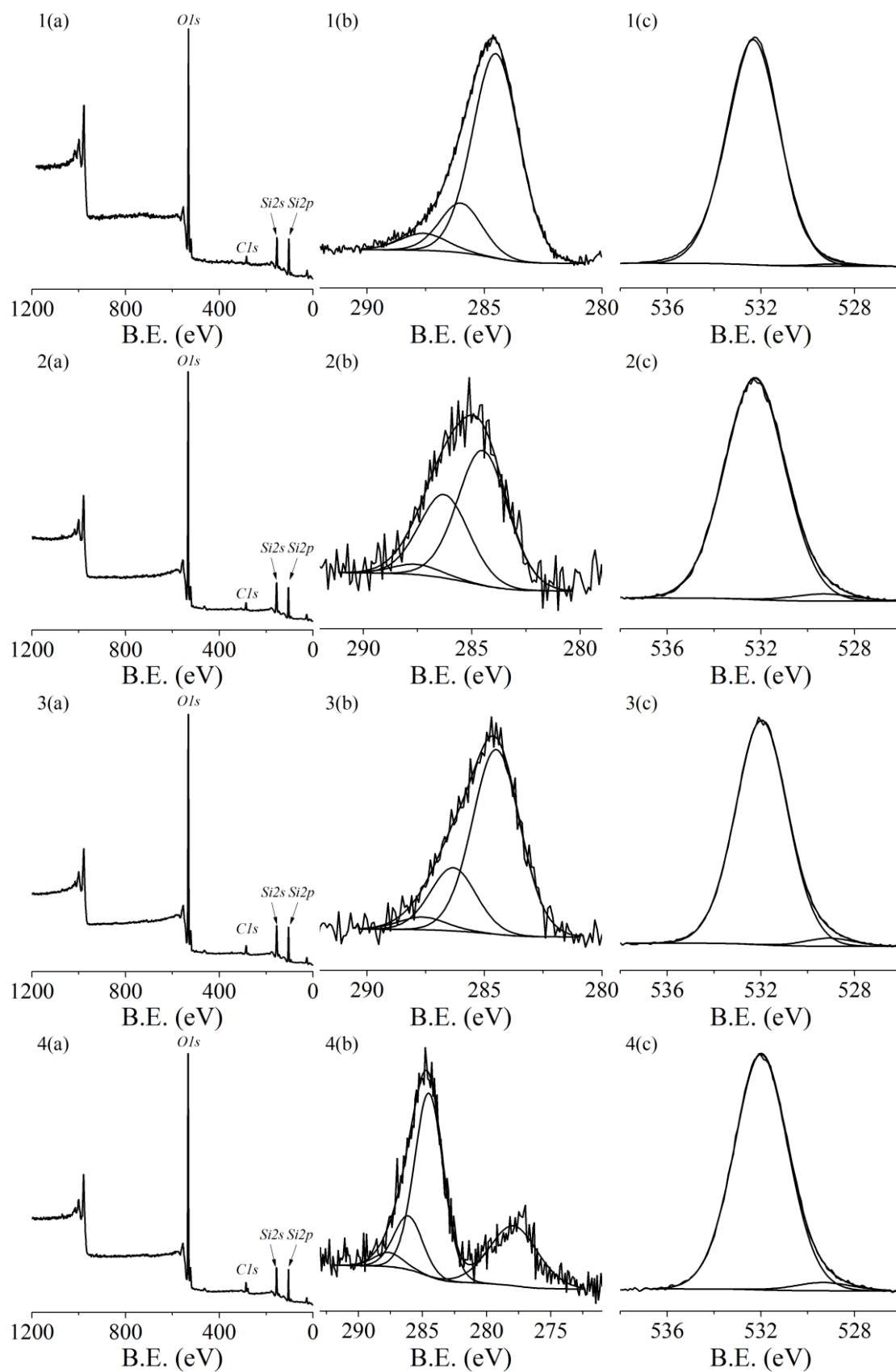


Figure 4.8: XPS spectra displaying (a) the wide scan and high resolution (b) C 1s and (c) O 1s scans of (1) Si_MP_Pristine (2) Si_MP_Processed (3) Si_MP_15a_5 and (4) Si_MP_15a_20.

The main features present on all the silica (micro and nano) samples included the core levels of SiO₂ by Si 2p and Si 2s photoemission peaks at ~103 eV and ~149 eV binding energies, and an O 1s peak at ~532 eV. High resolution spectra of the O 1s region permitted devolution into two chemical environments. The principal peak at $\sim 532.0 \pm 0.2$ eV is from oxygen species present in the Si-O-Si bonds^{29, 30} and Si-O-H bonds.³¹ The second, which is generally of a weak contribution, was detected at $\sim 529.2 \pm 0.4$ eV from C=O (carbonyl and carboxyl) oxygen species.³²

Additionally, a C 1s component of variable concentration was detected at ~285 eV binding energy for all the silica samples. This is presumably as a result of sample contamination for the unmodified samples. Otherwise, for the functionalised silica samples, altered C 1s contributions are likely an indication of the successful surface modifications. The C 1s peaks were devolved into several peaks, as directed from the generated XPS spectra. The first, present on all silica samples, was ascribed to adventitious carbon and hydrocarbon (C-C, C-H) and positioned at 284.5 eV binding energy. Additionally, carbon atoms with single bonds to oxygen (C-O) were detected at $\sim 286.1 \pm 0.1$ eV and carbonyl (C=O) at $\sim 287.1 \text{ eV} \pm 0.1 \text{ eV}$. Extra C 1s peaks can be observed for some of the silica samples, namely modified silica Si_NP_15a (Figure 4.7 and Si_MP_15a (Figure 4.8) and unmodified Si_NP_Processed (Appendix-Chapter 3). These doubled C 1s peaks are attributed to altered sample charging according to whether the analysed section of the silica pellet sample was in contact directly with the sample copper stub or additionally in contact with the carbon tape (used to affix the sample to the copper stub). This is assumed, as the peak cannot be attributed to any other element markers and is supported by the fact that the signal was present on both unmodified and modified samples. As a result, the duplicate C 1s peaks for these samples have not been used in the peak area calculations to determine the surface elemental composition.

Lastly, the XPS surface analysis demonstrated a good sample purity for the unmodified and modified silica samples, as no contamination by any of Na, K, Cl was observed, in contrast to the high number of contaminants that were detected for the modified silica samples in Chapter 3.

4.3.1.4. CHN

Combustion analysis (Table 4.8) was performed to all the silica samples as a secondary method to XPS in order to further determine changes in the elemental content to the silica after carbene treatment.

Table 4.8: CHN elemental analysis of pristine and modified silica nanoparticles.

Sample	CHN (%)	
	C	H
Si_MP_Prisine	0.46	1.50
Si_MP_Processed	1.69	1.39
Si_MP_15a_5	2.69	1.49
Si_MP_15a_20	2.19	1.24
Si_NP_Pristine	0.42	1.46
Si_NP_Processed	0.37	1.08
Si_NP_15a	2.81	1.34
Si_NP_15b	2.09	1.39

The results for the modified nanosilica particles support evidence of the surface modification by the increased carbon content of 3 % and 2 %, for hexyl and dodecyl terminated silica, compared to the <1 % detected for the unmodified nanosilica samples. Further, this result is consistent with the increased carbon content as observed by XPS analysis for the modified nanosilica. This result is replicated by the increased carbon content of 3 % for Si_MP_15a_5, however the detected carbon content of 2 % for Si_MP_15a_20, is close to that of processed microsilica. This highlights the limitations of the bulk analysis technique for surface analysis, especially without the inclusion of nitrogen elemental markers, but also the higher degree of error of the results close to the detection limit of the combustion measurements (0.1 %).

4.3.1.5. SSNMR

Solid-State NMR (SSNMR) permitted further analysis of the surface chemistry of the microsilica and nanosilica and direct evidence was immediately presented by ^{13}C CP MAS (cross-polarisation magic-angle spinning) spectra (Figure 4.9).

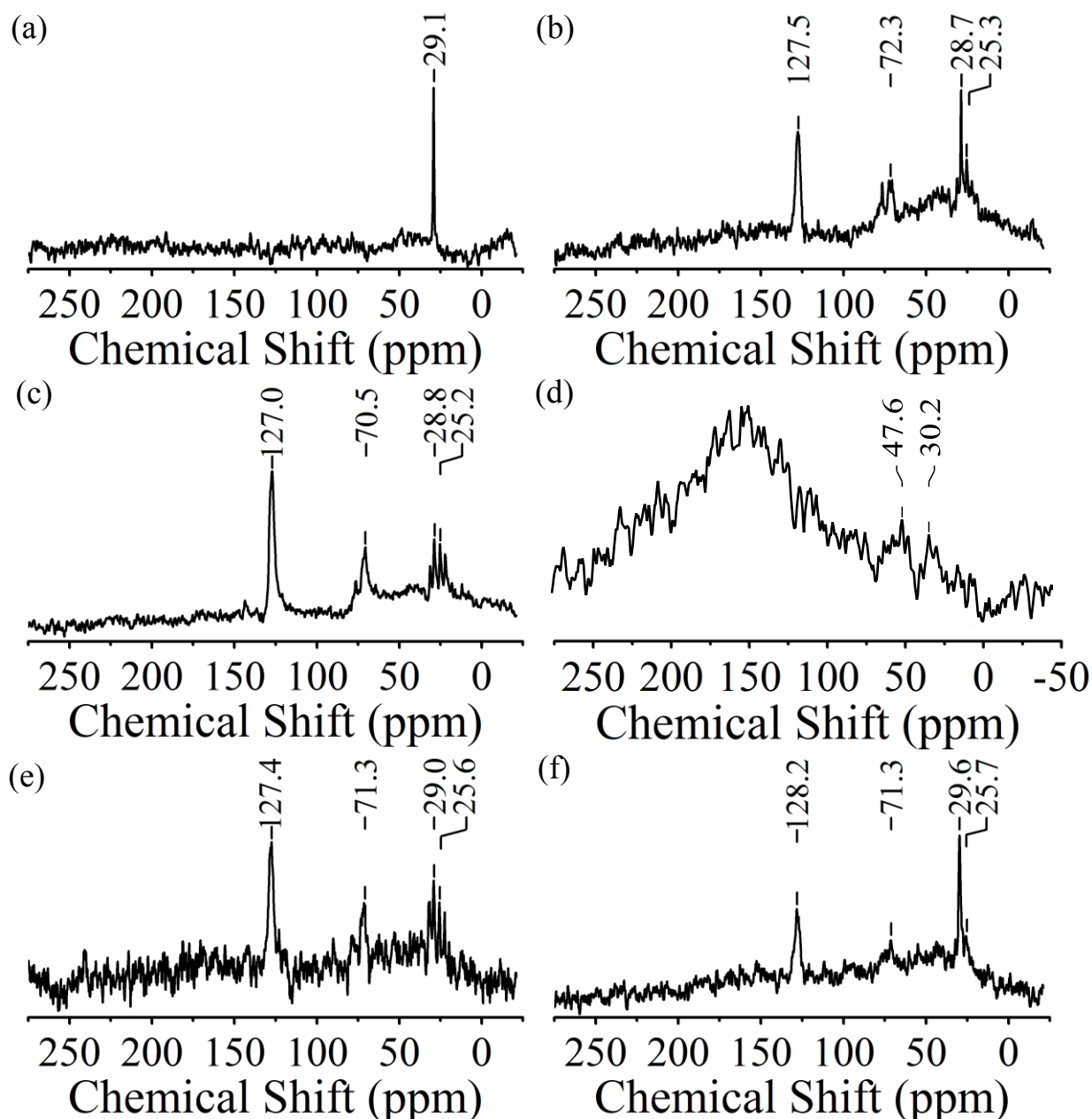


Figure 4.9: ^{13}C CP MAS SSNMR of (a) Si_MP_Processed (b) Si_MP_15a_5 (c) Si_MP_15a_20 (d) Si_NP_Processed (e) Si_NP_15a and (f) Si_NP_15b.

The presence of the modification for all four functionalised silica samples is indicated by assignment of the benzene rings at ~ 127 - 128 ppm, the ether group at ~ 66 - 72 ppm and the

hydrocarbon chains at ~12-25 ppm. Additionally, there is evidence of acetone for some of the unmodified (Si_MP_Processed and Si_NP_Processed) and modified (Si_MP_15a_5 and Si_NP_15b) samples, as indicated by the peak at ~28-30 ppm.³³ The peaks corresponding to the presence of the Si-O-C bond, usually observed at ~66 ppm,³⁴ unfortunately cannot be identified for this silica modification as the signal indicating the presence of the ether groups is observed in the same region on the ¹³C SSNMR spectra.

Further, evidence of functionalisation was investigated by ²⁹Si CP MAS and ²⁹Si DP MAS (direct-polarisation) for some of the silica samples, included for reference in the Appendix. However, no significant alterations to the contribution of the silicon species of the silica could be observed between the unmodified and modified samples, in a similar result to Chapter 3. This is attributed to the expectation that the carbene reacts with Si-O₂, rather than directly to Si, coupled with the low degree of surface functionalisation present.¹⁵

4.3.1.6. ATR-IR

ATR-IR measurements were conducted on all the pristine and modified microsilica nanosilica. Peaks were detected in the broad range of ν 2340-1800 cm⁻¹ as a result of the diamond attachment used for the ATR-IR measurements. Otherwise, characteristic absorbances for silica were observed for the unmodified and modified silica samples at ν ~1077 cm⁻¹, ν ~954 cm⁻¹ and ν ~799 cm⁻¹ corresponding to asymmetric Si-O-Si stretches, Si-OH and symmetric Si-O-Si stretches, respectively.³⁵⁻³⁷ The only sample to display any extra peaks was Si_NP_15b, Figure 4.10.

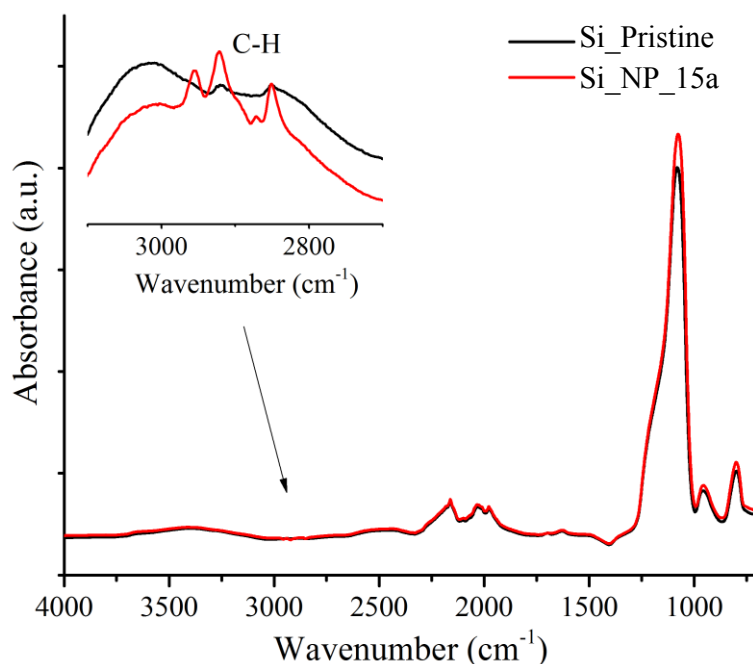


Figure 4.10: ATR-IR spectra of pristine and modified silica Si_NP_15b (insert shows the introduction of the C-H bonds in the 3100-2700 cm^{-1} region.)

Upon first inspection, it appears that there is little difference between the modified Si_NP_15b spectra and the pristine nanosilica, however a closer examination of the C-H stretching region reveals new peaks (Figure 4.10, insert). The peaks detected at ν 2851 cm^{-1} and ν 2872 cm^{-1} , are attributed to C-H symmetric stretches, and at ν 2921 cm^{-1} and ν 2956 cm^{-1} , to C-H asymmetric stretches.³⁸ Further, these new peaks now observed for the modified silica surface correspond directly to C-H peaks at ν 2853 cm^{-1} , ν 2871 cm^{-1} , ν 2923 cm^{-1} and ν 2954 cm^{-1} detected for the benzophenone modifier (**12b**), from the synthesis procedure to produce Si_NP_15b and stable enough to be tested by ATR-IR. This result is therefore attributed to the dodecyl termination now present on the modified silica.

4.3.1.7. Silica Characterisation Summary

In summary, evidence provided by thermal analysis and ^{13}C SSNMR experiments confirm the successful surface functionalisation of microsilica and nanosilica by reaction with diaryl carbenes terminated in hexyl and dodecyl hydrocarbon chains. These results

were further supported by an increase in the elemental carbon surface content as demonstrated by XPS and CHN measurements, as well as the identification of the dodecyl termination by ATR-IR.

4.3.2. Carbon Based Nanoparticle Characterisation

This section presents a detailed surface analysis of the unmodified and carbene-treated carbon-based nanomaterials CB, ACB and CNT. The previous chapter demonstrated that processed CB, when subjected to the modification procedure in the absence of the addition of the diazo precursor displayed the same surface properties as pristine CB. Therefore, these results have not been re-discussed in this work, however for comparison, results of processed CB have been included in tabulated summary data, as appropriate. Additionally, for the new nanomaterials in this study, ACB and CNTs, processed samples have been analysed and will be discussed in comparison to the equivalent modified samples.

4.3.2.1. BET

Surface area analysis by nitrogen sorption was performed to ACB and CNT, as well as CB, as presented in Chapter 3. The key data extracted from the BET measurements are displayed in Table 4.9, and the adsorption and desorption isotherms are included in the Appendix.

Table 4.9: BET summary data of pristine CB, ACB and CNT.

Sample	BET Surface Area (m ² /g)	t-Plot Micropore Area (m ² /g)	t-Plot External Surface Area (m ² /g)	BJH Adsorption Average Pore Diameter (Å)	BJH Desorption Average Pore Diameter (Å)
CB_Pristine ^a	72.5 (0.0) ^c	10.1 (0.2)	62.5 (0.2)	366.6 (13.7)	354.3 (5.5)
ACB_Pristine ^b	79.8 (0.1)	6.7 (0.3)	73.1 (0.3)	122.8 (0.9)	123.1 (0.9)
CNT_Pristine	112.6	12.1	100.5	235.6	228.7

^a Average of 2 repeat BET measurements.

^b Average of 3 repeat BET measurements.

^c The standard deviation of the repeated measurements is included in brackets.

The surface areas indicate that ACB displays an overall similar BET surface area to CB, but with nanopores of smaller diameters and a reduced t-plot micropore area. Alternatively, CNT displays the largest surface area of the three carbon-based nanomaterials.

4.3.2.2. Thermal analysis

Extensive thermal analysis of the pristine, processed and modified carbon-based nanomaterials provides excellent evidence supporting successful surface modification. Discussing first the CB nanoparticles, the TGA, DTG and DSC thermal analysis results are displayed in Figure 4.11 and the derived data for all the carbon-based nanomaterials is included in Table 4.10.

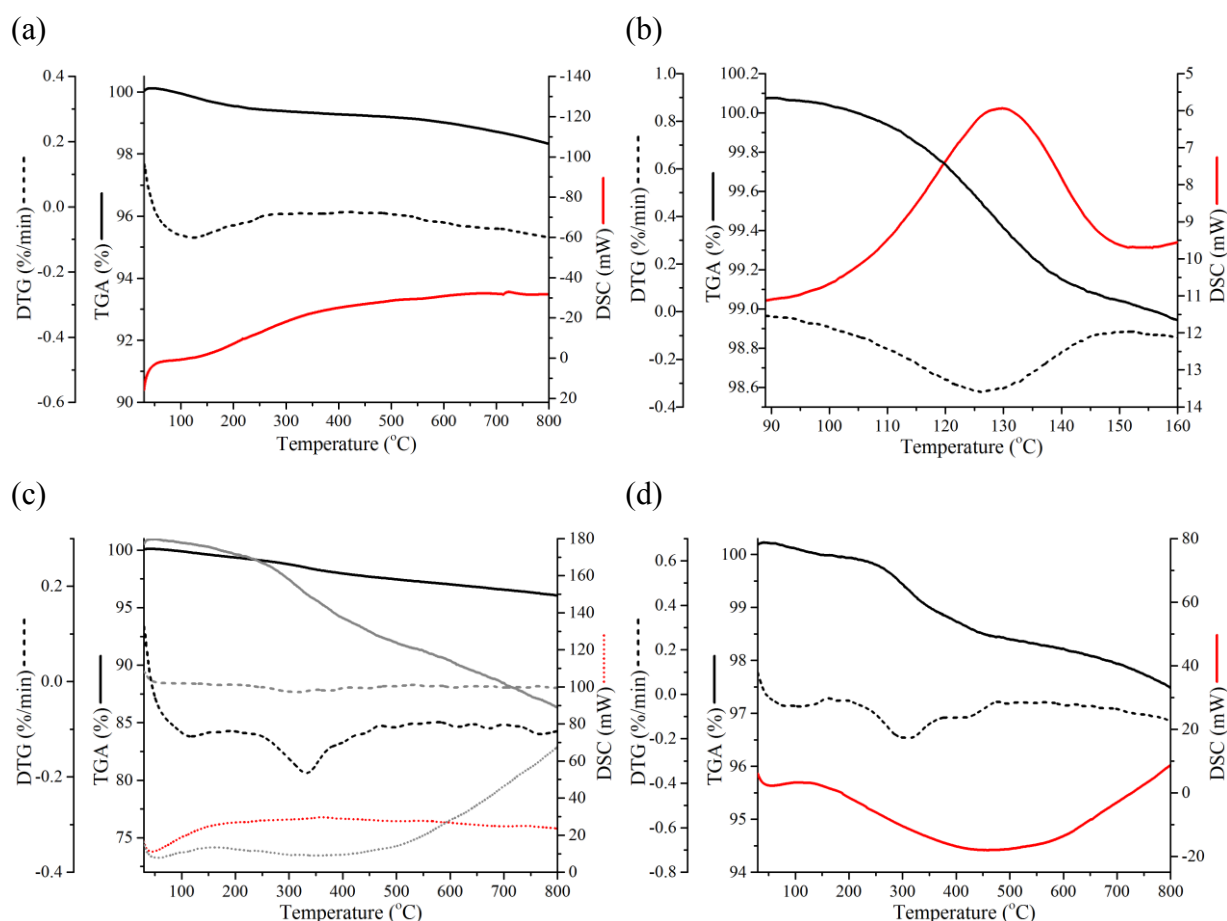


Figure 4.11: Thermal analysis data displaying TGA, DTG and DSC curves (heat flow endo down) under nitrogen flow of (a) CB_Pristine (b) CB_15a_Mod, in which the surface modification reaction was performed in the STA instrument of CB coated in the diazo precursor **14a** to produce the modified sample, CB_15a_STA (c) CB_15a (black), modified by the usual modification procedure, and CB_15a_STA (grey), after the modification procedure in the STA instrument and (d) CB_15b. Adapted with permission from the American Chemical Society © 2016.¹⁶

Table 4.10: Extracted TGA, DTG and DSC peak data from thermal analysis runs (30-800 °C) of the carbon-based nanomaterials. The thermal events for each of the samples are labelled by a numbered superscript, the same numbers that identify the observation of the same thermal event by the different thermal analyses techniques. The same TGA, DTG, DSC thermal events observed in multiple samples are organised in the same columns and the major DTG peak corresponding to the loss of the modifier is in bold.

Sample	TGA Onset (°C)			DTG Peak (°C)						DSC (°C)
	T _o	T _o	T _o	T _p	T _p	T _p	T _p	T _p	T _p	T _p
	Solvent Residue	N ₂ Removal	Mod.	Solvent Residue	N ₂ Removal	Modification				Mod.
CB Pristine				119.3 ¹						
CB Processed				119.1 ¹						
CB 15a Mod		112.0 ¹			126.1 ¹					
CB 15a STA			265.7 ¹				315.9¹	375.8 ¹	448.4 ¹	
CB 15a			276.3 ¹				333.8¹	398.0 ¹	441.4 ¹	
CB 15b			254.5 ²				308.0²	421.3 ²		107.9 ¹
ACB Pristine										142.6 ¹
ACB Processed										121.9 ¹
ACB 15a Mod		119.3 ¹			126.9 ¹					
ACB 15a			323.3 ¹			280.1 ¹	368.8¹	424.4 ¹	461.3 ¹	
CNT Pristine				129.8 ¹						
CNT Processed	100.1 ¹									134.6 ¹
CNT 15a Mod										
CNT 15a			256.8 ²			234.4 ²	290.1 ²	352.2²	445.5 ²	132.4 ¹

^a T_o, onset temperature.

^b T_p, peak temperature.

^c Mod., modification.

Pristine CB, as presented in Chapter 3 in more detail, initially displays a small TGA weight loss step in the 30-200 °C temperature range and concomitant with a broad DTG curve with a peak maximum of 119.3 °C attributed to the volatilisation of water or residual solvents.³⁹ Above 500 °C to the end of the thermal run ~800 °C, the second broad weight loss step can be ascribed to the loss of appreciable non-graphitic fractions present on the CB.⁴⁰ Figure 4.11(b) displays the thermal analysis results of the performed carbene reaction in the STA instrument, in an experiment labelled CB_15a_Mod. Pristine CB coated with diazo **14a** (~15 mg), was subjected to a thermal analysis run of 30-280 °C at a ramp rate of 10 min⁻¹, to give modified CB_NP_15a_STA, terminated in a hexyl hydrocarbon chain. The thermal analysis results readily demonstrate the diazo decomposition reaction via the exothermic peak on the DSC thermogram, with a reaction enthalpy of -45.6 J/g, and an extrapolated peak onset at 107.9 °C and peak decomposition temperature at 129.2 °C. Additionally, the TGA thermogram indicates that the initial

weight loss of the sample begins at ~ 90 °C and plateaus at ~ 160 °C, with an onset of 112.0 °C and a total weight loss of 0.165 mg (1.13 %), and corroborated by the DTG peak maxima at 126.1 °C. This result is attributed to the loss of N_2 upon generation of the reactive carbene species.^{41, 42} Figure 4.11(c) displays CB_15a, modified by the usual protocol, and CB_15a_STA (~ 3 mg), recovered after the modification in the STA followed by washings in acetone. First, the similarity of onsets of 276.3 °C and 265.7 °C for the two samples, CB_15a and CB_15a_STA, respectively, affirms that it is indeed the carbene insertion reaction that is observed by the STA experiment in Figure 4.11(b). Second, the success of the modification is confirmed by the similar DTG thermogram patterns, in which the prominent peaks are observed in the same temperature region at 333.8 °C and 315.9 °C for each CB_15a and CB_15a_STA, although the DTG for the latter sample is somewhat broadened. It can be noted that this is a similar thermal pattern to that observed for the modified silica. Additionally, the larger, extended weight loss step observed for CB_15a_STA indicates a more efficient carbene insertion reaction in the STA instrument, corresponding to a maximum conversion of the diazo compound to diarylcarbene of 33 %, compared to 6 % for CB_15a, modified by the usual protocol. Dodecyl modified CB_15b presents a similar thermal analysis result. The TGA weight loss step with an onset of 254.5 °C is accompanied by the prominent DTG maximum at 308.0 °C affirming the success of the modification reaction.

The thermal analysis results of pristine and processed ACB (Figure 4.12(a-b)) displays unremarkable but similar thermal data, with a negligible weight loss of ~ 0.1 % during the 30 - 800 °C thermal program.

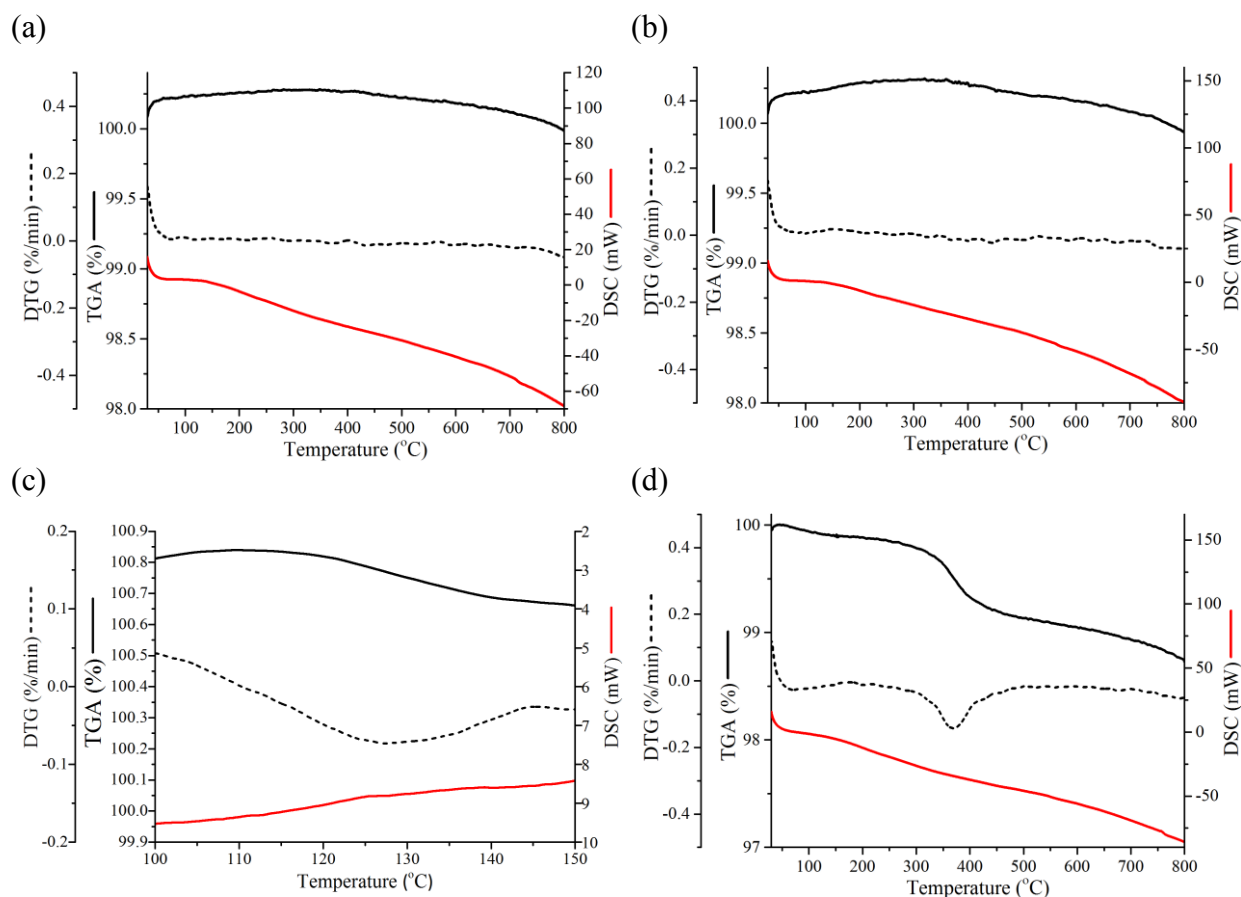


Figure 4.12: Thermal analysis data displaying TGA, DTG and DSC curves (heat flow endo down) of (a) ACB_Pristine (b) ACB_Processed (c) ACB_15a_Mod, in which the surface modification reaction was performed in the STA instrument of ACB coated in the diazo precursor **14a** and (d) modified ACB_15a.

The only noteworthy feature for both samples is the observable buoyancy effect at the beginning of the thermal runs, in which the changing density of the nitrogen gas flow as the temperature increases, leads to a surge in the sample mass.⁴³ This is reflected in the DTG curves and by the DSC peaks at 142.6 °C and 121.9 °C for pristine and processed ACB, respectively. For previous samples, this effect has been negligible compared to the immediate weight loss of physisorbed water or solvent residues. The observation of the buoyancy effect for ACB, and indeed the low mass loss during the thermal program, can therefore be attributed to the high purity of this type of carbon nanomaterial.

Figure 4.12(c) displays the thermal analysis of the performed carbene reaction of pristine ACB coated with diazo **14a** (~4 mg), under the same conditions as for the silica and CB samples. Unfortunately, the thermal analysis result is not as distinct as was observed for

CB_15a_STA, possibly due to the lowered mass used in the experiment or the fact that a 10 wt. % diazo loading was used, compared to the 66 wt. % for CB. Nonetheless, a broad diazo decomposition reaction can still be observed by the TGA thermogram, in which a weight loss step is evident, starting ~ 110 °C and plateauing at ~ 150 °C with an onset of 119.3 °C. The weight loss of 0.007 mg (0.18 %) is detected and is again attributed to the loss of N_2 upon generation of the reactive carbene species. This can be more easily observed by the broad DTG peak with maxima of 126.9 °C, notably at the same temperature as the DTG peak observed for the CB modification in the STA. In Figure 4.12(d) the analysis of the functionalised ACB_15a, prepared by the usual modification protocol, exhibits the decomposition of the surface modification. The TGA onset at 323.3 °C is reflected by the principal DTG peak at 368.8 °C. However, the low degree of the ACB modification is presumably explains the absence of a peak in the DSC thermogram. Finally, the thermal analysis results for the CNT samples are included in Figure 4.13, on the next page. Pristine and processed CNT display generally similar thermal analysis data, with a low mass loss <2 % during the thermal program. Initially, processed CNT displays a weight loss with a TGA onset at 100.1 °C, shadowed by a DSC exothermic peak at 134.6 °C, expected to be due to the loss of water and solvent residues present on the samples, as seen for the other carbon-based samples.³⁹ Additionally, both samples display sharp TGA weight loss steps of ~ 8 % and ~ 9 % at ~ 671 °C and ~ 658 °C, for pristine and processed CNT, respectively, replicated by peaks in the DTG and DSC curves. It is supposed that these are artefacts from some disturbance to the sample or the STA machine during the thermal runs, and therefore do not need to be compared to the modified samples. Repeated attempts were made to measure the pristine CNT, however the results displayed similar artefacts at different temperatures, ~ 164 °C and ~ 390 °C (figures are included in the Appendix).

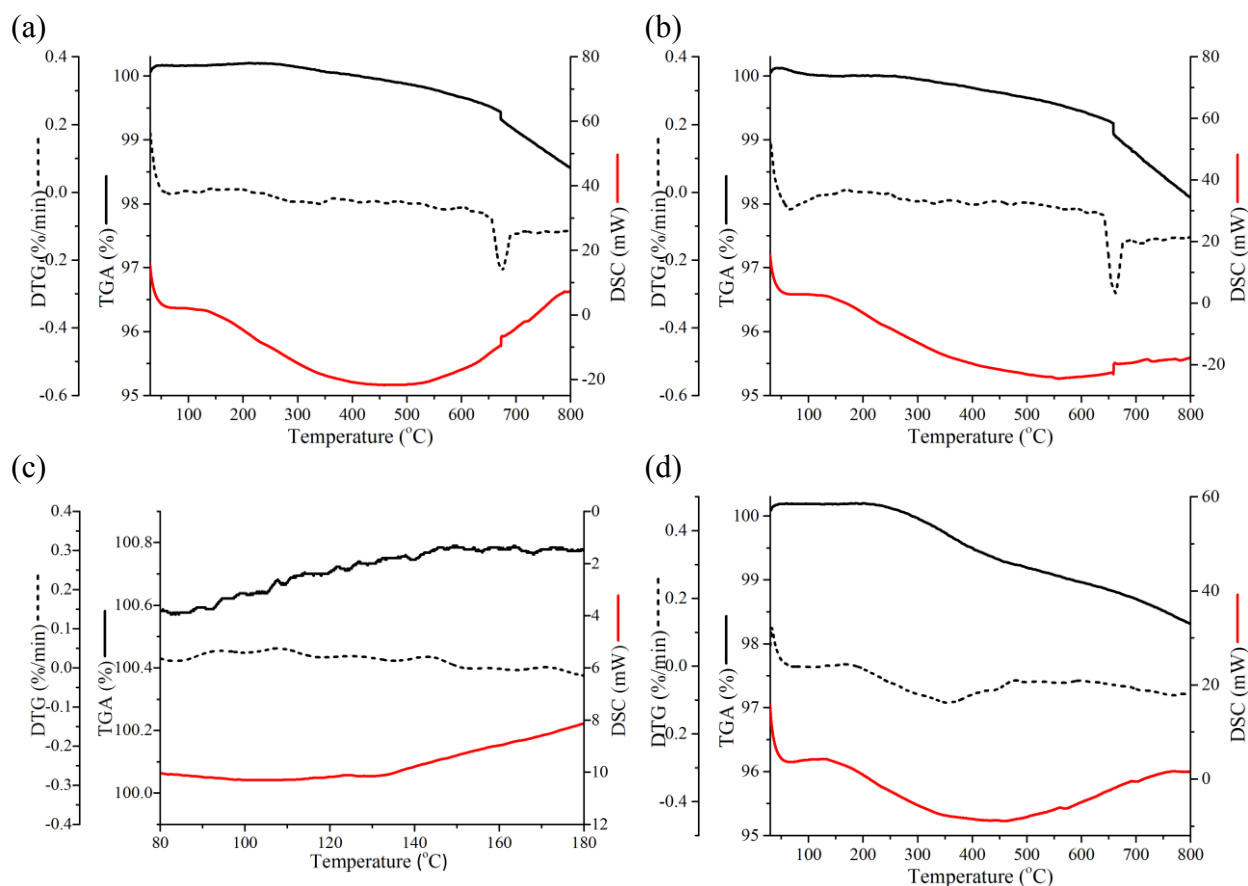


Figure 4.13: Thermal analysis data displaying TGA, DTG and DSC curves (heat flow endo down) of (a) CNT_Pristine (b) CNT_Processed (c) CNT_15a_Mod, in which the surface modification reaction was performed in the STA instrument of CNT coated in the diazo precursor **14a** and (d) modified CNT_15a.

The diazo reaction was also followed in the STA using pristine CNT coated in the diazo compound **14a** at 5 wt. % diazo loading (Figure 4.13(c)). Unfortunately, the thermal analysis does not provide evidence of the diazo decomposition reaction, similar to the nanosilica experiment, possibly due to the low diazo addition to the CNT samples combined with the low mass of CNT samples tested (~4 mg). Alternatively, the thermal analysis of the modified CNT_15a samples (Figure 4.13(d)), prepared by the usual modification procedure, readily demonstrates the presence of the surface modification by the TGA onset at 256.8 °C and a series of DTG peaks with the prominent peak observed at 352.2 °C.

The informative thermal analysis results for all the modified carbon-based nanoparticles clearly demonstrate the decomposition of the surface functionalisation. Further, once

again, the weight loss data of the modified samples, compared to that of the equivalent unmodified samples, can be used to calculate the degree of loading based on the knowledge of the modification added to the surfaces and the experimentally determined BET surface areas of CB (72.5 g/m²), ACB (79.8 g/m²) and CNT (112.6 g/m²). The raw data and results of these surface loading calculations are displayed in Table 4.11.

Table 4.11: Thermogravimetric analysis weight loss data and calculated surface modification loadings of carbon-based nanomaterials. Adapted with permission from the American Chemical Society © 2016.¹⁶

Sample	TGA Weight Loss (%)						Surface Loading ^b		Surface Coverage ^c	
	30-200 °C	200-500 °C	500-800 °C	Sample Wt. Loss due to the Mod. (g)	Theoretical Wt. Loss Expected due to the Mod. (g)	Efficiency (%)	Moles /g	Molecules /cm ²	Diazo precursor 14a-b (Figure 4.5(b))	Diaryl Core (Figure 4.5(c))
CB_Pristine	0.52	0.34	0.82							
CB_Processed	0.75	0.38	0.70							
CB_15a_STA	0.91	7.98	5.64	3.5×10^{-4}	1.0×10^{-3}	33	5.1×10^{-4}	4.3×10^{14}	410	217
CB_15a	0.70	1.90	1.40	2.9×10^{-4}	4.7×10^{-3}	6	8.5×10^{-5}	7.1×10^{13}	68	45
CB_15b	0.26	1.54	0.92	9.7×10^{-5}	3.6×10^{-3}	3	2.9×10^{-5}	2.4×10^{13}	31	15
ACB_Pristine ^a	+0.17	0.04	0.24							
ACB_Processed ^a	+0.22	0.08	0.27							
ACB_15a	0.06	0.75	0.40	1.4×10^{-4}	1.1×10^{-3}	13	4.0×10^{-5}	3.1×10^{13}	29	19
CNT_Pristine ^a	+0.13	0.32	1.32							
CNT_Processed	0.04	0.35	1.56							
CNT_15a	0.11	1.00	0.88	6.3×10^{-5}	5.5×10^{-4}	14	1.8×10^{-5}	1.3×10^{13}	13	9

^a +weight losses for these samples is noted as was an increase in weight in the 30-200 °C temperature range, due to the observed buoyancy effect for these samples.

^b Assumes a monolayer surface coverage of the determined BET surface areas of CB (72.5 m²/g), ACB (79.8 m²/g) and CNT (112.6 m²/g).

^c Note the surface coverage is calculated from the found surface loading compared to the expected surface loading per unit, according to the predicted projection areas as displayed in Figure 4.5.

The surface loading calculations of the modified carbon-based nanoparticles ranges from $1.3 - 7.1 \times 10^{13}$ molecules/cm², a result which is consistent with the presented silica modification loadings and in the literature.¹⁵ These results can also be compared to the theoretical estimations for the surface loadings for this modification, as discussed in the silica section of this Chapter (Figure 4.5), and accordingly the percentage surface coverage can be estimated (Table 4.11). The results are reasonable for nanoparticles prepared by the usual procedure, but CB_15a_STA, modified during the STA experiment, surpasses the monolayer surface coverage by the estimations at 410 % or 217 %. This

demonstrates the efficiency of this modification approach, resulting in the highest surface of 4.3×10^{14} molecules/cm² compared to the rest of the modified particles. It is interesting to note the general similarity of the loadings for the carbon-based nanomaterials considering the different surface areas of these substrates and the diazo **14a** loading additions at 66 %, 10 % and 5 % for CB, ACB and CNT, respectively.

4.3.2.3. XPS

XPS analysis was performed to pristine, processed and modified CB, ACB and CNT nanoparticles to assess the changed surface chemistry and to determine the relative elemental abundance (Table 4.12). Further information, including the charge correction, binding energies and FWHM, of the peaks analysed can be found in the Appendix.

Table 4.12: Chemical percentage of the carbon and oxygen composition of pristine, processed and modified carbon-based nanoparticles by XPS analysis. Adapted with permission from the American Chemical Society © 2016.¹⁶

Sample	XPS (%)	
	C	O
CB_Pristine	98.4	1.6
CB_Processed	97.2	2.8
CB_15a	94.4	5.6
CB_15b	97.0	3.0
ACB_Pristine	99.5	0.5
ACB_Processed	99.1	0.9
ACB_15a	99.3	0.7
CNT_Pristine	99.1	0.9
CNT_Processed	98.6	1.4
CNT_15a	98.8	1.2

As discussed in the XPS analysis of the silica samples, the challenge in this CB modification is the absence of an elemental marker inserted to the surface, and instead only carbon and oxygen are introduced to the predominantly carbon substrates. Accordingly, all the samples displayed dominant C 1s photoemission peaks at ~285 eV binding energy and small O 1s features at ~532 eV binding energy. Key results can therefore only be inferred by the observed increase in the oxygen elemental percentage for all the modified samples, compared to the equivalent pristine nanomaterial, due to the

introduction of the ether linkage of the inserted modifier to the surface. Unfortunately, however the presence of the modifications is not obvious as both the processed and modified nanofillers demonstrate an increased oxygen content compared to the pristine samples. This increase in the oxygen content for all the processed samples is likely a result of the physisorption of impurities or the presence of residual solvents following the modification procedure. This is consistent with the thermal analysis data, in which all the processed samples, compared to the pristine, displayed greater TGA weight losses <200 °C.

In detail, the high resolution spectra of the C 1s region of all the carbon-based samples was deconvoluted into 6 photoelectron peaks of different chemical environments, as also presented in Chapter 3. The principle peak was positioned at 284.5 eV (C-C, C-H) and subsequent peaks, due to contributions from carbon coordinated to oxygen, were at ~286.0 eV (C-O, ± 0.0 eV), ~287.4 eV (C=O, ± 0.2 eV) and ~289.0 eV (COOH, ± 0.2 eV) binding energies. Weaker $\pi-\pi^*$ features were also observed at ~290.6 eV ($\pi-\pi^*$, ± 0.2 eV) and ~292.1 eV ($\pi-\pi^*$, ± 0.2 eV). The O 1s peaks present on the samples at ~532 eV are attributed to C-O and C=O.

The XPS analysis of pristine CB and hexyl and dodecyl modified CB are presented in Figure 4.14. The increased surface oxygen content is immediately evident for the hexyl modified CB, CB_15a, at 5.6 % elemental composition, compared to pristine CB at 1.6 % and processed CB at 2.8 %. This is consistent the highest modification loading as detected by thermal analysis, compared to the other carbon-based samples. Dodecyl-terminated modified CB, CB_15b, indicates an increased oxygen content at 3.0 % compared to pristine CB. This result is however close the oxygen content found for processed CB at (2.8 %). Additionally, the peak areas of the C 1s deconvoluted peaks do not indicate significant contribution alterations between the modified and unmodified CB samples,

however the increased contribution of $\sim 2\%$ of the C-O peaks can be observed for the modified samples. The relative peak areas can be found in the Appendix.

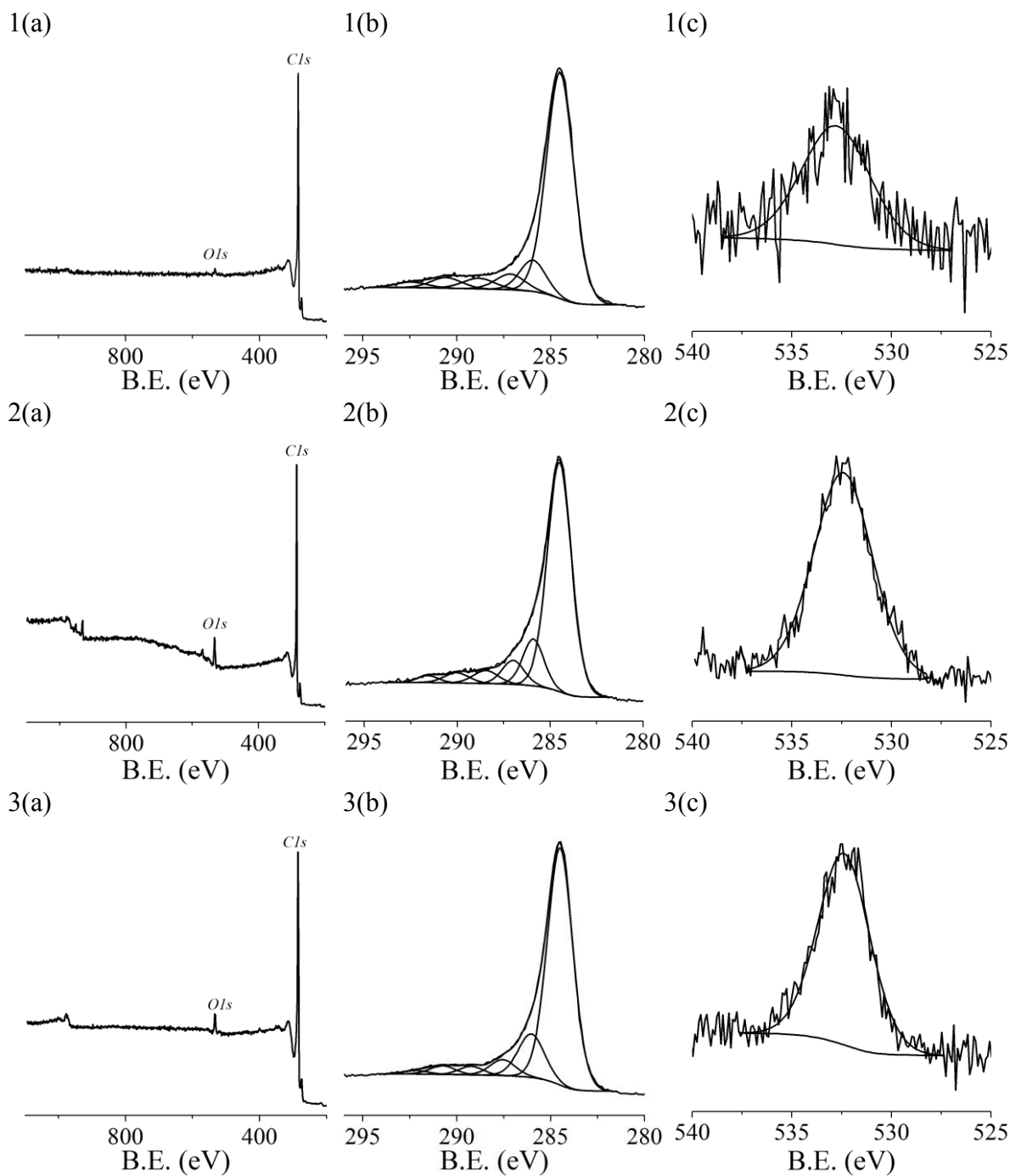


Figure 4.14: XPS (a) wide scan spectra and (b) C 1s and (c) O 1s high resolution spectra of 1. CB_Pristine 2. CB_15a and 3. CB_15b. CB_Processed can be found in the Appendix- Chapter 3.

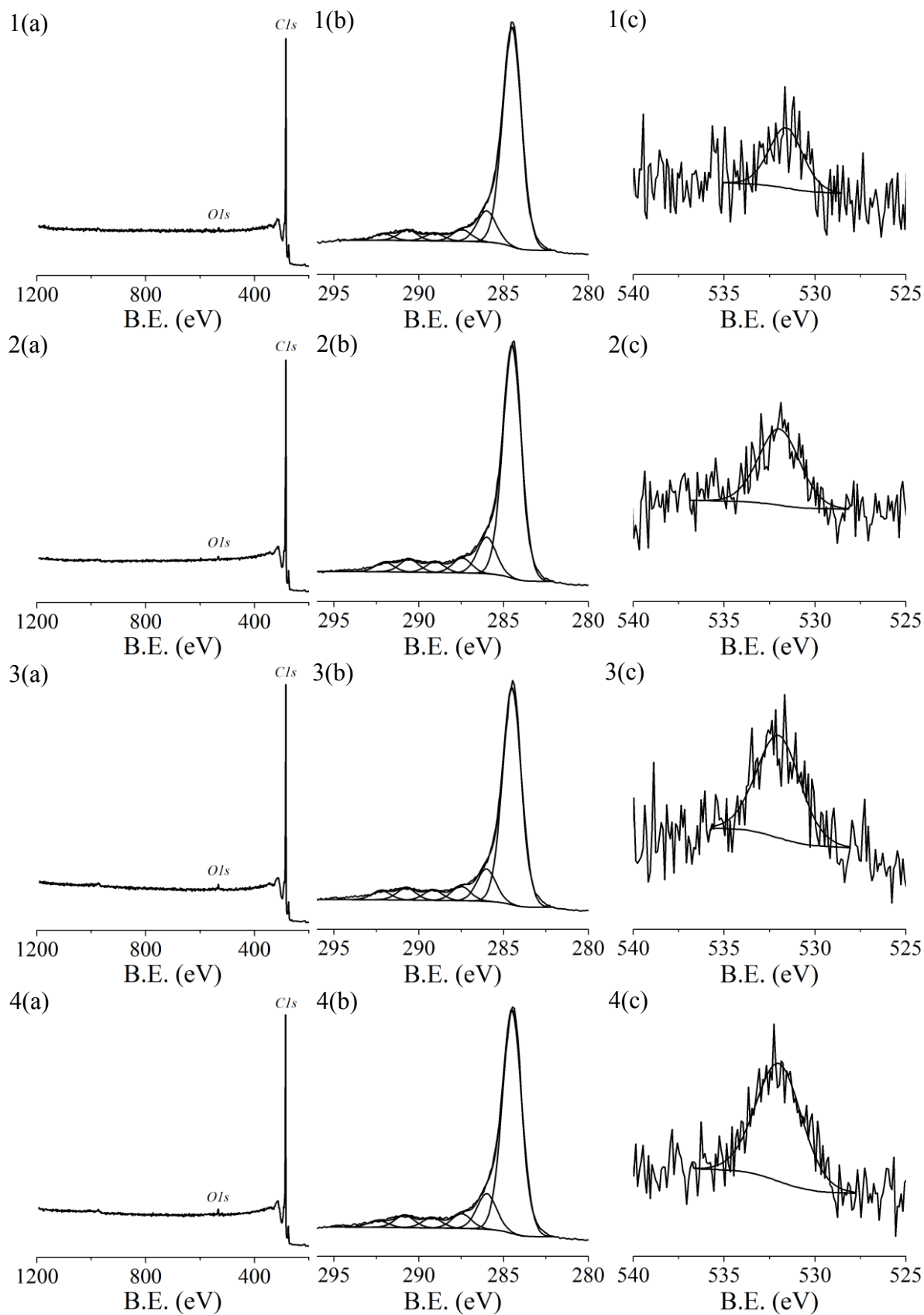


Figure 4.15: XPS (a) wide scan spectra and (b) C 1s and (c) O 1s high resolution spectra of 1. ACB_Pristine 2. ACB_15a 3. CNT_Pristine and 4. CNT_15b.

The XPS analysis comparing pristine ACB and CNT and the hexyl modified ACB and CNT are displayed in Figure 4.15, on the previous page. For reference the figures for processed ACB and CNT and the C 1s deconvoluted peak areas can be found in the Appendix. The low oxygen content of ACB and CNT, compared to CB, is immediately evident, as expected for these higher quality carbon-nanofillers. The small increase in oxygen content for the modified samples of 0.7 % and 1.2 %, can be observed, compared to the pristine samples at 0.2 % and 0.3 %, for ACB and CNT samples, respectively. However, this is an insignificant result, as this increased oxygen content of the modified samples is unfortunately lower than that of the equivalent processed samples. Therefore, this result cannot be directly attributed to the inserted modification.

Nevertheless, the XPS results demonstrate the high degree of purity of the modified samples, as there was no evidence of contamination, which was otherwise observed by the presence of potassium in the carbene modified CB samples in Chapter 3.

4.3.2.4. CHN

Combustion analysis was performed on the carbon-based nanomaterials to further evaluate the changed elemental composition following the performed carbene surface modifications (Table 4.13).

Table 4.13: CHN elemental analysis of pristine and modified carbon-based nanoparticles. Adapted with permission from the American Chemical Society © 2016.¹⁶

Sample	CHN Raw Data (%)		
	C	H	N
CB_Pristine	96.46	1.15	0.00 ^a
CB_Processed	96.82	0.91	0.00
CB_15a	96.67	1.36	0.00
CB_15b_1	95.64	0.94	0.39
CB_15b_2	96.19	1.28	0.32
ACB_Pristine	95.31	0.00	0.00
ACB_Processed	99.14	0.00	0.00
ACB_15a	98.76	0.00	0.00
CNT_Pristine	99.11	0.00	0.00
CNT_Processed	95.41	0.00	0.00
CNT_15a	94.99	1.09	0.00

^a Abundance below the detection limit of the analysis (<0.10 %).

The combustion analysis results of the samples provide limited evidence. Following the XPS results, a reduced carbon content, coupled with an increased hydrogen content, might suggest modification. However, this pattern or any other pattern is not obvious for the three different modified substrates concerned here. It is worth noting that nitrogen was detected at 0.4 % on CB_NP_15b and upon resubmission nitrogen was again detected at 0.3 %. This is unexpected as this method of carbene modification does not introduce nitrogen, and it was not detected on this or any other sample by XPS analysis. This result is therefore attributed to sample contamination.

4.4. Concluding Remarks

To conclude this section of work, a number of silica and carbon-based nanomaterials have been surface functionalised using a tailored precursor diaryldiazo compound terminated in hydrocarbon chains variable in length. The success of the modification was analysed by a number of techniques including BET, thermal analysis, XPS, CHN, SSNMR and ATR-IR. Accordingly, this investigation has presented a number of conclusions:

- A four-step synthesis procedure was optimised to produce a tailored diaryldiazo compound of high purity permitting a one-step surface modification of selected nanomaterials of varied surface chemistries.
- Thermal analysis proved to be a principal method in this work for both types of nanomaterials functionalised. Thermogravimetric measurements upon heating from ~30-850 °C identified the presence of the surface modifications by distinctive weight loss profiles above 200 °C. Surface loadings were determined at 4.2×10^{12} to 4.3×10^{14} molecules/cm², corresponding to a maximum conversion of the diazo compound to the reactive carbene at 3-37 % efficiency. Additionally, for two of the samples analysed, CB and ACB, thermal analysis permitted observation of the diazo

decomposition reaction by the loss of nitrogen upon generation of the carbene species, at a peak rate at 126 °C for both samples under the thermal analysis conditions used.

- SSNMR analysis of the modified silica further affirmed the presence of the inserted diaryl modification by the observation of the aromatic rings, the ether group and hydrocarbon chains compared to the background noise and contaminant solvent peaks present on the unmodified samples.
- BET, XPS, CHN and ATR-IR provided less informative results as this modification did not insert any element markers to the particles surfaces. Nonetheless, these techniques did highlight the purity of this surface modification, especially compared to the variation of results for the carbene modification presented in Chapter 3.

Following the preliminary work discussed in Chapter 3, this study provides an optimised one-step method for tailoring nanoparticle surfaces. Consequently, a general strategy for the functionalisation of nanomaterials of variable surface properties, size and aspect ratios has been demonstrated. Further, this modification presents potential for use in the pursuit of improving nanoparticle compatibilisation in polymer matrices in the technology of polymer nanocomposites.

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5. Nanocomposites Prepared with Covalent Functionalised Nanoparticles

5.1. Introduction

5.1.1. Background

The addition of nanoparticles to polymers presents an opportunity to develop advanced materials for high-tech and engineering applications in the electronic, automotive, aerospace, defence and medical sectors.¹ However, the anticipated superior multifunctional properties of polymer nanocomposites are compromised by the poor compatibility of the two components and the tendency for the nanomaterials to agglomerate as a result of the attractive interactions which exist between them.

Polyolefins, such as polypropylene (PP) and polyethylene (PE), are amongst the most common commodity thermoplastics due to their low cost, relatively simple processability and low chemical reactivity.² As such, these polymers are widely used in automotive and aviation industries as well as household items, for example bottles, stationary and food packaging.³ However, the potential for further application of PP in the engineering sector is undermined by its low compressive strength and low resistance to crack propagation.⁴ The addition of nanomaterials can be used to alleviate this problem, by the introduction of the reinforcing nanofillers with strong adhesive interfaces with the polymer matrix.⁵ Further, PP can be made more relevant as a multifunctional material for other industries through the introduction of new properties, for example electrically conductive polymers are widely sought for electronic devices.^{6, 7}

Accordingly, the addition of silica, arguably one of the most promising nanomaterials due to its high surface area and tuneable porosity, to polymers at low loadings (<10 wt. %) presents an opportunity to improve the mechanical strength, fire retardance as well as to introduce improved thermal, optical and barrier polymer properties.^{2, 8} Polymer

composites prepared with reinforcing fillers at the nano-scale are expected to deliver improved mechanical properties compared to more traditionally used micro-scale particles, as directed by enlarged stiff interfacial regions with the polymer due to the larger surface areas and higher aspect ratios of nanofillers. The superior reinforcing phase in the polymer nanocomposite is however dependent on a uniform dispersion of the nano-scale filler in the polymer matrix. Unfortunately, this is more difficult to achieve because more often nanoparticles will possess greater surface energy than the micro counterparts, especially in polymer matrices, where agglomeration is likely to occur due to the associated stronger filler-filler interactions (Figure 5.1).^{9, 10}

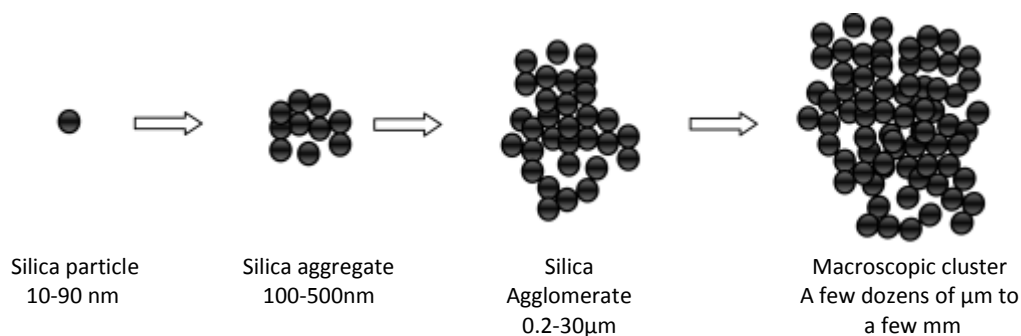


Figure 5.1: A scheme to show the tendency for silica nanoparticles to agglomerate and cluster in polymer nanocomposites. Adapted with permission from John Wiley and Sons © 2013.¹¹

In the case of silica nanomaterials, agglomeration is further promoted by hydrogen bond formation between silanol groups on neighbouring particles.¹² Agglomeration will not only inhibit effective translation of the rigid silica properties to the polymer matrix, but importantly can initiate failure if force is applied to the polymer nanocomposite.¹³ As such, silica surface functionalisation routes are employed as a method to inhibit the attractive filler-filler interactions as well as to improve the filler-matrix compatibilisation so as to encourage a good reinforcing effect to the PP matrix. Further, if uniform dispersion can be achieved, this results in an enhanced interfacial region which can improve the mechanical properties of the polymer nanocomposite. As explained in more

detail in the Introduction Chapter, the interfacial region describes the area surrounding nanoparticles in which the polymer properties differ from the bulk.^{14, 15}

One active area of research into silica functionalisation uses silane coupling agents ($\text{Si}(\text{OR})_3\text{R}'$) (as detailed in Chapter 1) to engineer improved interfacial compatibilisation with polymer matrices.¹⁶ In terms of silica polymer nanocomposites, silica reinforcement has been generally directed towards epoxy resin nanocomposites, with a number already commercially produced.¹ Alternatively, the homogeneous dispersion of hydrophilic silica in hydrophobic polyolefins, such as PP and PE, presents a greater challenge, and improving the interfacial adhesion between the two incompatible components is a key consideration for this nanocomposite system.¹⁷ Accordingly, surface initiated-polymerisation of polypropylene has been performed to the surface of silica nanoparticles in order to produce 'hydrophobic' silica in an effort to diminish the filler agglomeration.¹⁸ Investigation into the effect of tailored interfaces leading to the functionalisation of nanosilica by grafting polymer chains has found that homogeneous filler dispersions were best achieved at the lower filler additions and at lower degrees of chemical grafting.¹⁹ It is considered that the attractive rigid properties of silica can be compromised by high levels of grafting (i.e. when the interfacial region is too large) and therefore the stiff, rigid desirable properties of the silica cannot be effectively translated to the polymer matrix, even if good dispersion in the nanocomposite is achieved.²⁰ Therefore, methods for lower degrees of surface modifications or the incorporation of specific compounds are topical routes being pursued in the interest of polyolefin nanocomposites.

Another application of interest for polyolefins, is for the production of electrically conductive nanocomposites by the addition of carbon-based nanomaterials. Potential applications for these materials include as electronic devices, anti-static coatings and films as well as static dissipative materials for electromagnetic interference (EMI) and

radio frequency (RF) shielding.²¹ Conductive polyolefin nanocomposites are already commercially available using PP and PE polymers with CB, CNT and carbon fiber (CF) fillers, amongst other carbon-based nanomaterials. For example, SIMONA[®] PP-EL is a CB/PP nanocomposite with an electrical conductivity $\sim 10^6 \text{ Scm}^{-1}$ used to shield electrostatic discharge (ESD) in welding rod applications.⁷ The development of high performance electrical nanocomposite materials has, however, also been hindered by tendency of super-agglomerates to form in CB type systems, or entangled fibers for CNTs and CFs nanocomposites. Filler agglomeration is promoted by attractive Van der Waals interactions which exist between carbon-based nanomaterials, as well as the poor compatibility with the polymer matrix. This is unfavourable, as high filler loadings are therefore required to achieve electrical conductivity, compromising the processability properties and attractive innate mechanical characteristics, such as fracture toughness, of the original polymer.^{22, 23} Additionally, the conductive fillers are expensive compared to the polymer component, especially if graphene and CNT nanomaterials are used, and therefore for economically viable conductive polymer nanocomposites, lower filler additions is a key requirement.²⁴

In detail, the addition of conductive carbon-based fillers dispersed in insulating polymers induces electrical conductivity at a critical filler concentration, termed the percolation threshold (Figure 5.2).²⁵ Before the percolation threshold is reached, upon addition of the nanofiller into the polymer matrix, the level of electrical conductivity rises gradually from the original polymer matrix. At the percolation threshold, the formation of continuous three-dimensional networks permits the passage of electrons through the nanocomposite, resulting in a significant increase in conductivity over a small range addition of nanofiller content to the system.^{26, 27} After the critical concentration has been reached, continued filler addition leads to a gradual increase in the conductivity measurements as the

nanocomposite sample approaches the peak electrical conductivity of the filler, which is $\sim 10^2 \text{ Scm}^{-1}$ for CB.²⁸

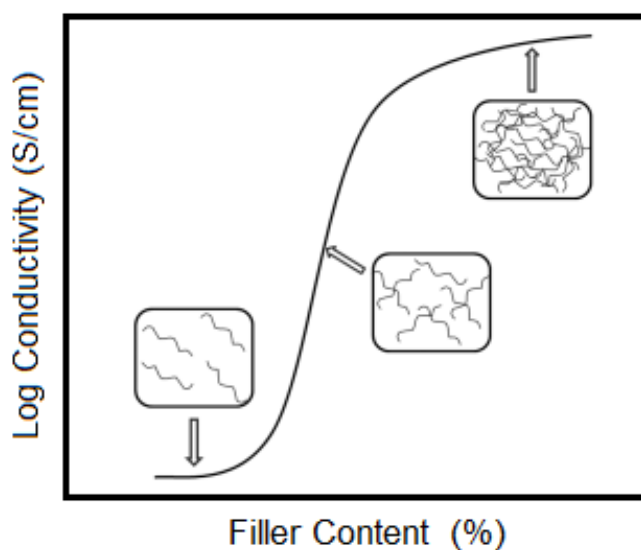


Figure 5.2: The formation of the percolation network as a function of conductive filler loading. Adapted with permission from John Wiley and Sons © 2013.⁷

For example, The TEM image in Figure 5.3(a) demonstrates the formation of the conductive pathways above the percolation threshold in the types of nanocomposite samples which will be prepared and analysed in this Chapter.

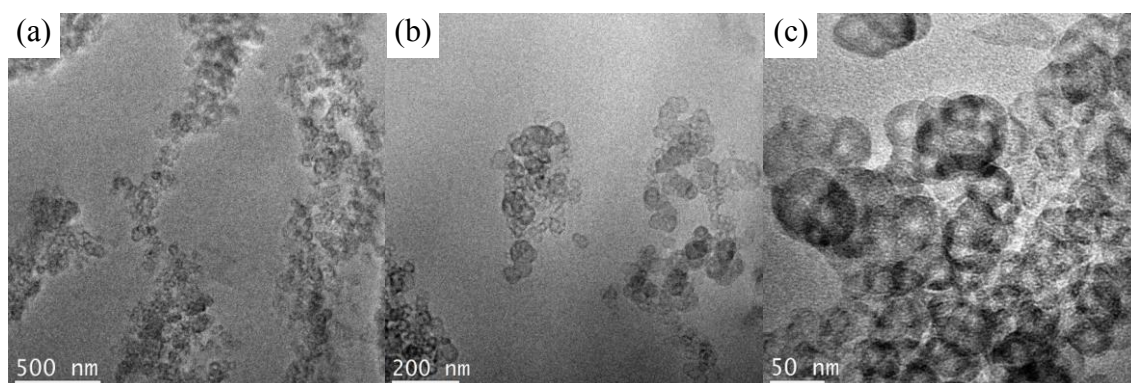


Figure 5.3: TEM images of a solvent-mix prepared CB_Pristine/PP nanocomposite at 30 % wt. loading at (a) 500 nm (b) 200 nm and (c) 50 nm resolution. The CB is the same as used in Chapters 3 and 4.

Closer inspection of the TEM images indicates the presence of isolated agglomerates in the PP matrix (Figure 5.3(b)) as well as the high level of CB agglomeration in the conductive pathways (Figure 5.3(c)). In this example, it is evident that the conductive

networks of CB could be formed more efficiently, and therefore there is potential for the percolation threshold to be achieved at lower filler loadings in the PP matrix. More accurately, the production of electrically conductive polymer nanocomposites at lowered filler loadings requires an effective balance of filler dispersion and distribution as illustrated in Figure 5.4.

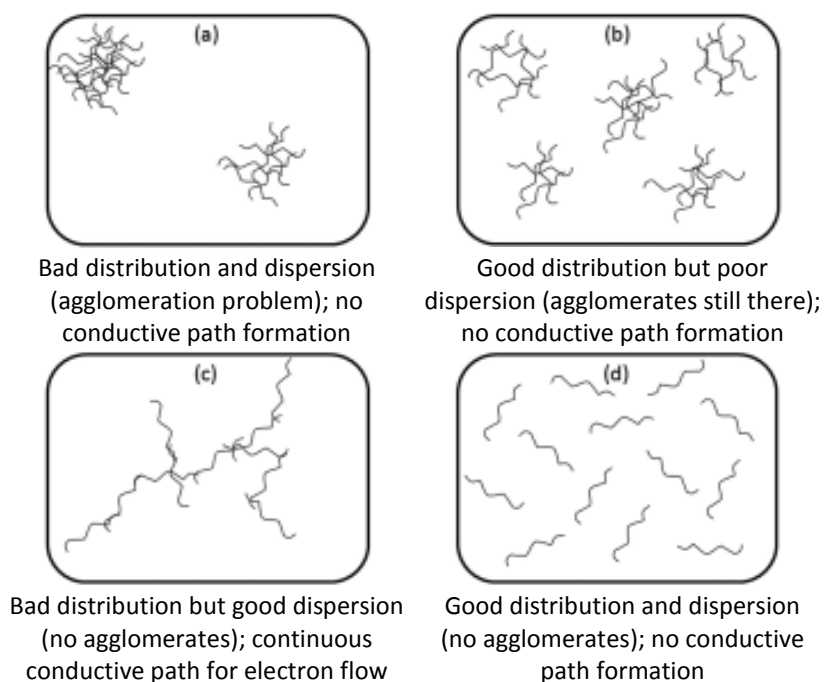


Figure 5.4: The importance of dispersion and distribution upon the conductive path formation in the polymer matrix. Adapted with permission from John Wiley and Sons © 2013.⁷

As previously mentioned, good dispersion is a pre-requisite for good electrical properties, otherwise large agglomerates are formed as depicted in Figure 5.4(a-b) and shown in Figure 5.3(b-c). However, the distribution of the nanofiller is also an important consideration as it needs to be relatively homogeneous in order to achieve effective percolation networks across the PP. On the other hand, the dispersion of the conductive nanofiller in the polymer matrix can become too effective (Figure 5.4(d)). This results in an isolated nanofiller in the PP matrix, which will also lead to poor electrical conductivity for the nanocomposite at low filler loadings. In terms of CB/PP nanocomposites, it is in fact the presence of CB aggregates – the defined units of fused primary CB nanoparticles

– which enables electrical conductivity at lower loadings than are otherwise predicted for a system with separate primary spherical particles.²⁹ That said, a relatively good distribution can still lead to good conductivity as the aggregates do not necessarily need direct contact because electron tunneling can facilitate conduction if they are close enough, $\sim <10$ nm.³⁰ Therefore, the principal aim in this work is to improve the CB/PP filler-matrix interface in order to achieve good dispersion and relatively good distribution in order to minimize the amount of conductive CB nanofiller required to achieve conductive nanocomposites.

In summary, the ultimate properties of polymer nanocomposite are dependent upon a multitude of factors, including the polymer fabrication method, the selected polymer and filler type as detailed extensively in the Introduction Chapter. However, in order to gain control of nanocomposite properties, nanofiller functionalisation has been widely employed. The global aim is for the modification to improve the filler-matrix interfacial interactions leading to the inhibition of unfavourable agglomeration, ultimately for the improved dispersion and optimal distribution of the nanofiller.³¹ In Chapter 4, microsilica, nanosilica and CB, selected as commonly used nanofiller candidates, were modified using diarylcarbene derivatives with terminal hexyl and dodecyl chains to tailor their surface chemistries to PP. In this Chapter, the preparation of nanocomposites with these nanofillers using polypropylene (PP) will be reported in order to explore the possibility of chemical surface functionalisation leading to enhanced nanocomposite properties.

5.1.2. Aims of the Project

This chapter explores the potential for diaryldiazo modified silica and CB nanomaterials for use in the production of PP nanocomposites with superior properties.

The major objectives in the section of work included:

- To develop in-house nanocomposite fabrication methods to produce silica/PP and CB/PP nanocomposites;
- To evaluate whether the treatment to the nanomaterial surfaces by diaryldiazo compounds, terminated in hydrocarbon chains of variable lengths, promotes improved compatibilisation, and therefore enhanced properties in the resulting PP nanocomposites;
- To identify whether the thermal and mechanical properties of PP are altered in the prepared silica/PP nanocomposites, and by comparing microsilica and nanosilica results, evaluate the effect of the filler size on the final material properties;
- To determine if the modified CB leads to superior electrical conductivity at lowered filler loadings and improved thermal properties of the CB/PP nanocomposites.

Ultimately, the aim of this study is to establish whether diaryldiazo nanomaterial surface modification routes proposes a useful and viable strategy for polymer nanocomposite technology.

5.2. Experimental Details

5.2.1. Materials

Microsilica (Si_MP) was purchased as Merck Geduran Si 60 silica gel (40-63 μm) and nanosilica (Si_NP, 10-20 nm, density 2.2-2.6 g/mL) was sourced from Sigma-Aldrich. Commercial Monarch® Carbon Black (CB, M 430, 27 ± 10 nm, density 1.1 - 1.9 g/cm³) was supplied from Cabot Corporation (Billerica, MA, USA). Commercial grade polypropylene (PP, 2440TC polypropylene copolymer with ethylene as the co-monomer, MFI 55 g/10 min) was provided by IRPC Ltd., Thailand. All other reagents were used as supplied from Alfa Aesar Chemicals Ltd., Sigma-Aldrich Chemicals and Lancaster Chemicals Ltd.

The nanomaterials were modified by carbene functionalisation from precursor diaryldiazo compounds terminated in hexyl or dodecyl hydrocarbon chains (Figure 5.5), as presented and characterised in detail in Chapter 4.

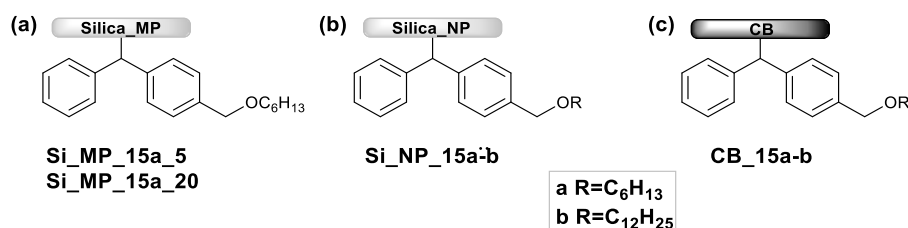


Figure 5.5: A scheme to show the modified nanomaterials used for PP nanocomposites in this Chapter: (a) Si_MP_15a_5 and Si_MP_15a_20, that is modified microsilica (Si_MP) at 5 and 20 % diazo wt. loading with the hexyl termination, (b) Si_NP_15a-b, modified nanosilica (Si_NP) at 16 % diazo wt. loading with hexyl and dodecyl terminal groups and (c) CB_15a-b, modified Carbon Black (CB) at 66 % diazo wt. loading with hexyl and dodecyl termination.

5.2.2. Preparation of Polymer Nanocomposites

Nanocomposite samples were prepared by solvent mixing methods, adapted from general procedures in the literature.^{7, 32, 33} For the preparation of Si/PP nanocomposites, PP pellets (0.5 g) were dissolved in toluene (20 mL) under reflux (130 °C) for 40 min. Subsequently, in a hot suspension in toluene (2 mL), pristine and modified microsilica, at 1, 3 and 5 wt. % of PP, and for nanosilica, at 1, 3, 5 and 10 wt. % of PP, were added to the dissolved PP in toluene under reflux. After 10 min, the Si/PP suspension was sonicated for 30 min in an ultrasonic bath and dried *in vacuo* to give Si/PP nanocomposites (Figure 5.6(a)).

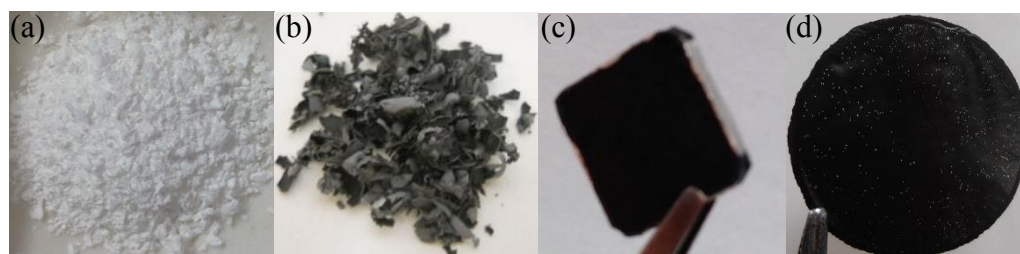


Figure 5.6: Photos of the solvent-method fabricated nanocomposites of (a) Si/PP (b) CB/PP and compression moulded CB/PP (c) silver pasted plaque for conductivity measurements and (d) film for TEM analysis.

For the preparation of CB/PP nanocomposites, PP pellets (0.15 g) were dissolved in toluene (10 mL) under reflux (130 °C) for 30 min. Subsequently, in a hot suspension in

toluene (2 mL) pristine, processed and modified CB at 10, 15, 20, 25 and 30 wt. % of PP were added to the dissolved PP in toluene under reflux. Following 10 min stirring, the PP/CB suspension was sonicated for 30 min in an ultrasonic bath and dried *in vacuo* to give CB/PP nanocomposite (Figure 5.6(b)).

For DMA, TEM and dielectric analysis, nanocomposite samples were pressed into films (29 mm diameter) at selected thicknesses (15-500 μm), using a Specac Film Maker assembly set up in a Specac Atlas hydraulic press (Figure 5.6(c)). The selected steel spacer (A-F) for the required film thickness was fitted between two optically polished platens, in which the sample was placed between non-stick aluminium foil sheets. Custom set heat and pressure methods were used to prepare the films of each thickness. The nanocomposite samples for DMA were prepared at a film thickness of 500 μm (spacer 'F'); the nanocomposite sample (~300 mg) was heated at 180 $^{\circ}\text{C}$ for 5 min and then, a pressure of 1 Torr was applied for 1 min, before removal to a cooling plate. For dielectric analysis, films at a thickness of 50 μm (spacer 'C') were prepared; the nanocomposite sample (~45 mg) was heated at 175 $^{\circ}\text{C}$ for 2.5 min, and then a pressure of 1 Torr applied for 45 s before removal and cooling. For TEM/SEM analysis and visual characterisation of the prepared nanocomposites, films at a thickness of 15 μm (spacer 'A') were prepared; the sample (~20 mg) was heated at 170 $^{\circ}\text{C}$ for 30s, and then a pressure of 0.5 Torr was applied for 30s, before removal and cooling.

Nanocomposite samples for conductivity measurements were prepared by compression moulding into plaques ($1 \times 1 \times 0.1 \text{ cm}^3$ (Figure 5.6(d))) using a custom made mould in the Specac Film hot press treated at a sequential temperature profile of: 200 $^{\circ}\text{C}$ -5 min, 190 $^{\circ}\text{C}$ -10 min, 195 $^{\circ}\text{C}$ -10 min and 200 $^{\circ}\text{C}$ -5 min. After 30 min in the hot press, the mould was removed and immediately cooled under running cold water for ~5 min.

5.2.3. Nanocomposites Characterisation

The nanocomposite samples were all characterised using simultaneous thermal analysis (DSC, TGA), and for the CB/PP nanocomposites, by volume electrical conductivity measurements. Selected samples were additionally analysed by DMA, dielectric analysis, TEM, SEM. The experimental procedures for these analysis techniques are detailed in Chapter 2.

5.3. Results and Discussion

The assessment of the altered PP nanocomposite properties is detailed in two sections according to the addition of the covalent modified inorganic (silica) and organic (CB, ACB, CNTs) nanofiller type to PP.

5.3.1. Silica-PP Nanocomposites Characterisation

Modified microsilica, Si_MP_15a_5 and Si_MP_15a_20, with the hexyl terminated modification at 5 and 20 wt. % loadings, and modified nanosilica, Si_NP_15a-b, with a hexyl and dodecyl termination (16 % loading), were used to prepare PP nanocomposites (1 - 10 %). SEM images of unmodified nanosilica and thermal analysis measurements, including DSC, TGA and DMA, were used to evaluate the changed macroscopic properties of the nanocomposites with particular focus upon the thermal stability and mechanical properties.

5.3.1.1. Morphological Properties

The morphology of blank nanosilica/PP nanocomposites (prepared at 5 % wt.) was examined by SEM (Figure 5.7).

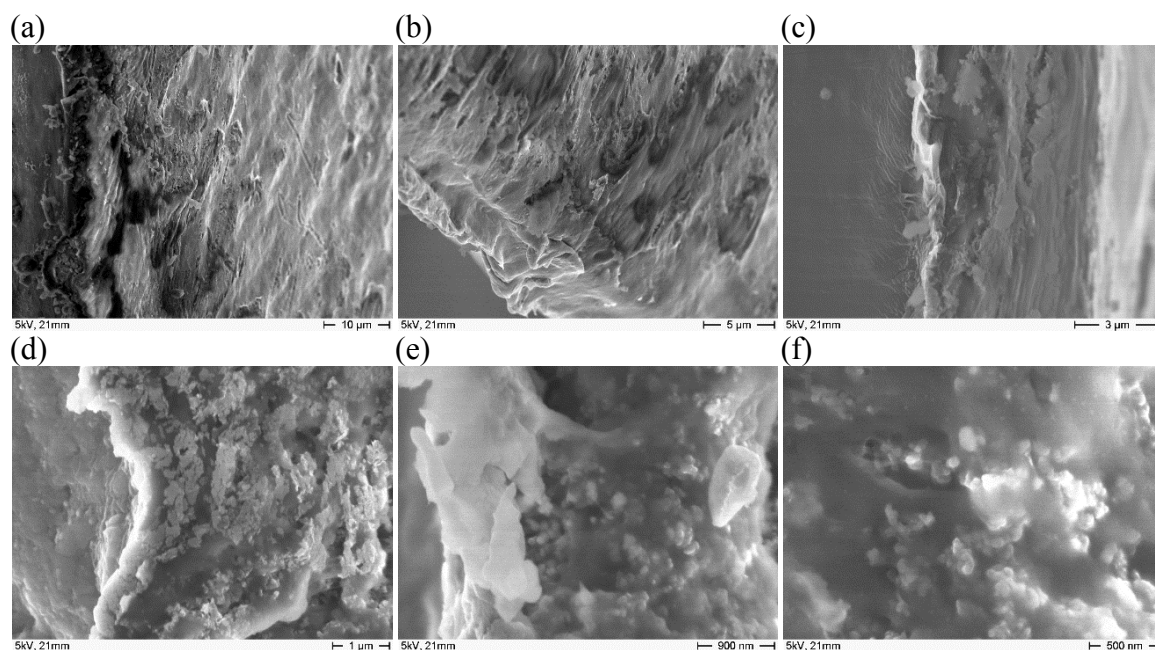


Figure 5.7: SEM images of Si_NP_Pristine/PP at 5 wt. % loading at (a) 10 μm , (b) 5 μm , (c) 3 μm , (d) 1 μm , (e) 0.9 μm and (f) 0.5 μm magnification.

The light areas, particularly visible in the high resolution images, show the nanosilica and clearly demonstrates the tendency for aggregation in clusters as large as 900 nm in the PP matrix. The inhomogeneity of the dispersion and poor distribution of the silica is immediately evident, emphasising the need for some optimisation to improve the compatibility between the nanocomposite components.

5.3.1.2. Thermal Analysis

Thermal analysis measurements of the prepared Si/PP nanocomposites were used to evaluate the influence of the silica types and the performed functionalisation by characterisation of the crystallisation, melting and decomposition behaviours. Reference polymer blank samples, PP as received in pellet form (PP_Pristine), and PP as received and then treated in the nanocomposite process without the addition of nanofiller (PP_Processed), were each tested three times and the silica nanocomposite samples twice. As an introduction to the thermal analysis investigation for PP and the Si/PP

nanocomposites, Figure 5.8 displays the typical thermal analysis curves for processed PP for the thermal program used: Step 1, 30-250 °C; step 2, 250-30 °C and step 3, 30-850 °C.

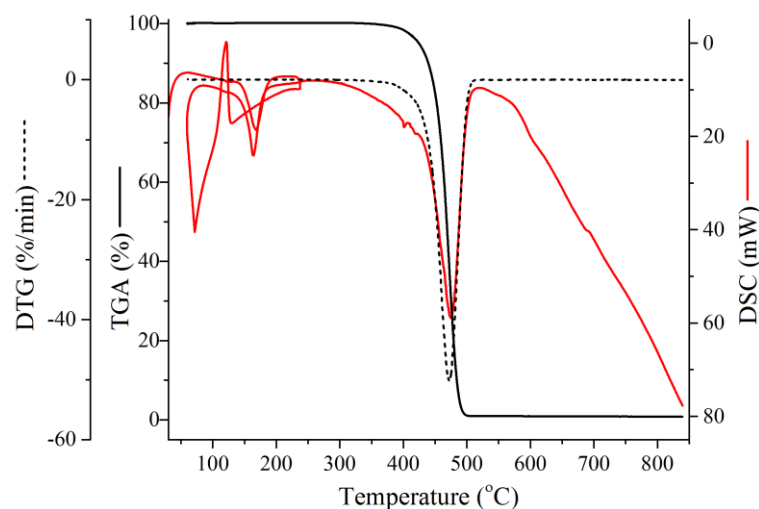


Figure 5.8: Thermal analysis data displaying the DSC, TGA, and DTG curves of PP_Processed.

The initial heating run is performed to erase the thermal history of the polymer, and accordingly in literature the melting temperature (T_m) is generally determined by a second heating run. In this work a second advantage of an initial melting peak, is that when the samples (~12 mg) are set up in the STA analyser they are dissimilar in size, the nanocomposite is made up of small flakes, whereas the as-received PP is a halved pellet. However, once melted after the first heating scan, satisfactory, similar thermal contact with the crucible can be ensured, enabling better comparative data for the rest of the thermal run. During the cooling run on the STA program the crystallisation temperature was found to be ~121 °C and then during the second (final) heating step, the melting temperature was at ~165 °C and the onset of the decomposition of PP was found to be at ~475 °C. The PP decomposition is additionally evident in Figure 5.8 from the TGA signal, which has an extrapolated onset at ~446 °C, and a derivative peak maximum at ~472 °C.

For the thermal events of PP and considering the potential for silica nanocomposites, it is worth reiterating the PP used is a semi-crystalline random co-polymer with ethylene as a co-monomer. The broad melting peaks are therefore the result of the large size distribution of crystallites as a semi crystalline polymer. The addition of an inorganic nanofiller to the semi-crystalline PP is anticipated to alter and improve the melting, the crystallisation and degree of crystallinity for the resulting nanocomposites.³⁴ Additionally, the thermal decomposition of the used co-polymer PP is improved by ~100 °C, compared to isostatic PP in non-oxidizing (N₂) conditions. The thermal decomposition mechanism for PP is a complex radical chain process by radicals present on carbon backbone initiating carbon-carbon chain scission.³⁵ PP however demonstrates a lower thermal stability compared to PE, as the methyl side groups in PP enable intermolecular hydrogen transfer, which enhances the degradation mechanism,³⁶ hence the improved decomposition temperature of the co-polymer with ethylene observed here. Accordingly, another aim of dispersed micro or nanosilica in the PP nanocomposites is for further enhancement of the decomposition temperature, as it has been reported in the literature that in an inert atmosphere, a dispersed nanofiller can yield a ‘shielding’ effect in which the loss of volatile by-products formed as the polymer decomposition is hindered.³⁷

Following thermal analysis, measurements were taken of the PP and Si/PP nanocomposite samples. The averaged data extracted for the main peaks and onsets of interest are reported in Table 5.1, and further details, including the repeat measurements, can be found in the Appendix. The determined degree of crystallinity (X_c) was calculated as follows:

$$X_c = \frac{H_m}{(1 - x)H_0} \times 100 \quad \text{(Equation 5.1)}$$

where H_m is the sample melting enthalpy, as measured by DSC, H_0 is the melting enthalpy of 100 % crystalline PP, which is reported to be 207.1 J/g,^{38, 39} and x is the weight fraction of silica present in the nanocomposite.⁴⁰

Table 5.1: Extracted DSC, TGA and DTG data from thermal analysis runs of pristine and modified microsilica and nanosilica PP nanocomposites.

Sample	Silica Loading (Wt. %)	DSC						TGA	DTG	
		T _{oc} ^a (°C)	T _{pc} ^b (°C)	T _{om} ^c (°C)	T _{pm} ^d (°C)	ΔH _m ^e (J/g)	X _C ^f (%)	T _{pd} ^g (°C)	T _{od} ^h (°C)	T _{pd} ⁱ (°C)
S.D. sample set ^j		0.3	0.9	0.7	1.3	3.4	1.7	1.0	2.0	0.9
Average PP_Pellet ^k	0	121.1	116.5	150.8	163.0	77.0	37.2	470.9	444.6	468.5
S.D. PP_Pellet		0.0	0.1	0.5	0.1	0.6	0.3	1.1	0.7	0.2
Average PP_Processed ^k	0	127.6	122.9	149.1	163.2	71.1	34.3	474.0	446.3	472.3
S.D. PP_Processed		1.7	1.9	1.8	0.7	0.7	0.3	0.8	2.1	1.0
Si_MP_Pristine	1	126.9	120.8	148.9	163.7	65.5	31.9	474.4	442.0	471.6
	3	127.6	120.9	147.3	165.7	57.9	28.8	476.6	438.9	474.3
	5	128.0	121.6	148.1	164.4	62.1	31.6	474.8	438.3	473.2
Si_MP_15a_5/PP	1	128.5	123.7	147.0	163.8	79.9	38.9	473.2	443.3	471.0
	3	127.6	121.0	148.8	163.7	68.4	34.0	473.2	440.4	471.3
	5	128.3	122.0	148.2	165.3	74.7	38.0	474.0	439.2	471.6
Si_MP_15a_20/PP	1	126.9	120.9	148.0	163.9	68.1	33.2	474.1	435.4	470.8
	3	127.5	122.5	146.8	163.0	76.1	37.9	471.3	436.7	469.6
	5	128.1	122.1	147.4	164.8	66.6	33.9	472.2	441.4	472.6
Si_NP_Pristine/PP	1	126.8	120.8	149.4	164.9	75.6	36.9	474.8	443.9	470.5
	3	127.8	121.0	147.8	165.0	72.7	36.2	471.2	444.3	468.3
	5	127.3	118.7	147.1	167.0	71.8	36.5	471.1	442.3	468.3
	10	126.7	120.0	146.3	161.7	66.3	35.6	471.6	443.7	470.2
Si_NP_15a/PP	1	127.1	121.8	146.9	161.6	67.1	32.6	473.3	443.7	471.5
	3	127.5	120.7	147.1	166.6	73.9	36.8	471.3	443.6	469.3
	5	128.7	122.4	146.9	165.2	74.5	37.8	470.4	441.7	467.2
	10	127.0	120.9	147.1	162.4	74.1	39.7	470.9	439.3	469.9
Si_NP_15b/PP	1	128.0	122.3	148.4	163.8	68.2	33.3	474.7	450.2	471.9
	3	127.5	120.5	148.9	165.5	71.9	35.8	473.7	446.7	470.1
	5	127.1	119.3	148.4	166.4	71.4	36.3	471.4	443.5	468.6
	10	125.7	119.2	146.2	162.2	70.7	38.0	468.0	436.8	464.5
Average Si/PP		127.5	121.2	147.7	164.3	70.4	35.4	472.7	441.7	470.3
S.D. Si/PP		0.7	1.2	0.9	1.5	5.0	2.7	2.0	3.5	2.2

^a T_{oc}, onset crystallisation temperature.

^b T_{pc}, peak crystallisation temperature.

^c T_{om}, onset melting temperature (second melting cycle).

^d T_{pm}, peak melting temperature (second melting cycle).

^e ΔH_m, enthalpy of melting (second melting cycle).

^f X_C, is the degree of crystallinity.

^g T_{pc}, peak decomposition temperature (DSC).

^h T_{pc}, onset decomposition temperature (TGA).

ⁱ T_{pc}, peak decomposition temperature (DTG).

^j average standard deviation across the sample set for two repeated measurements of each nanocomposite sample.

^k The average PP samples were determined from three repeat measurements.

The average standard deviation between the duplicate repeats of the Si/PP nanocomposites for each of the measured events, labelled ‘S.D. sample set’, are included in Table 5.1 in order to aid interpretation of the significance of the generated results.

Taking into account this error and the small variation of the results of the prepared

nanocomposites it is difficult to identify a clear trend from either data of the silica types or the effect of the silica surface modification. The data set for all the Si/PP nanocomposites was also averaged and the standard deviation calculated for all the loadings and modification types, highlighting some small general changes across the thermal events by the augmented standard deviations. Most notably, a general unexpected effect of lowered peak crystallisation (T_{oc}), onset of melting (T_{om}) and decomposition (T_{od}) temperatures is indicated after silica addition. Additionally, it can be observed that the crystallisation and decomposition properties of PP appear to be altered during the solvent mixing process, indicating that the processing conditions generally appear to have had a greater effect on the thermal analysis results than the silica addition.

The STA thermal analysis results for the microsilica/PP and nanosilica/PP nanocomposites therefore generally do not indicate any significant improvements following the diaryl carbene treatments to the silica reinforcing filler.

DMA

Dynamic Mechanical Analysis (DMA) is a technique in which the modulus, the stiffness, and the damping behaviour, related to the energy the sample can absorb, is measured and therefore presents a useful technique for the detection of altered interfacial interactions for nanofillers in polymer nanocomposites. After the generally uninformative thermal analysis data of the prepared silica/PP nanocomposites, a selection of unmodified and hexyl and dodecyl terminated nanosilica/PP nanocomposite film samples at 3 % wt. loading were analysed by DMA.

For semi-crystalline polymers, such as PP, the principal transitions that can be identified by DMA are the glass-rubber transition temperature (T_g) and the melting point (T_m), which will be the highest temperature transition with the largest modulus change. The T_g of PP is reported to be $\sim 10^\circ\text{C}$ (from the $\text{Tan } \delta$ peak position at 1 Hz) and for PE is

generally accepted at ~ 20 °C.⁴¹ The results of the damping factor ($\tan \delta$ – the ratio of the loss modulus (E'')/storage modulus (E')) for the PP and Si/PP nanocomposites indicate three relaxations at ~ 50 °C (γ), ~ 0 °C (β) and ~ 65 (α) °C, as determined from the peak temperature in the $\tan \delta$ curves (Figure 5.9, Table 5.2).

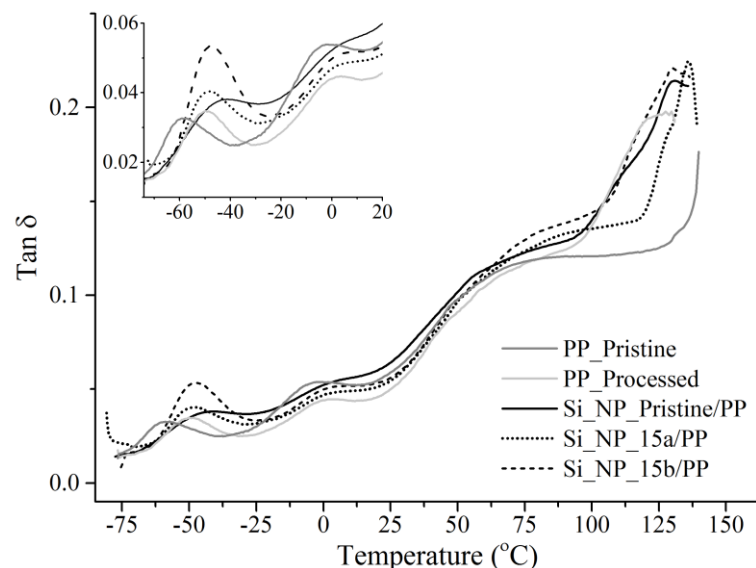


Figure 5.9: $\tan \delta$ (measured at 1 Hz at a heating rate of 5 °C/min) as a function of temperature for PP and nanosilica/PP nanocomposite film samples. Insert shows the γ and β relaxation peaks at the beginning of the thermal program ~ -75 – 20 °C.

Table 5.2: Extracted DMA data including α , β and γ relaxation peak data, as determined from the $\tan \delta$ curves, and the extrapolated onset of the major transition of the storage modulus (E') at -70 °C, the melting transition (T_m).

Sample	Tan δ						Storage E'	
	Relaxation γ		Relaxation β		Relaxation α		At -70 °C T_m Onset (Pa)	°C
	(°C)	Height	(°C)	Height	(°C)	Height		
PP_Pristine	-59.6	0.013	-5.3	0.012	67.5	0.038	3.2×10^9	136.0
PP_Processed	-50.0	0.015	-0.9	0.007	57.6	0.015	3.2×10^9	104.5
Si_NP/PP	-46.5	0.014	1.3	0.006	64.2	0.023	3.1×10^9	119.3
Si_NP_15a/PP	-49.1	0.015	0.5	0.005	66.4	0.027	3.4×10^9	130.6
Si_NP_15b/PP	-48.4	0.029	0.6	0.006	64.5	0.019	3.0×10^9	119.0

At the lowest temperature at the beginning of the analysis, the γ -relaxation process occurs in the amorphous regions due to short range motions of chain segments, such as methyl groups in side chain ends of the polymer. Next, the principal β -relaxation phase is attributed to the glass-rubber transition. An increase in the peak temperature of the $\tan \delta$, as well as a reduced peak intensity for these relaxations, can signify restricted segmental

mobility, which is the capacity for the polymer chains to form different physical orientations in the amorphous phase.⁴² Last, α -relaxation at higher temperatures closer to the melting point of the sample, represents motions of the crystallites in the interphase regions, such as lamellar slip and rotation.⁴³ For the Si/PP nanocomposites, the Tan δ peak temperatures therefore provides an important indication of the viscoelastic properties between the nanomaterial and polymer matrix interphase layers. The small general increase recorded for each of the relaxations, compared to the PP only samples, indicates the restricted polymer chain movements due to the reinforcing effect of the added silica nanoparticles.⁴³ Nevertheless, it should be noted that the difference in the Tan δ data of the PP_Pristine films, prepared from the as-received pellets, and the PP_Processed films, prepared from PP treated in the nanocomposite solvent mixing procedure, might indicate altered amorphous content as a result of the nanocomposite solvent processing methods used. Additionally, the height of Tan δ γ -relaxation peaks are similar for Si_Pristine/PP and Si_NP_15a/PP to the PP samples, however for Si_NP_15b/PP, the height is doubled. This suggests that the expected lowered segmental mobility due to the addition of the rigid silica is perhaps compensated by the longer dodecyl terminated functionalisation which is promoting the molecular movement of the PP. A similar effect, whereby silica nanoparticles have demonstrated altered Tan δ peak heights as a result of differing degrees of grafting density has previously been reported.¹⁹ The Storage modulus (E') displays the α , β and γ relaxations as well as the major transition (T_m) at ~ 100 - 150 °C due to the samples reaching the melt region (Figure 5.10).

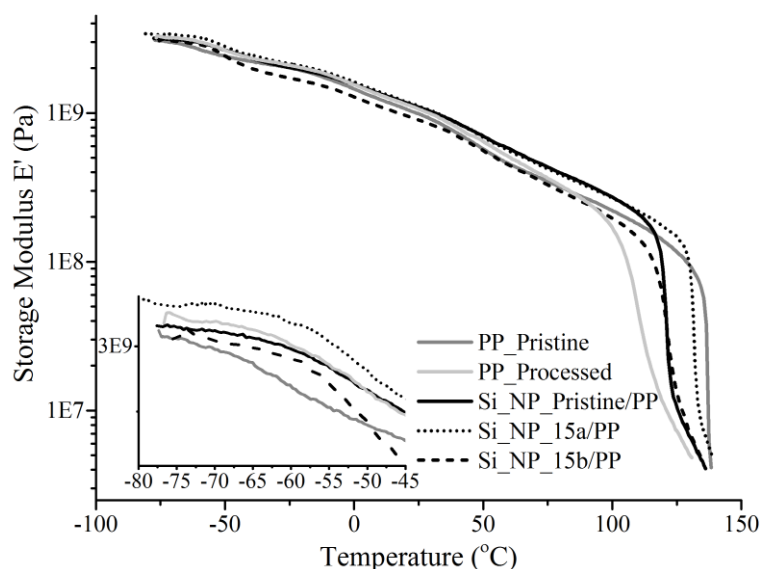


Figure 5.10: Storage modulus (E') (measured at 1 Hz at a heating rate of 5 °C/min) as a function of temperature for PP and nanosilica/PP nanocomposites. The insert displays the Storage modulus (E') at the beginning of the thermal program ~ -80 – -45 °C.

The major transition does not display a sharp decrease, as expected, due to the range of melting points for the polymer sample. This is a consequence of the different molecular weights present in the PP copolymer used.⁴¹ The range of the extrapolated onset temperatures for the melt transition of the samples of 104.5–136.0 °C (Table 5.2) does not indicate any significant results or pattern between the samples. Indeed, important changes in the melt region would have been more easily observed in the DSC thermal analysis results presented above. However, the key result in this data is the small enhancement of the storage modulus of Si_NP_15a/PP (with the hexyl termination) by 200 MPa at -70 °C (Figure 5.10(Insert), Table 5.2), consistent with the expected stiffening effect from the added silica nanofiller. Albeit a small change, it might be that the hexyl silica functionalisation for this sample improved the interactions with the PP matrix, thereby improving the dispersion and promoting an augmented storage modulus. The lowered storage modulus of Si_NP_15b/PP compared to Si_NP_Pristine/PP and PP_Processed by 100 and 200 MPa, respectively, indicates a poorer stiffening effect for the dodecyl silica modification. It could be that the longer chain silica surface modification is promoting

molecular movement of the PP as suggested by the Tan δ peak height result, which has compromised the impact of the rigid silica on the PP matrix.

Considering the small alterations discussed in the DMA results following the addition of pristine and modified silica to PP, it is worth highlighting that care was taken for the samples to be exposed to exactly the same thermal conditions, from nanocomposite preparation through to film preparation. Additionally, the nanocomposite preparation by solvent mixing was optimised for the silica nanocomposites to allow for the low filler additions (1-10 wt. %) in this work. Nevertheless, the nanocomposite film preparation for the DMA experiments exposed the similar, high levels of clustering of the nanosilica for all the samples (Figure 5.11).

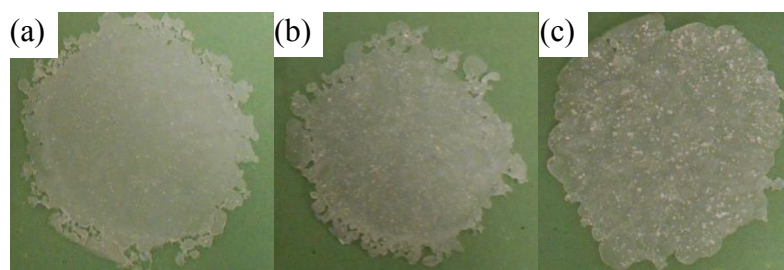


Figure 5.11: Nanocomposite (0.5 mm) films of (a) Si_NP_Pristine/PP, (b) Si_NP_15a/PP and (c) Si_NP_15b/PP prepared at 3 % wt. filler loading used for DMA analysis.

In summary, the generally unremarkable thermal analysis by STA and DSC for the microsilica and nanosilica/PP nanocomposites suggests that silica remains highly agglomerated in the PP nanocomposites. Either the functionalisation approach was insufficient to promote filler dispersion, or the solvent mixing method was inadequate to permit evaluation of the effects of the functionalisation. Alternatively, it may be that the equipment and analysis techniques were not sensitive enough to determine the changed properties.

5.3.2. CB-PP Nanocomposites Characterisation

Pristine, processed and modified CB, CB_15a-b with the terminal hexyl and dodecyl diaryl functionalisation, were used to prepare PP nanocomposites at 10-30 wt. % loadings. Accordingly, the volume electrical conductivity of the nanocomposites, along with further analysis by dielectric analysis, TEM and STA techniques were used to evaluate the changes to the nanocomposite properties after surface functionalisation.

5.3.2.1. Volume Resistivity

Improved electrical conductivity is a key aim for the CB/PP nanocomposites and additionally it provides a useful indication on the nano-scale of the altered filler-filler and filler-polymer interfacial interactions following the carbene filler functionalisation. The introduction of electrical conductive properties to insulating polymers using carbon-based filler is detailed in the Introduction of this Chapter. However, it is worth reiterating the importance of the percolation threshold. This term describes the critical filler concentration at which the point the nanocomposite induces electrical conductivity by the formation continuous three-dimensional networks in the polymer matrix.²⁵ The aim for high performance nanocomposites for electrical applications is to achieve the percolation threshold at low filler loadings, in order to avoid the loss of attractive innate mechanical and the good processability properties of the neat polymer.⁴⁴ The volume conductivities, calculated from the measured sheet resistance of prepared pristine, processed and modified CB/PP nanocomposite plaque samples ($1.0 \times 1.0 \times \sim 0.1 \text{ cm}^3$), are presented in Figure 5.12 as a function of filler loading. Further details can be found in the Appendix, including the initial resistance measurements, dual measurements of the plaques as well as the calculated error from the repeated unmodified CB/PP nanocomposites.

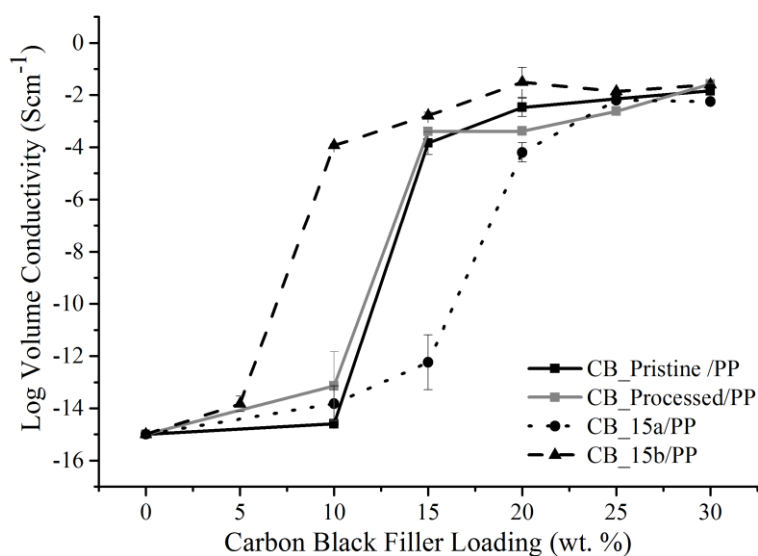


Figure 5.12. Logarithm of the volume electrical conductivity of pristine and modified CB/PP nanocomposites as a function of CB nanofiller loading. The error bars indicate the error of the measurements taken across the perpendicular sides of the nanocomposite plaque samples. Adapted with permission from the American Chemical Society © 2016.⁴⁵

The electrical conductivity of the CB_Pristine/PP nanocomposites increased significantly in the region from 10 to 20 wt. % filler loading, identifying the percolation threshold starting to be reached ~15 wt. %, with a conductivity in the order of $4.66 \times 10^{-4} \text{ Scm}^{-1}$. The high filler loading required to induce electrical conductivity is expected based on the low aspect ratio and low structure of the CB used, and this result is consistent with previous work on similar nanocomposite systems.⁴⁶ The CB_Processed/PP nanocomposites demonstrate similar results to the CB_Pristine/PP nanocomposites, indicating the sonication step or indeed any part of the modification process (excluding the addition of the carbene compound) does not lead to altered CB/PP nanocomposite properties. As such, the altered electrical conductivities of the modified CB/PP nanocomposites can be considered a direct result of the performed CB carbene surface modification. Additionally, the CB_Processed/PP nanocomposite results highlight the general reproducibility of the electrical measurement protocol used, whilst the greater variability in the region of the percolation threshold (~10-20 %) can be observed, as would be expected.

For the modified CB nanocomposites, CB_15a/PP – in which the CB was covalently modified with a terminal hexyl chain – an increased critical concentration of ~20 wt. % was required, compared to the unmodified CB (~15 wt. %). This result suggests the presence of even one polar ether group in the short side chain modifying group leads to poor CB-PP matrix compatibilisation in the nanocomposite. By contrast, CB_15b/PP, functionalised with a terminal dodecyl chain, displayed high electrical conductivities at reduced filler loadings. Top conductivities of $2.51 \times 10^{-1} \text{ Scm}^{-1}$ were observed with the percolation threshold beginning to be realised near a loading of 10 wt. %, at a conductivity of $1.19 \times 10^{-4} \text{ Scm}^{-1}$ (Figure 5.12). This result suggests improved compatibilisation between the CB and PP components following the surface functionalisation. Further, it is likely that steric stabilisation from the modification hinders CB agglomeration of aggregates, assisting dispersion of the nanofiller in the nanocomposite. Interestingly, this reveals that the terminal dodecyl chain present on CB_15b, compared to hexyl-terminated modification on CB_15a, is a viable nanoparticle modification for the production nanocomposite with improved conductive properties. It is important to note here that the difference between the two covalently modified nanoparticles is unlikely to be as a result of the surface loading of the modifiers as they were similar, at values of 7.1×10^{13} and 2.4×10^{13} molecules/cm² for CB_15a and CB_15b, respectively, as estimated by TGA (Chapter 4).

Additionally, the volume conductivity was measured across both sides of the nanocomposite plaques, permitting estimation of the error bars in Figure 5.12. The bidirectional analysis indicated an excellent level of sample homogeneity for the dodecyl modified CB_15b/PP and a poorer level for the hexyl modified CB_15a/PP, especially at lower filler concentrations, consistent with greater agglomeration in the latter nanocomposite.

5.3.2.2. Dielectric Analysis

Altered percolation thresholds of carbon-based polymer nanocomposites have been shown to exhibit promising dielectric properties, for example in electromagnetic interference (EMI) shielding applications.⁴⁷ Further, testing nanocomposite samples close to the percolation threshold can provide useful information about the conductive mechanism which cannot be identified by DC conductivity measurements, such as the microstructure, connectivity and electrodynamics of the nanocomposite samples.⁴⁸⁻⁵¹ Figure 5.13 displays the real (ϵ') and imaginary (ϵ'') parts of the complex permittivity as a function of frequency of pure PP and pristine and modified CB/PP nanocomposite samples at 20 wt. % loading in the range 10 MHz - 10 GHz.

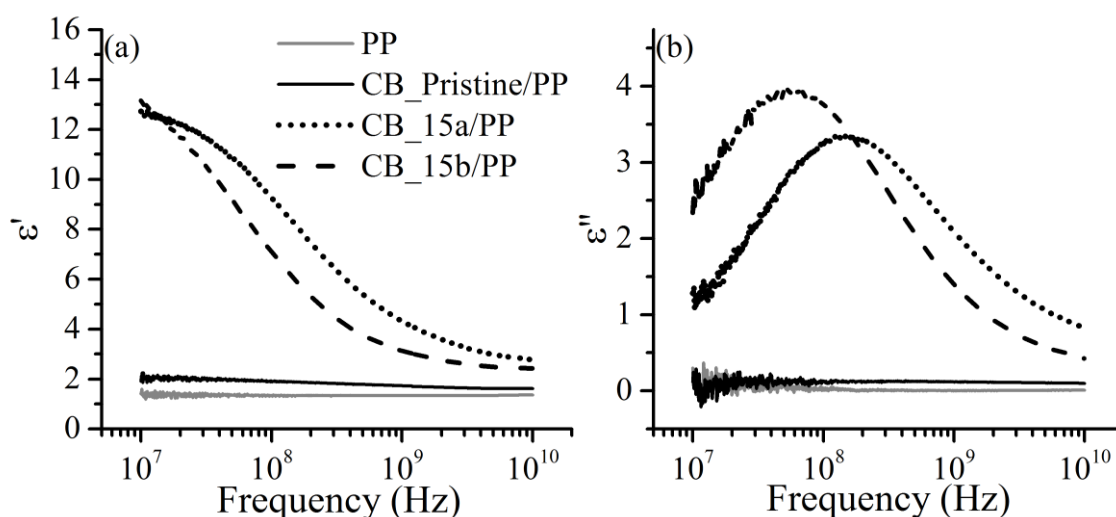


Figure 5.13. (a) Real part (ϵ') and (b) the imaginary part (ϵ'') of the complex permittivity as a function of frequency, averaged over 50 repeat measurements at different points, of pure PP and CB_Pristine/PP, CB_15a/PP and CB_15b/PP nanocomposite film samples (50 μm), at 20 wt. % loading in the range 10 MHz - 10 GHz. Adapted with permission from the American Chemical Society © 2016.⁴⁵

For the real part (ϵ') of the complex permittivity, which represents the capacity for electric energy storage,⁵² pure PP displays a frequency independent response at a value of 1.3 and CB_Pristine/PP a low frequency dependent response at ~ 1.8 . However, for the modified CB nanocomposite samples, CB_15a/PP and CB_15b/PP, major differences in the percolative conduction can be observed. Both display dielectric relaxation responses

as the frequency is increased, confirming changed CB-CB and CB-PP interfacial interactions following the covalent modifications. In detail, CB_15a/PP displays an increased real permittivity of 12.7 at lower frequency measurements, reducing to 2.8 at the highest frequency recorded. In a similar trend, sample CB_15b/PP displays the greatest increase of real permittivity of 13.2 at lower frequency measurements, levelling to 2.4 at the highest frequency recorded. The imaginary part (ϵ'') of the complex permittivity is related to the energy dissipation, accounting for conductive and relaxation effects of the nanocomposite sample.⁵³ Similar to the real permittivity results, PP demonstrates a frequency independent response at a value of 0.03 and CB_Pristine/PP a flat low frequency dependent response at ~ 0.1 , both exhibiting non-conductive behaviour at this frequency range. Alternatively, CB_15b/PP displays a typical dielectric relaxation response with a maximal value $\sim 5.0 \times 10^7$ Hz and CB_15a/PP a weaker dielectric response, which has shifted towards higher frequencies $\sim 1.5 \times 10^8$ Hz. This is an interesting result, as whilst the PP flat response is expected, the difference between the unmodified and modified CB/PP nanocomposites provides evidence of the altered conduction mechanisms, compared to the DC conductivity results which demonstrated relatively similar macroscopic conductivity values at this loading (20 wt. %) for all the samples.

An advanced frequency dependence for both modified nanocomposite samples compared to the CB_Pristine/PP sample can be observed. Further, comparing the modified nanocomposite samples, it is also slightly larger for CB_15b/PP compared to CB_15a/PP. The sample frequency dependence is indicative of the conducting features of nanocomposites with increasing percolative correlation length as the percolation threshold is approached.^{54, 55} Therefore, at this measured loading, it is evident that the electrical conductivity is influenced by inter-filler tunnelling.⁵⁵ In detail, the observed

frequency dependence is a result of the Maxwell-Wagner-Sillars effect, common to highly inhomogeneous systems, such as nanocomposites comprising of conductive fillers embedded in an insulating polymer matrix.⁵⁶ In the presence of an alternating current, interfacial polarisation can be induced at the interface between adjacent conductive CB clusters embedded in the PP matrix, resulting in a system of nanocapacitors, whereby the CB filler aggregates act as nanoelectrodes and the PP matrix in between as nanodielectrics.^{33, 57} The frequency dependent response of CB nanocomposites is largely directed by the CB loading and dispersion as well as the interfacial polarisation effects.^{58, 59} Additionally, the surface chemistry of the filler, in this case the covalent modifications, can also have a direct effect on the electron tunnelling mechanism between adjacent CB clusters in the PP matrix, as demonstrated by these results as well as in other systems.⁶⁰ Accordingly, as the sample is subjected to the alternating current, at lower frequencies the interfacial polarisation follows the change in the electric field and maximal interfacial polarisation is obtained. As the frequency is increased, the alternating electrical field becomes too fast to induce polarisation effects leading to dielectric relaxation and a reduced contribution to the real permittivity.⁴⁵ In the imaginary part of the complex permittivity, there is a corresponding relaxation response associated with induced oscillating interfacial polarisations.³³

The greater frequency dependence upon the CB_15b/PP sample indicates a more dispersed filler structure in this nanocomposite sample, as the greater number of nanocapacitors present is concomitant with a greater polarisation density.⁶¹ On the other hand, the reduced frequency dependence of the CB_15a/PP sample is indicative of a more aggregated structure following the hexyl-terminated CB surface functionalisation. This supports the conclusion of the DC conductivity results, which found that the percolation threshold had increased as a result of increased CB agglomeration. Nevertheless, it is

worth highlighting that despite the poorer DC conductivity results of CB_15a/PP the dielectric results of this nanocomposite compared to CB_Pristine/PP importantly indicate that the CB surface hexyl modification assists the electron tunnelling mechanism in the polymer nanocomposite.

The variance of the repeat dielectric measurements (~ 50) at different points on the nanocomposite films provides further evidence of the uniformity of the CB filler dispersion and distribution, Figure 5.14. The wider range of the relaxation peaks for the real part (ϵ') and the imaginary part (ϵ'') of the complex permittivity observed for CB_15a/PP, further suggests that the dispersion is non-uniform over the length scale of the measurement (the probe has a 1.6mm aperture). By contrast, the repeat relaxation peaks for CB_15b/PP are more regular, a further indication of the better dispersion and uniformity of the sample across measurement length scales.

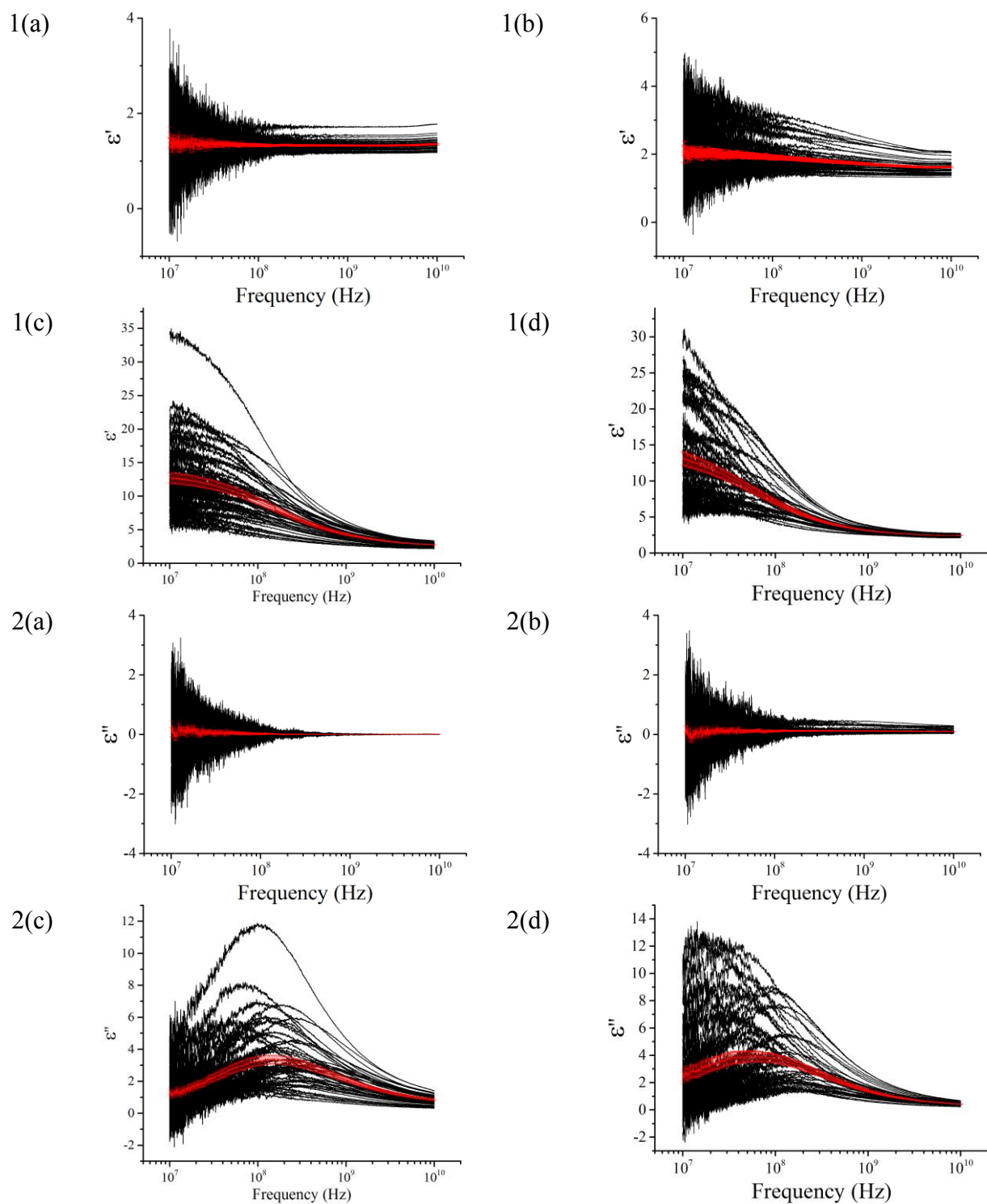


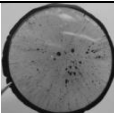
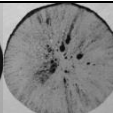
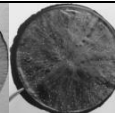
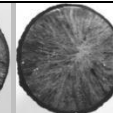
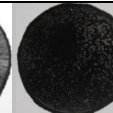
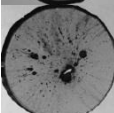
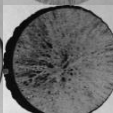
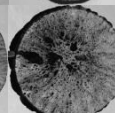
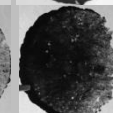
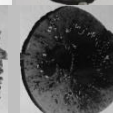
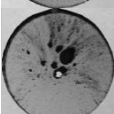
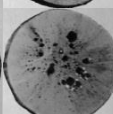
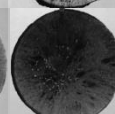
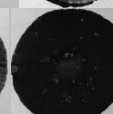
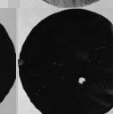
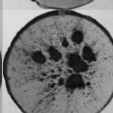
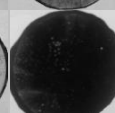
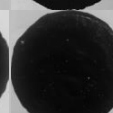
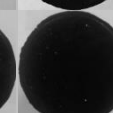
Figure 5.14: Repeat measurements of 1. the real part and 2. the imaginary part ϵ'' of the complex permittivity of (a) PP (b) CB_Pristine/PP (c) CB_15a/PP and (d) CB_15b/PP nanocomposite film samples (50 μm) with the average and calculated error in red. Adapted with permission from the American Chemical Society © 2016.⁴⁵

5.3.2.3. Morphological Properties

CB-Nanocomposite Films

Preparation of compressed moulded thin films (15 μm) of the CB/PP polymer nanocomposites proved a useful immediate visual indication, albeit a crude one, of the level of dispersion and distribution of the filler at different loadings and after carbene surface treatment (Table 5.3).

Table 5.3: Photos of thin films (15 μm) of unmodified and modified CB/PP nanocomposites at 10-30 wt. % loadings. Adapted with permission from the American Chemical Society © 2016.⁴⁵

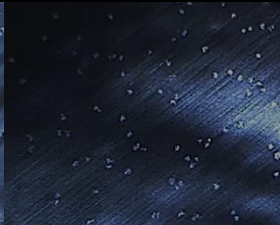
Sample	Wt. % of CB in PP nanocomposites				
	10	15	20	25	30
CB_Pristine/PP					
CB_Processed/PP					
CB_15a/PP					
CB_15b/PP					

It is evident that the unmodified CB, CB_Pristine and CB_Processed, PP nanocomposite films display similar high levels of CB agglomeration, especially at the lower CB wt. % loadings. Alternatively, the modified CB/PP nanocomposites both display altered CB dispersion, indicating the macroscopic effect following surface modification on the nano-scale. CB_15a/PP, in which the CB is modified in the hexyl termination, films display generally high CB aggregation at the lower wt. % additions of 10-20 %, however at 25 and 30 % the filler dispersion appear to have improved compared to the unmodified CB/PP samples. This result is consistent with the poor conductivity results of this modified nanocomposite at lower filler loadings. CB_15b/PP, with the dodecyl functionality films appear across the range of loadings to demonstrate the minimal CB

agglomeration, notably with remarkable filler dispersion at 10 % wt. loading, with an exception at 15 wt. %. This film at 15 wt. % indicates poor levels of agglomeration comparable to, if not greater, than the rest of the samples at this loading. This result appears anomalous to the rest of the CB_15b/PP sample set and is therefore potentially a result of inconsistent nanocomposite processing, highlighting the sensitivity of filler dispersion to the processing conditions. The visible, generally, good level of CB_15b dispersion in the PP nanocomposite films is highly consistent with the level of DC conductivity as well as the high reproducibility of the DC conductivity and dielectric results reported.

Closer inspection of films of CB_Pristine and CB_15b PP nanocomposites at 10 and 30 wt. % loadings using a tabletop microscope further reveals the presence of PP clusters (Table 5.4).

Table 5.4: Microscopy images of CB_Pristine/PP and CB_15b/PP (dodecyl functionalised) nanocomposites at 10 and 30 wt. % loadings at $\times 20$ magnification.

Sample	Wt. % of CB in PP Nanocomposites	
	10	30
CB_Pristine/PP		
CB_15b/PP		

The images highlight the poor compatibility of CB and PP in the unmodified CB/PP nanocomposite samples at both the high and low loadings. Moreover, the significant reduction of PP clusters in the CB_15b/PP samples, especially for the image of the

nanocomposite at the higher filler loading of 30 wt. %, signifies the improved CB dispersion after the CB carbene surface modification.

TEM

TEM micrographs of the pristine and modified CB/PP nanocomposites thin films (Table 5.3) at 20 wt. % loading provided further visual indication of the altered dispersion of the CB nanofiller in the region of the percolation threshold (Figure 5.15).

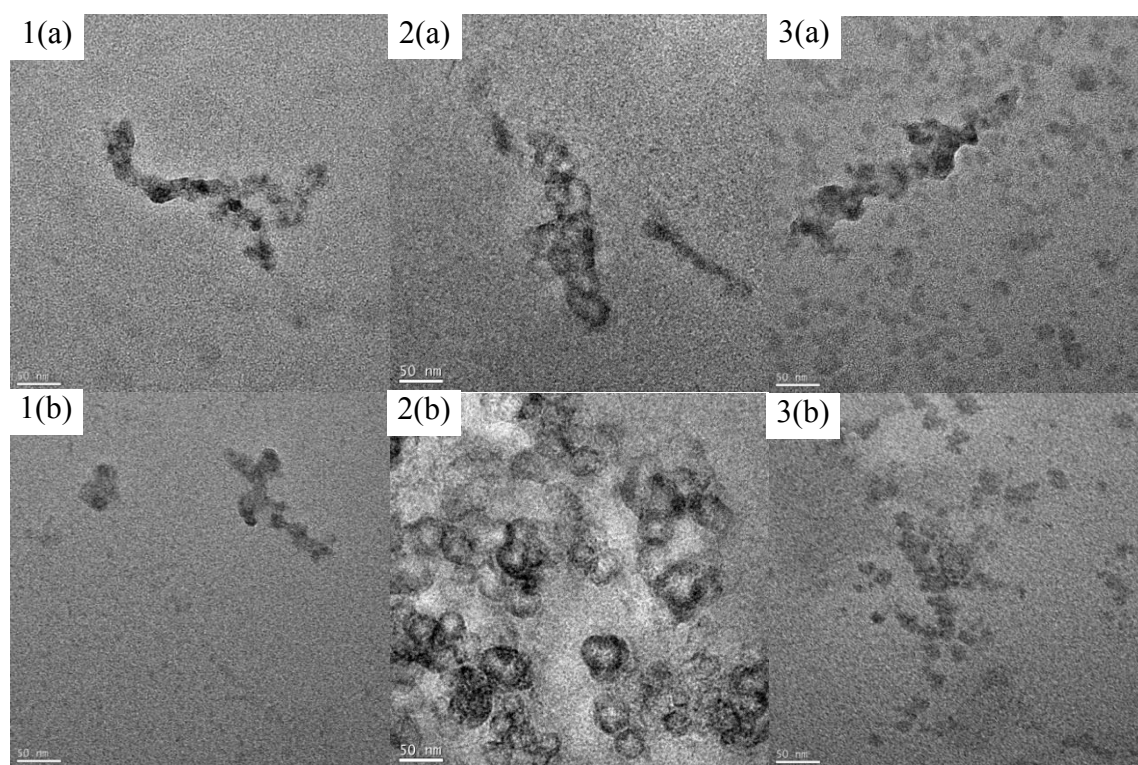


Figure 5.15. TEM micrographs for 1. CB_Pristine/PP 2. CB_15a/PP 3. CB_15b/PP nanocomposites at a loading of 20 wt. % at 50 nm. Adapted with permission from the American Chemical Society © 2016.⁴⁵

Pristine CB displays, in both images (Figure 5.15(1a-b)), large isolated agglomerates in the PP matrix. CB agglomerates can also be seen for the modified CB_15a/PP film, Figure 5.15(2(b)), and additionally clustered PP appears to be visible. This further indicates the poor filler-polymer compatibilities and equally, the unhindered attractive filler-filler interactions following the hexyl-terminated nanoparticle functionalisation. However, for modified CB_15b, good nanofiller dispersion in PP can be observed by the TEM image, particularly in Figure 5.15(3(a)). A small agglomerate, or part of a

conductive nanoparticle network is visible, and furthermore a small dispersed CB aggregates are distributed across the TEM micrograph in accordance with the reported superior conductivity results. This result further indicates that covalent modified CB_15b has improved the compatibilisation between the filler and PP matrix.

5.3.2.4. Thermal Analysis

The melting, crystallisation and decomposition behaviour of pure PP and CB/PP nanocomposites extracted from the DSC, TGA and DTG thermal analysis curves are reported in Table 5.5.

The determined degree of crystallinity (X_C) was calculated by the same method as the silica nanocomposites by:

$$X_C = \frac{H_m}{(1-x)H_0} \times 100 \quad (\text{Equation 5.2})$$

where H_m is the sample melting enthalpy, as measured by DSC, H_0 is the melting enthalpy of 100 % crystalline PP, which is reported to be 207.1 J/g,^{38,39} and x is the weight fraction of CB present in the nanocomposite.⁴⁰

The CB/PP nanocomposite thermal analysis results are from single sample measurements, since the repeated silica results generally indicated good reproducibility of the derived thermal data. For reference, the standard deviation found across the repeated silica samples is also included in Table 5.5, and can be compared to the S.D. for the averaged set of CB/PP nanocomposites, immediately highlighting that the addition of CB has indeed altered the thermal properties.

Table 5.5: Extracted DSC, TGA and DTG data from thermal analysis runs of pristine and modified CB_15a/PP and CB_15b/ PP nanocomposites. Adapted with permission from the American Chemical Society © 2016.⁴⁵

Sample	CB Loading (Wt. %)	DSC						TGA		DTG
		T _{oc} ^a (°C)	T _{pc} ^b (°C)	T _{om} ^c (°C)	T _{pm} ^d (°C)	ΔH _m ^e (J/g)	X _c ^f (%)	T _{pd} ^g (°C)	T _{od} ^h (°C)	T _{pd} ⁱ (°C)
S.D. sample set ^j	0	0.3	0.9	0.7	1.3	3.4	1.7	1.0	2.0	0.9
Av. PP_Pristine ^k	0	121.1	116.5	150.8	163.0	77.0	37.2	470.9	444.6	468.5
S.D. PP_Pristine	0	0.0	0.1	0.5	0.1	0.6	0.3	1.1	0.7	0.2
Av. PP_Processed ^k	0	127.6	122.9	149.1	163.2	71.1	34.3	474.0	446.3	472.3
S.D. PP_Processed	0	1.7	1.9	1.8	0.7	0.7	0.3	0.8	2.1	1.0
Pristine CB/PP	10	128.9	124.1	145.6	161.9	68.0	36.5	475.9	449.2	475.1
	15	125.1	119.9	149.3	164.2	62.7	35.6	477.3	450.5	475.7
	20	132.5	125.5	146.7	165.5	59.4	35.9	477.7	456.4	477.2
	25	131.5	123.8	146.8	165.1	60.0	38.6	476.1	458.9	476.1
	30	133.8	126.6	147.6	166.0	59.2	40.8	484.5	464.9	483.2
CB_15a/PP	10	121.3	115.8	151.9	162.5	57.7	31.0	476.5	453.0	474.5
	15	125.2	117.4	149.0	166.2	57.8	32.8	476.4	450.5	474.4
	20	126.3	120.7	150.0	163.7	57.3	34.6	476.1	456.5	476.9
	25	127.7	121.2	148.2	165.8	56.8	36.6	478.1	458.9	477.4
	30	129.1	121.7	149.3	167.4	54.8	37.8	488.9	467.4	487.6
CB_15b/PP	10	133.3	126.7	146.6	165.7	67.3	36.1	482.8	458.6	481.6
	15	127.8	122.8	146.8	163.7	62.3	34.3	476.2	454.3	473.9
	20	134.0	127.3	148.5	166.9	62.2	37.5	485.2	464.3	484.3
	25	132.1	124.7	148.8	165.6	60.4	38.9	485.4	465.0	483.9
	30	133.9	126.5	148.7	166.2	59.6	41.1	486.5	466.8	485.2
Average CB/PP		129.5	123.0	148.4	165.1	60.2	36.5	480.2	458.3	479.1
S.D. CB/PP		3.9	3.5	1.6	1.6	3.4	2.7	4.7	6.2	4.6

^a T_{oc}, onset crystallisation temperature.^b T_{pc}, peak crystallisation temperature.^c T_{om}, onset melting temperature (second melting cycle).^d T_{pm}, peak melting temperature (second melting cycle).^e ΔH_m, enthalpy of melting (second melting cycle).^f X_c, is the degree of crystallinity.^g T_{pc}, peak decomposition temperature (DSC).^h T_{pc}, onset decomposition temperature (TGA).ⁱ T_{pc}, peak decomposition temperature (DTG).^j The average standard deviation across the sample set for the silica nanocomposites, in which each sample was measured twice.^k The average of the PP samples was determined from three repeat measurements.

As a function of filler content, an increased nucleation efficiency of all the nanocomposite systems is indicated by the general increase in onset and peak crystallisation temperatures (T_{oc}, T_{pc}) and calculated degree of crystallinity (X_c). Although CB nanoparticles are expected to collect in the amorphous regions of semi-crystalline polymers like PP, it is established that they can influence the crystalline structure.⁶² Accordingly, nanofillers can act as heterogeneous nucleation sites, initiating nucleation at higher temperatures closer to the melting temperature resulting in smaller, less uniform spherulites.^{43, 63} As a result, this can increase the rate and degree of crystallinity when a filler is embedded in the polymer matrix of nanocomposites.^{54, 64} Comparison of the samples at equal filler loading permits further consideration of the changes to the nucleation ability of the CB filler following

surface modification. Once more, these changes can be attributed to changes in the filler-filler interfacial interactions as well as polymer-filler interfacial interactions, controlling the filler dispersion. Good filler dispersion provides an important indication for the potential of preserved mechanical properties of the polymer nanocomposite.⁶⁵ Figure 5.16 displays the cooling and the melting thermograms of the pristine and the modified CB/PP nanocomposites at 20 wt. % loading.

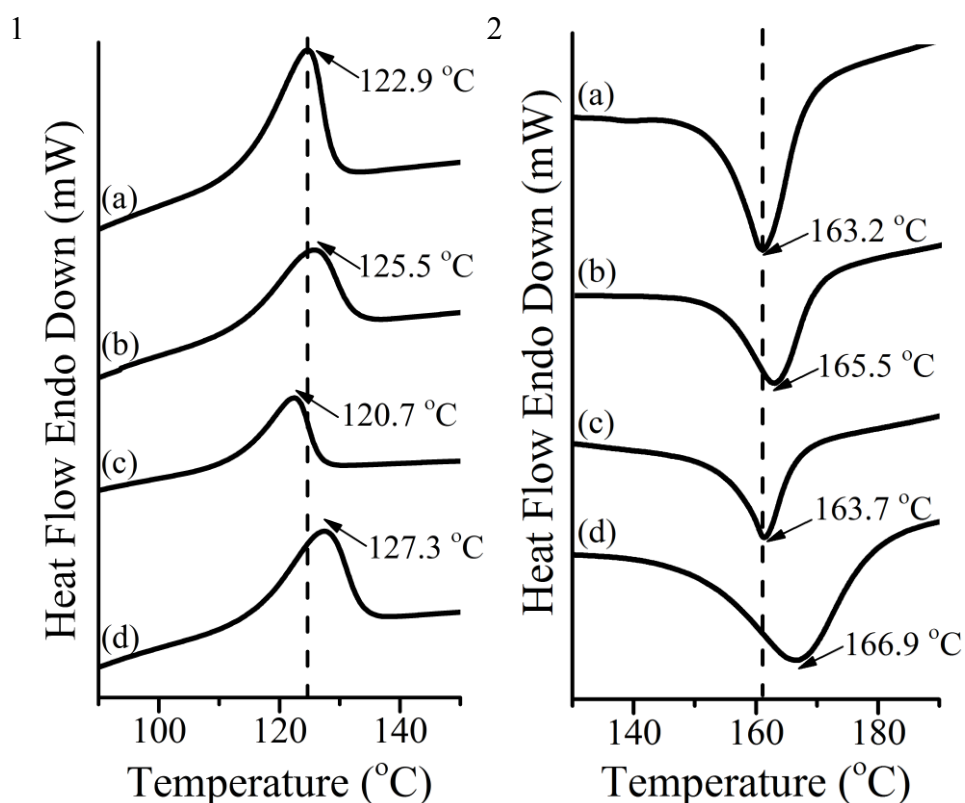


Figure 5.16: DSC thermal analysis of 1. cooling thermograms and 2. melting thermograms (second heating cycle) of (a) PP_Processed (b) CB_Pristine/PP (c) CB_15a/PP and (d) CB_15b/PP nanocomposites at 20 wt. % filler loading. Adapted with permission from the American Chemical Society © 2016.⁴⁵

It is evident from the crystallisation values, T_{pc} , that a similar trend to the conductivity measurements can be observed. CB_15b/PP shows the largest T_{pc} increase compared to pure PP by ~ 4 °C, which can be compared to an increase of ~ 2 °C for CB_Pristine/PP. While only a small change, this result further supports improved filler dispersion following modification, which is directing an increased number of nucleation sites present at the same filler loading. Conversely, the T_{pc} of CB_15a/PP is lower than

CB_Pristine/PP by ~ 5 °C, and is also lower than pure PP by ~ 2 °C. This further supports the evidence of the poor compatibility and poor dispersion of this hexyl-terminated CB modification with PP. Figure 5.16-2 also reveals a similar trend for the melting, T_{pm} , values, with the most dispersed system, CB_15b/PP, showing the highest melting temperature. Raised T_m values following filler addition is indicative of decreased lamellar thickness in a more ordered PP matrix and is observed due to the increased nucleation ability of the most dispersed CB_15b/PP system.⁶⁶

With regards to the degree of crystallinity results (Table 5.5), it can be observed that at low filler additions of 10 wt. % and 15 wt. %, CB_15a/PP nanocomposite displayed low X_c values of 31 % and 33 %, respectively. It is worth noting that this is lower than the X_c of pure PP, 34 %, and this result can be attributed to the presence of large CB agglomerates, clearly visible in the film samples at these wt. % loading (Table 5.3), resulting in restricted PP chain movement as well as hindered effective polymer chain packing.⁶⁵ Finally, above 20 wt. % filler loading of CB_15a/PP, the X_c of the nanocomposite surpasses pure PP with an eventual X_c of 38 % at maximum loading. CB_Pristine/PP and CB_15b/PP nanocomposites both immediately display increase X_c compared to PP, with the CB_15b/PP nanocomposite displaying a notably higher degree of crystallinity at 20 wt. % loading, a result again indicative of the nucleation capability of this modified CB filler. Finally, it is evident that the reported degree of crystallinity (Table 5.5) follows a similar trend to the nanocomposite conductivity measurements (Figure 5.12). Previous studies have also found corresponding results between the nucleation effect of filler nanoparticles and the conductivity measurements above the percolation threshold.⁶⁷

5.4. Concluding Remarks

In summary, the application of tailored diaryldiazo modified silica and CB nanomaterials for PP nanocomposites was investigated and this work has led to a number of key conclusions:

- Silica and CB/PP nanocomposites were prepared by development of in-house solvent mixing methods. Protocols were established for production of compression moulded plaque samples, for electrical conductivity measurements, and thin films (15-500 μm), for DMA, SEM, TEM, and dielectric analysis.
- Microsilica/PP and nanosilica/PP nanocomposites prepared at different loadings (1-10 %) were evaluated by thermal analysis techniques (DSC, TGA and DMA) to identify if the tailored diaryldiazo modifications resulted in altered macroscopic properties. From the extracted DSC data, the addition of the silica to PP led to a small reduction of the peak crystallisation, onset of melting and decomposition temperatures and no trends could be identified to indicate the effect of the silica modification or even a difference between the two silica types used in the PP nanocomposites. DMA analysis of PP and nanosilica/PP nanocomposites at 3 % wt. loading suggested the introduction of a stiffening effect from the reinforcing fillers by an increase in the T_g for all the Si/PP nanocomposites and additionally a small increase in the storage modulus for Si_15a/PP, with the hexyl termination.
- Ultimately however, the results suggest that silica remains highly agglomerated in the PP nanocomposites and the analysis techniques could not identify any significant advantage or disadvantage of the silica surface functionalisation strategy. Changes between the microsilica and nanosilica could not be realised, which further suggests that the solvent mixing method was inadequate for the preparation of the silica/PP nanocomposites.

- The application of modified CB_{15a-b} to produce electrically conductive PP nanocomposites was investigated and samples prepared at various loading (10-30 %). Macroscopic property changes, including electrical, dielectric and thermal as well as visibly altered filler dispersion, in the resulting CB/PP nanocomposites were demonstrated. Consequently, the changed CB surface chemistries following the carbene functionalisation approach presented altered CB-CB and CB-PP interfacial interactions as nanofillers in PP nanocomposites.
- CB_{15a}/PP, hexyl-terminated CB, resulted in an increased percolation threshold compared to CB_{Pristine}/PP nanocomposites, which is suggestive of increased CB agglomeration in the nanocomposite system after carbene treatment. TEM micrographs, dielectric analysis and STA thermal properties further corroborated this result. This effect might be a result of enhanced CB filler-filler interactions or reduced CB-PP compatibility, or a combination of the two effects, following the performed modification leading to aggregated, poorly dispersed and distributed hexyl modified CB in the PP matrix. Nevertheless, interestingly the dielectric analysis also revealed that the hexyl diaryl surface modification, compared to pristine CB, promoted conduction by electron tunnelling in the PP at 20 % wt. loading in the analysed nanocomposite films.
- TEM micrographs of CB_{15b}/PP, dodecyl terminated CB, visibly demonstrated improved dispersion of CB aggregates and reduced CB agglomerate formation. Correlation with STA data illustrated increased crystallisation temperatures following CB modification, and indicated an increased number of nucleation sites owing to separated and dispersed CB aggregates present in the nanocomposite. Correspondingly, enhanced dielectric and electrical properties were observed. The electrical percolation threshold of the covalent modified CB_{15b}/PP was reduced to

~10 wt. % filler addition, almost half the required filler loading to achieve conductivity for unmodified CB_Pristine/PP nanocomposites.

To conclude, the preparation and analysis of silica/PP and CB/PP nanocomposites investigated the macroscopy properties changes following the nano-scale filler surface carbene modification. Whilst the Si/PP nanocomposites were unable to generate conclusive evidence of the effect of the modification, the CB/PP nanocomposites did and furthermore clearly demonstrated the potential of this tailored functionalisation strategy in the pursuit of superior, multifunctional nanocomposites.

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Part II:

Physical Nanoparticle Modification Routes

6. Surfactant CB Functionalisation for PP Nanocomposites

6.1. Introduction

Previous work demonstrated a promising route for the development of CB/PP nanocomposites with improved macroscopic properties, using tailored diarylcarbenes to functionalise CB. In particular, the electrical conductivity of CB/PP nanocomposites was dramatically improved by the steric stabilising functionality of the dodecyl hydrocarbon chain introduced to the CB nanofiller. This Chapter alternatively aims to identify if a simpler surface functionalisation approach, namely physisorption, can introduce the same agglomeration inhibiting properties to nanomaterials in the pursuit of superior polymer nanocomposites. Following the more promising results from the CB/PP nanocomposite results in the previous Chapter (compared to silica/PP), the functionalisation of CB by surfactant physisorption is investigated to establish the effect of this nano-scale modification upon the properties of the PP nanocomposites.

6.2. Background

The opportunity to tune the interfacial properties of carbon-based nanoparticles using physisorption in a non-covalent approach presents a promising simpler, non-destructive functionalisation method. The adsorption of surfactants onto the surface of particles has been used to promote stable dispersions in aqueous or organic solvents and more recently, to polymeric systems in the field of nanocomposites.¹⁻³ In one study, the uniform dispersion of surfactant modified MWCNTS in water soluble (poly(ethylene glycol)) and water in-soluble (PP) polymers was investigated. It found that for MWCNT/PP nanocomposites prepared by solution mixing methods, the addition of the non-ionic surfactant polyoxyethylene octyl phenyl ether (Triton X-100), promoted the homogeneous dispersion of MWCNTs in the PP matrix, and demonstrated an improved

degree of crystallinity and nucleation efficiency by DSC thermal analysis.⁴ In other work, an epoxy/MWCNTs nanoparticle nanocomposite system treated with the non-ionic surfactant Triton X-100 demonstrated improved dispersion of CNTs due to a lowered polymer viscosity during nanocomposite preparation,⁵ and in another study the improved dispersion by result of the surfactant modification directed improved electrical conductivity above the percolation threshold, compared to pristine MWCNTs.⁶

Based on this previous work, Triton X-100 has been selected as a suitable surfactant modification candidate for CB in this project. Further, non-ionic surfactants have been shown to be effective as a dispersant for non-polar organic solvents, as the adsorption mechanism is dominated by hydrophobic interactions between the surfactant and the CB and the disaggregation mechanism is driven by the steric stabilisation by the surfactant modification. Alternatively, for ionic modified CB, disaggregation is promoted by electrostatic repulsive effects and charge dissociation is most effective in aqueous media.⁷ This adsorption mechanism of non-ionic surfactants is also an important advantage for the employed nanocomposite solvent mixing, procedure, which uses toluene, and equally is likely to exhibit good compatibilisation with the PP matrix, which is apolar. Further, the relatively low hydrophile-lipophile balance (HLB) of Triton X-100 makes this surfactant an ideal candidate to achieve the balance between effective adsorption onto the CB nanoparticles, whilst aiming not to impair compatibility with the PP matrix by the moderately short hydrophilic polyethylene oxide chain (9-10 units).⁴ Triton X-100 is in fact part of a commercially available series of surfactants, the 'Triton X family' (a trade mark of Rohm and Haas), in which the polyethylene oxide chain can vary from 1.5 to 55 units.^{8,9}

The functionalisation mechanism of Triton X-100 onto CB is shown in Figure 6.1.

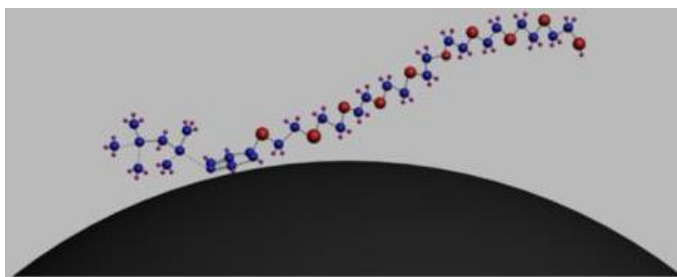


Figure 6.1: Schematic of the adsorption of Triton X-100 onto CB. Adapted from.¹⁰

Below the CMC, which is 0.24 mM for Triton X-100 at 25 °C,¹¹ the random adsorption onto carbon-based nanoparticles is expected to be directed by attractive hydrophobic interactions, namely from the branched trimethyl pentane tail group, as well as π - π stacking interactions between the benzene ring of Triton X-100 and those present on the surface of the graphitic CB. These interactions anchor the surfactant to the CB at low surfactant concentrations at ‘perpendicular’ orientation to the CB surface, enabling the hydrophilic polyethylene oxide chain ‘head’ group to extend from the surface, as shown in Figure 6.1.^{1, 4, 10} Additionally, if the selected solvent media is water, the polarity of this media is likewise expected to aid the orientation of the surfactant adsorption, further promoting hydrophobic interactions between the hydrophobic ‘tail’ group and CB. When the dispersion concentration is at the CMC, Triton X-100 will self-assemble at the carbon-based nanoparticle surface. The nanoparticle will become encapsulated as the surface is saturated by the surfactant at ‘perpendicular’ orientation (to the CB), promoted by favourable hydrogen bonding interactions between parallel hydrophilic polyethylene oxide chain groups. Further, at concentrations above the CMC, as the surface concentration of the particles and packing density increases, hemi-micelles and micelles will begin to form at the surface, as depicted for the surface functionalisation of CNTs in Figure 6.2(d).^{6, 12} Triton X-100 adsorption investigations have focused largely upon the surface modification of CNTs, but a similar adsorption mechanism for CB might be expected.

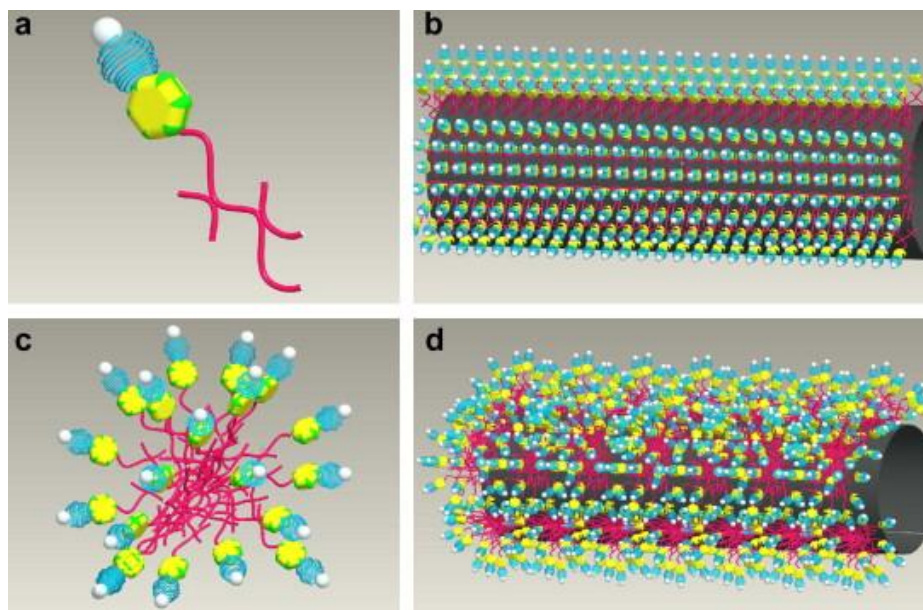


Figure 6.2: Schematic of (a) Triton X-100 (b) the modified surface of CNT at the CMC (c) a Triton X-100 micelle and (d) the formation of micelles or hemi-micelles at the surface of CNT at 10 CMC. Used with permission from Elsevier ©2008.⁶

Despite a vigorous research effort into the mechanism of surface functionalisation of carbon-based nanomaterials, and some studies translating this research to polymer nanocomposite, few studies have used the surfactant modification to produce the dry surfactant modified nanomaterial which can then be selected for polymer nanocomposite production or other applications.¹⁰ More often the Triton X-100/carbon-based nanoparticle dispersion solution is directly added to the polymer, in solution or in the melt, to produce the polymer nanocomposite.^{4, 6} Herein, it was of interest to investigate if dried nanocarbon particles, pre-surface modified by Triton X-100, could be produced and tested for use in polymer nanocomposites. If the resulting material properties demonstrate promising improvements, this could be more easily translated for application in industry, for example compared to the covalent nanofiller functionalisation approaches described earlier.

Important considerations will be the development of a simple effective modification protocol with an optimised Triton X-100 surface functionalisation concentration. It might be that at a very low Triton X-100 concentration, the steric stabilisation effects of the

surface modification will not be adequate to prevent agglomerate formation. Equally, it might be that in the case of a high surfactant concentration, the attractive steric stabilisation effects of the polyethylene oxide hydrophilic group might compromise the compatibility of the CB with PP. Further, perhaps CB aggregates could be totally ‘encapsulated’ by the surfactant surface functionalisation, thereby insulating the conductive CB and ultimately inhibiting electronic conduction by electron tunnelling between neighbouring CB aggregates in the PP matrix. Lastly, the potential for hydrogen bonding between the hydrophilic ‘head’ groups of adjacent surfactant modified CB has been suggested, which can lead to the formation of a loose network of bridged aggregates,^{4, 10} and would also likely affect the conductive and mechanical properties of resulting nanocomposites.

6.2.1. Aims of the Project

This Chapter presents the surface functionalisation of CB by Triton X-100 for the production of CB/PP nanocomposites with modified macroscopic properties. The key aims of this work include:

- To determine a modification procedure for the functionalisation of CB using Triton X-100, in particular the choice of the dispersion solvent media, organic or aqueous, and the Triton X-100 surfactant concentration;
- To identify the presence of the Triton X-100 surface modification on dried CB nanoparticles after treatment and establish the degree of modification;
- To evaluate if the Triton X-100 surfactant functionalisation procedure endows CB/PP nanocomposites with improved properties.

Ultimately, the aim is to determine if this simpler modification approach using the commercially available Triton X-100 dispersant can produce CB/PP nanocomposites with

superior properties, and if this functionalisation approach could be promising for implementation in industry.

6.3. Experimental Details

6.3.1. Materials

Commercial Monarch® Carbon Black (CB, M 430, 27 ± 10 nm, density 1.1 - 1.9 g/cm³) was supplied from Cabot Corporation (Billerica, MA, USA). The non-ionic surfactant Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_n$ (n=9-10)) was purchased from Sigma Aldrich. Commercial grade polypropylene (PP, 2440TC polypropylene copolymer with ethylene as the co-monomer, MFI 55 g/10 min) was provided by IRPC Ltd., Thailand. Triton X-100 solutions were prepared using ultrapure water (>18 MΩcm, Millipore Water systems) and the organic solvents used (toluene, chloroform and m-xylene) were of analytical grade and supplied by Sigma-Aldrich.

6.3.2. Preparation of Surfactant Modified CB

The preparation of Triton X-100 modified CB was optimised in different sections in this Chapter and the protocols are summarised below.

6.3.2.1. Triton X-100 Functionalisation of CB: Study A - Which solvent?

CB (150 mg, 50 mL) dispersions using 4 different solvents (water, toluene, chloroform and m-xylene) were sonicated for 10 min. At the same time, Triton X-100 solutions (50 mL), prepared in each of the same solvents, were also sonicated for 10 min. Afterwards, the CB dispersions and Triton solutions, for each solvent, were combined. The resulting CB/Triton X-100 (150 mg, 100 mL, 0.24 mM) dispersions in each water, toluene, chloroform and m-xylene solvents were sonicated for a further 2 hrs before leaving to rest for 7 days to assess the CB dispersion over time in the different solvents. Additionally, a second round of CB/Triton X-100 dispersions were prepared using water and toluene

solvents and left for only 24 hr, before extraction of the Triton X-100 functionalised CB. This was achieved for the CB/Triton X-100/water dispersion using a Beckman GS-15R centrifuge, in which the sample was spun for 1 hr at 10000 rpm at 8 °C before removal of the supernatant from the separated layers by pipette. For the CB/Triton X-100/toluene dispersion, the toluene supernatant was removed *in vacuo* on a rotary evaporator. Finally, upon extraction the modified CB was dried in an oven (80 °C) overnight.

6.3.2.2. Study B - Optimisation of Triton X-100 loading

In a similar method to Study A, aqueous Triton X-100 solutions (100 mL) at a range of 5 different concentrations and CB dispersions (600 mg, 100 mL) were each sonicated for 10 min, before combining. Afterwards, the CB/Triton X-100/water dispersions (600 mg, 200 mL, 0.024-0.48 mM) were sonicated for a further 1 hr in the ultrasonic bath and left to settle for 24 hrs. The dispersion was then filtered using a Whatman™ Glass Vacuum Membrane Filter, the supernatant with any residual Triton X-100 retained, and the modified CB dried in an oven at 80 °C.

6.3.3. Characterisation of the Triton X-100 Modified CB

The pristine, processed and Triton X-100 modified CB nanoparticles were analysed by TGA, BET, XPS and ATR-IR surface analysis techniques. Additionally, the supernatant solutions, retained after filtration of the Triton X-100 modified CB, were analysed by UV-Vis to determine the residual surfactant concentration. The experimental protocols of these analyses are all detailed in Chapter 2.

6.3.4. Preparation of CB Based PP Nanocomposites

6.3.4.1. Fabrication of CB - PP Nanocomposites

Nanocomposite samples were prepared by solvent mixing (SM) methods, adapted from general procedures in the literature, as used and presented in Chapter 5.¹³⁻¹⁵ Additionally,

CB/PP nanocomposites were prepared by melt mixing (MM) methods using lab-scale in-house prepared melt mixing equipment and temperature controller (Figure 6.3), in order to use a nanocomposite preparation method more applicable for industrial production.

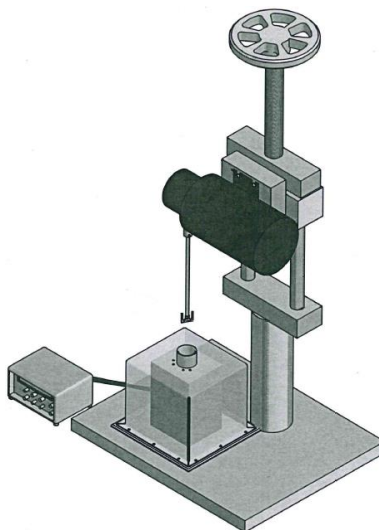


Figure 6.3: Schematic of the melt mixing equipment used to prepare CB/PP nanocomposite samples.

Accordingly, PP pellets (~ 0.5 g) and pristine or Triton-X100 modified CB at different wt. % of PP (5, 10, 15, 20, 25 %), were dry mixed together in a flat bottom test tube (1 min) prior to placing in the heated melt mixing apparatus, at the starting temperature of 160 °C. The sample was then heated and stirred at a sequential temperature program: 160 °C-5 min, 180 °C-5 min, 190 °C-5 min and stirring at ~ 50 rpm, 200 °C-15 min and stirring at 100-300 rpm. After 30 min in the melt mixing equipment, the test tube of the mixed sample was removed and left to cool before removal and clipping to nanocomposite pieces ~ 1 mm³, as shown in Figure 6.4(a-b).

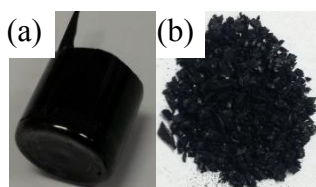


Figure 6.4: Photos of the CB/PP nanocomposite samples prepared by melt mixing of (a) the sample removed from the test tube after mixing and (b) the clipped sample prepared for further processing and analysis.

6.3.4.2. *Characterisation of the CB - PP nanocomposites*

The solvent mixed and melt mixed nanocomposites, labelled SM and MM, were then used to prepare plaques samples ($1 \times 1 \times \sim 0.1 \text{ cm}^3$) for conductivity measurements. Additionally, for selected samples, films ($50 \text{ }\mu\text{m}$ and $15 \text{ }\mu\text{m}$) were prepared for dielectric analysis and TEM, and each sample (neat.) was analysed by thermal analysis. These nanocomposite film and plaque samples were prepared by the same methods as described in Chapter 5 and using the same experimental procedures as presented in Chapter 2. Additionally, DMA analysis was performed to films of solvent-mix prepared nanocomposites of pristine and Triton X-100 modified CB at 15 and 25 wt. %, at a lower thickness of $250 \text{ }\mu\text{m}$, compared to the DMA films tested at $500 \text{ }\mu\text{m}$ presented in Chapter 5. The films at the new lower thickness ($250 \text{ }\mu\text{m}$) were pressed by a similar film preparation procedure as used in Chapter 5. The sample ($\sim 180 \text{ mg}$) was moulded using a Specac Film Maker assembly set up (with spacer 'E') in a Specac Atlas hydraulic press, in which it was heated at $180 \text{ }^\circ\text{C}$ for 5 min followed by a pressure of 1 Torr for 1 min, before removal to a cooling plate. The experiments were performed on a Mettler DMA 1 instrument as detailed in the Experimental Chapter.

6.4. Results and Discussion

This section outlines a number of Triton X-100 functionalisation treatments used for CB, in order to determine if the simple surfactant adsorption method can be used to improve the properties of CB/PP nanocomposites. Accordingly, it is divided into three parts, in which study A evaluates the selection of the solvent media for the Triton X-100 solutions for the treatment of CB, Study B examines the optimisation of the Triton X-100 surface loading for CB/PP nanocomposites and finally, Study C investigates the effect of the physisorption functionalisation upon CB/PP nanocomposites prepared by both solvent mixing and melt mixing methods at a series of filler loadings.

6.4.1. Study A: Which Solvent?

6.4.1.1. CB Triton X-100 Modification Protocol in Different Solvents

The aim of the first study was to design general conditions for a suitable Triton X-100 functionalisation protocol for CB from a selection of four solvents of various polarities: water (1.000), toluene (0.099), chloroform (0.259) and m-xylene (0.074).¹⁶ The protocol was developed based on reported studies of CB or CNT modification.^{3, 17} Accordingly, initial dispersion experiments were set up in which CB was added to Triton solutions in each of the solvents at a set concentration, the CMC (0.24 mM),¹¹ and left for a week, as detailed in the experimental section of this Chapter.

6.4.1.2. Dispersion Results

The expectation of this quick test was that if the solvent was suitable, it would facilitate a favourable interaction between the Triton X-100 and CB and then after a week the CB would remain dispersed. Photos documenting the CB dispersions of each of the solvents, with and without Triton X-100, immediately after preparation and after 7 days, are included in the Appendix. As a summary, the CB/Triton X-100 dispersions in water and toluene both demonstrated good dispersions after this period, whereas the chloroform/Triton X-100/CB dispersion displayed clear separation after one week. The m-xylene/Triton X-100/CB dispersion initially demonstrated improved dispersion with the addition of the surfactant, as separation was almost immediately observed in the neat m-xylene/CB dispersion. However, after one week, even with the addition of Triton X-100, it was evident that the dispersion had started to separate. The results of this screen test therefore suggest that poor adsorption of the surfactant onto the CB surface exists in the chloroform and m-xylene solvent dispersions.

Good CB/Triton X-100 dispersion in water was expected as the poor interactions that exist between the hydrophobic surfactant ‘tail’ group assists the effective interaction with

the hydrophobic CB surface. Accordingly, the hydrophilic polyethylene oxide ‘head’ group can extend from the CB, facilitating good dispersion in water.¹⁸ However, the good dispersion achieved in toluene demonstrates the dominance of the attractive hydrophobic properties between the CB and Triton X-100.

6.4.1.3. Thermal Analysis

TGA was performed to the dried CB after treatment with Triton X-100 in water and toluene following the promising dispersion experiments of these two solvents. The modified samples are labelled according to the solvent type and surfactant concentration used in the modification step: CB_Triton (Water, 0.24 mM) and CB_Triton (Toluene, 0.24 mM). Additionally, equivalent control samples were prepared, in which CB was subjected to the modification procedure without Triton X-100 in each of the solvents, labelled CB_Processed (Water) and CB_Processed (Toluene). The TGA thermograms are presented in Figure 6.5 and extracted data is summarised in Table 6.1. The raw data can be found in the Appendix.

Table 6.1: Thermogravimetric analysis weight loss data, calculated surface loading and extrapolated onset decomposition temperatures of pristine, processed CB and CB treated at 0.24 mM Triton X-100 solutions of water and toluene.

Sample	TGA Weight Loss (%) ^b			Surface Loading ^c		Onset Temp. (°C)
	30-150 °C	150-500 °C	Sample Wt. Loss due to the Mod. (g)	Moles /g	Molecules /cm ²	
CB_Pristine ^a	0.3	0.5				
CB_Processed (Water)	0.3	0.8				
CB_Processed (Toluene)	0.3	0.8				
CB_Triton (Water, 0.24 mM)	0.2	5.7	6.4×10^{-4}	8.7×10^{-5}	7.2×10^{13}	332.1
CB_Triton (Toluene, 0.24 mM)	0.6	13.5	1.1×10^{-3}	2.4×10^{-4}	2.0×10^{14}	303.5

^a Result are the average of 3 repeat runs of CB Pristine.

^b The TGA surface loading calculations were the same as used in Chapter 3 and 4 except the temperature of decomposition was measured at 150-500 °C.

^c Assumes monolayer surface coverage of the experimentally determined BET surface areas of CB_Pristine (72.5 m²/g).

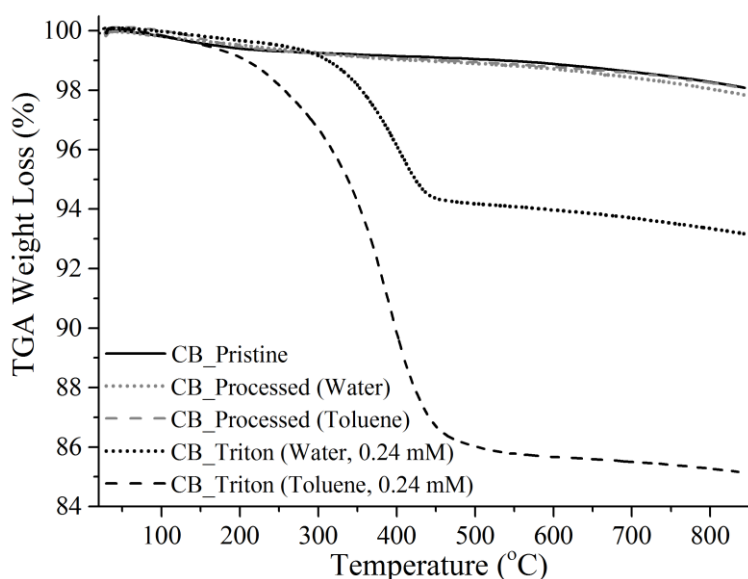


Figure 6.5: TGA thermograms of pristine, processed and Triton X-100 modified CB in water and toluene at 0.24 mM.

The TGA results of dried CB nanoparticles following treatment by Triton X-100 solutions in water and toluene indicates greater mass losses, at 5.7 % and 13.5 %, respectively, compared to pristine and the processed CB in water and toluene, at ~0.5 % and 0.8 %, in the temperature range 150-500 °C (Figure 6.5, Table 6.1). The extra weight loss is attributed to the evaporation of the Triton X-100, corresponding with the previously reported evaporation of neat. Triton X-100 at ~310 °C, under nitrogen (~50-100 °C higher than in air).¹⁹ Interestingly, the onset decomposition temperatures of 332.1 °C and 303.5 °C of the CB modified in water and toluene therefore also indicates an altered thermal stability of the Triton X-100 surfactant when adsorbed onto the CB surface, perhaps as a function of loading. This TGA result therefore indicates the successful surface functionalisation of Triton X-100 in both solvent systems, presenting calculated TGA surface loadings of 7.2×10^{13} and 2.0×10^{14} molecules/cm², for the CB modified in water and toluene respectively. This was evaluated by the greater weight losses of these samples, compared to pristine CB, in the 150-500 °C temperature range with the assumption of the average polyethylene oxide chain length of 9.5 units the Triton X-100

modification and the experimentally determined CB BET surface area ($72.5 \text{ m}^2/\text{g}$). These calculated surface loadings present a good comparison the covalent surface modified CB, as presented in Chapter 3 and 4. Further, the higher surface loading present on the CB sample modified in the toluene/Triton X-100 solution suggests this solvent system improves the CB-Triton X-100 compatibility, compared to the CB prepared in water, perhaps an unsurprising result for a non-ionic surfactant. Otherwise, it could also be considered that the different methods of extracting the modified CB from the dispersion in Toluene (rotary evaporator) compared to water (centrifuge followed by filtration), might also have affected the degree of Triton X-100 physisorbed on the resulting dried CB surface.

6.4.1.4. Summary

The modification of CB by Triton X-100 in water and toluene demonstrates a successful functionalisation approach, as indicated by the removal of the surfactant modification in the thermal analysis results. Additionally, dispersion studies for both solvents also demonstrated stable CB dispersions as a result of the treatment with Triton X-100. Alternatively, the initial dispersion experiments using chloroform and m-xylene demonstrated their unsuitability for use for CB Triton X-100 functionalisation. Despite the suitability of both water and toluene as a solvent for Triton X-100 functionalisation, water was selected the solvent choice for the next study as the modification protocol is simpler, without the requirement of the solvent removal using the rotary evaporator. Further, water as the solvent choice presents additional economical as well as ecological advantages, both important for industrial applications. Nonetheless, the stability of the Triton X-100 modification to CB in toluene is an important result if Triton X-100 modified CB/PP are prepared by solvent mixing methods, in which toluene is used as the solvent.

6.4.2. Study B: Optimisation of Triton X-100 Loading

Following the selection of water as the solvent for the modification of CB by Triton X-100, this section reports the investigation of different surfactant concentrations in the modification protocol in order to determine the optimal surfactant loading for CB/PP nanocomposites.

6.4.2.1. CB Triton X-100 Modification Protocol in Different Solvents

A set of 5 experiments were conducted in a range of Triton X-100 aqueous solution concentrations of 0.024-0.48 mM, in the region of the CMC (0.24 mM).¹¹ Additionally, changes to the general procedure of study A were made to further optimise the CB modification procedure. These included a halved sonication time, from 2 to 1 hrs, a doubled weight addition of CB to water (0.15 wt. % up to 0.3 wt. %) and a new filtration method, using a Whatman™ Glass Vacuum Membrane Filter, to separate the modified CB and aqueous supernatant solution, instead of using a centrifuge. The modified CB in this study are labelled according to the concentration of the prepared Triton X-100 solutions used for the modification protocol, as presented in (Table 6.2).

Table 6.2: The modified CB samples prepared by treatment in a range of aqueous Triton X-100 solution concentrations near the CMC of 0.24 mM.

Modified CB Samples by Triton X-100 Aqueous Solution	Solution Concentration to CMC of Triton X-100 Ratio
CB_Triton (0.024 mM)	0.1
CB_Triton (0.072 mM)	0.3
CB_Triton (0.12 mM)	0.5
CB_Triton (0.24 mM)	1
CB_Triton (0.48 mM)	2

6.4.2.2. Characterisation of the Modified CB by Triton X-100(aq)

Following treatment at various concentrations of Triton X-100 aqueous solutions, the modified CB was filtered, and dried in an oven overnight (80 °C). CB surface and supernatant analysis was performed in order to determine the success and the degree of functionalisation, as presented in this section of work.

BET

BET Surface area analysis by nitrogen adsorption was performed on the CB modified at both the highest Triton solution concentration (CB_Triton (0.48 mM)) and at the lowest (CB_Triton (0.024 mM)) and compared to pristine CB, in order to evaluate the effect of the surfactant surface loading upon the surface area (Table 6.3). The adsorption and desorption isotherms, t-Plots and BJH adsorption pore volume graphs comparing the three samples can be found in the Appendix.

Table 6.3: The BET surface analysis data of pristine CB, CB_Triton (0.024 mM) and CB_Triton (0.48 mM).

Sample	BET Surface Area (m ² /g)	t-Plot External Surface Area (m ² /g)	t-Plot Micropore Area (m ² /g)	BJH Adsorption Average Pore Diameter (Å)	BJH Desorption Average Pore Diameter (Å)
CB_Pristine ^a	72.5 (0.0) ^b	62.5 (0.2)	10.1 (0.2)	366.6 (13.7)	354.3 (5.5)
CB_Triton (0.024 mM)	62.5	58.6	3.87	397.1	376.4
CB_Triton (0.48 mM)	41.4	50.6	-	515.1	440.1

^a Average of 2 repeat BET measurements.

^b Standard Deviation has been included for repeated measurements in brackets.

The BET results demonstrate that as the CB nanoparticles are exposed to higher concentrations of Triton X-100 in the modification procedure, the resulting functionalised nanoparticles display a reduced BET surface area and t-plot external area, consistent with the smoothing of the nanoparticle surface by physisorption of the Triton X-100. A similar set of results was demonstrated for the pristine and modified silica samples in Chapter 4. Consequently, the greater reduction of the BET surface area observed for CB_Triton (0.48 mM), compared to CB_Triton (0.024 mM), suggests it has been functionalised at a higher surface loading, as would be expected. In detail, the surface analysis data indicates that as the Triton X-100 surface concentration increases, the surface micropores become capped preventing nitrogen adsorption in these regions of the CB surface. This results in a reduction of the detected t-plot micropore areas to 3.87 m²/g for CB_Triton (0.024 mM) compared to 10.1 m²/g for pristine CB. Further, for CB_Triton (0.48 mM) a negative

micropore volume was detected, indicating no micropores could be detected for this sample. This result is consistent with the increasing value of the average pore diameter.

Thermal Analysis

The modified CB samples were subjected to STA experiments to determine the surface loading and thermal stability of the physisorbed Triton X-100 (Figure 6.6, Table 6.4.) Further details of the extracted thermal analysis data and calculations for the surface loading are included in the Appendix.

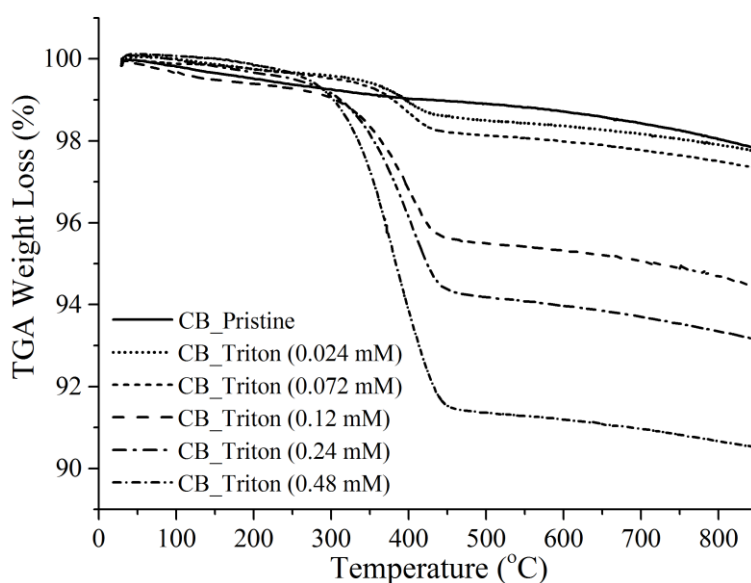


Figure 6.6: Thermogravimetric analysis under nitrogen flow of pristine and modified CB prepared by treatment at different aqueous concentration of Triton X-100.

Table 6.4: Thermogravimetric analysis weight loss data, calculated surface loading and extrapolated onset decomposition temperature of the Triton X-100 modification at different loadings onto CB.

Sample	TGA weight loss (%)			Surface Loading ^c		Onset Temp. (°C)
	30-150 °C	150-500 °C	Sample Wt. loss due to the Mod. ^b (g)	Moles /g	Molecules /cm ²	
CB_Pristine ^a	0.3	0.5				
CB_Processed (Water)	0.3	0.8				
CB_Triton (0.024 mM)	0.2	1.4	1.1×10^{-4}	1.4×10^{-5}	1.2×10^{13}	354.2
CB_Triton (0.072 mM)	0.4	3.2	3.0×10^{-4}	4.4×10^{-5}	3.6×10^{13}	353.6
CB_Triton (0.12 mM)	0.3	4.5	5.2×10^{-4}	6.7×10^{-5}	5.6×10^{13}	334.7
CB_Triton (0.24 mM)	0.3	5.6	6.4×10^{-4}	8.7×10^{-5}	7.2×10^{13}	316.1
CB_Triton (0.48 mM)	0.1	8.7	1.0×10^{-3}	1.4×10^{-4}	1.2×10^{14}	306.1

^a Results are the average of 3 repeat runs of CB Pristine.

^b The TGA surface loading calculations were the same as used in Chapter 3 and 4 except the temperature of decomposition was measured at 150-500 °C.

^c Assumes monolayer surface coverage of the experimentally determined BET surface areas of CB_Pristine (72.5 m²/g).

The thermal analysis results of pristine CB (presented in Chapters 3 and 4) demonstrate here the lowest weight loss of all the samples, as expected. Processed CB, treated in water without the addition of Triton X-100, displays a similar result to pristine CB, with a total weight loss up to 500 °C of only 1.1 % (Table 6.4). On the other hand, the thermal analysis results of the modified CB indicates a variation of mass losses of 1.4-8.7 % in the 150-500 °C temperature range, and the increasing mass loss of the modified samples directly correlates with the increased Triton X-100 concentrations used to treat the CB nanoparticles. This result confirms the success of the modification and is consistent with the thermal analysis data in Study A.

The weight loss of the modifications in this temperature range (150-500 °C), in comparison to the mass of pristine CB, was used to estimate the surface loadings, under the same assumptions as used in Study A, to give the calculated TGA loadings of 1.2×10^{13} to 1.2×10^{14} molecules/cm². Chemicalize predictive software can also be used to estimate the minimum and maximum loading of Triton X-100 that might be expected to surface functionalise CB in a monolayer coverage.²⁰ At the upper bound loading of Triton X-100, in which case the molecules would align ‘perpendicular’ to the CB surface, the surface coverage of the surfactant is estimated at 0.63 nm² per molecule, which would be 1.6×10^{14} molecules/cm² (Figure 6.7(a)).

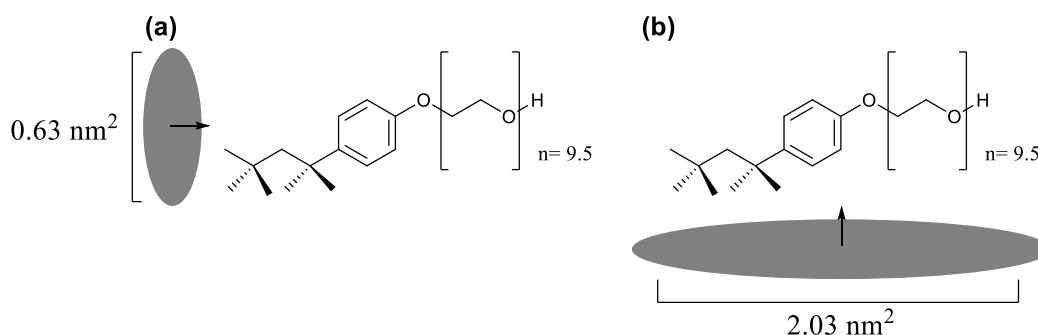


Figure 6.7: A scheme to show the calculated projection areas for the Triton X-100 modification if the physisorption was (a) perpendicular and (b) parallel to the CB surface.

In contrast, a lower bound estimation can be considered by Chemicalize predictive software if the Triton X-100 surfactant is aligned ‘parallel’ to the CB surface (Figure 6.7(b)), in which the surface coverage is 2.03 nm^2 per molecule, equating to 4.9×10^{13} molecules/cm².²⁰ A ‘parallel’ arrangement of the surfactant is a simplistic estimation, as the poor interaction between the hydrophilic polyethylene oxide chain group with the hydrophobic CB will expectedly promote extension from the surface. Nevertheless, this could be considered a basic theoretical estimation of the area the Triton X-100 might occupy at the CB surface at lower concentrations, at which point the surface adsorption is a random process (described in the Introduction of the Chapter (Figure 6.1)). Overall, the Chemicalize surface loading estimations are in good agreement with the calculated surface loadings by TGA, $\sim 10^{13}$ - 10^{14} molecules/cm². Interestingly, all the TGA calculated surface loadings of the Triton X-100 modified CB demonstrate surface loadings below the chemicalize upper loading estimation (‘perpendicular’ orientation to CB) of 1.6×10^{14} molecules/cm². This result suggests micellation at the CB nanoparticle surface might not have occurred (discussed in the introduction (Figure 6.2(d))).

Additionally, it is interesting to note that the highest onset temperatures for the evaporation of the Triton modification were observed for the CB modified at the lowest concentrations, at 354.2 °C for CB_Triton (0.024 mM) and at 353.6 °C for CB_Triton (0.072 mM). This suggests that at lower Triton X-100 loadings, stronger adsorption interactions exist between surfactant and the CB surface. In contrast, as the Triton loadings increase, the decomposition temperatures continued to decrease, with CB_Triton (0.48 mM), modified at the highest concentration, displaying a reduced onset decomposition temperature of 306.1 °C. This shift in thermal stability of the Triton X-100 CB modification might be an indication of the altering orientation of the surfactant as a function of concentration. It could be that at lower concentrations, physisorbed Triton X-

100 is perhaps positioned in a ‘parallel’ type orientation to the CB surface, (Figure 6.7(b)), allowing for a strong interaction between the CB surface and the hydrophobic ‘anchor’ group. But then, as the concentration increases, it may be that the orientation shifts to a ‘perpendicular’ type orientation to the CB (Figure 6.7(a)), promoted by favourable hydrogen bonding interactions between the polyethylene oxide of neighbouring Triton X-100 molecules. The alteration to the ‘perpendicular’ type orientation might however result in a reduced interaction of the hydrophobic group to the CB surface, thereby reducing the thermal stability of the functionalisation. This explanation is additionally supported by comparison of the Chemicalize estimations in the two orientations to the calculated TGA loadings of Triton modified CB.

UV-Vis Analysis

UV-Vis spectroscopy was used as a second method to estimate the degree of Triton X-100 functionalisation present on the surface of CB nanofillers. As a result of the UV-active nature of Triton X-100, the supernatant solutions retained from the modification protocol (when the CB was filtered) were analysed to determine the residual Triton concentration. Then, comparison to the initial solution concentration used in the modification procedure, permitted evaluation of the concentration at the surface of each of the modified CB. Solutions of known concentrations were measured for a calibration plot (included in the Appendix) and the absorbance of the supernatant solutions, at 224 nm, was measured (Figure 6.8), and the concentration of the supernatant solutions determined (Table 6.5.)

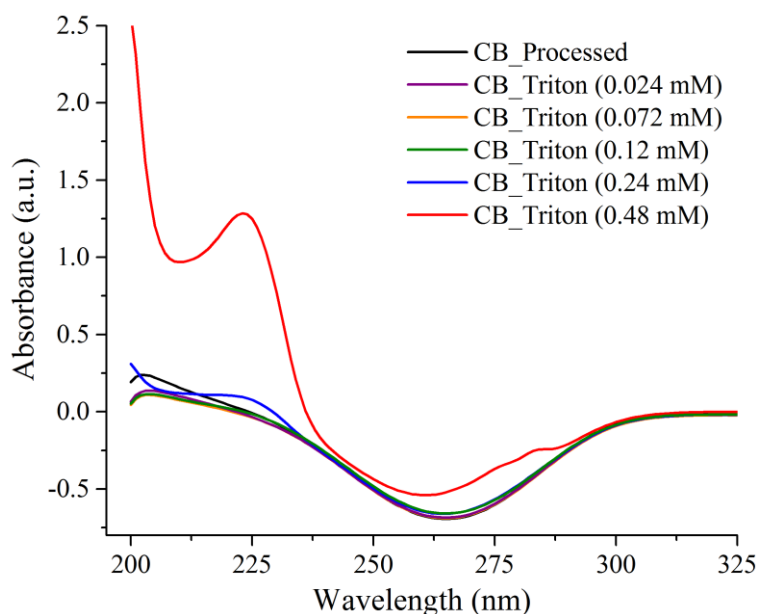


Figure 6.8: The UV-Vis absorbance spectra of the supernatant solutions from the Triton X-100 modified CB, prepared in aqueous Triton X-100 solutions at 0.024 - 0.48 mM.

Table 6.5: Surface loading calculation data from the UV-Vis absorbance peak at 224 nm of the supernatant solutions of the prepared Triton X-100 modified CB at different concentrations.

Sample	$\lambda_{\max}$ (a.u.)	Supernatant Triton Solution Conc. (mM)	Triton Conc. that modified the CB (mM)	Moles/g	Molecules /cm ²
CB_Processed	0				
CB_Triton (0.024 mM)	0	>0.012	0.012-0.024	$1.6-3.2 \times 10^{-5}$	$1.3-2.7 \times 10^{13}$
CB_Triton (0.072 mM)	0	>0.012	0.06-0.072	$8.0-9.6 \times 10^{-5}$	$6.6-8.0 \times 10^{13}$
CB_Triton (0.12 mM)	0	>0.012	0.108-0.12	$1.4-1.6 \times 10^{-4}$	$1.2-1.3 \times 10^{14}$
CB_Triton (0.24 mM)	0.10	0.01	0.23	3.1×10^{-4}	2.6×10^{14}
CB_Triton (0.48 mM)	1.29	0.11	0.37	4.9×10^{-4}	4.1×10^{14}

Triton X-100 exhibited a strong absorbance at 224 nm, used in this analysis, but also a second weaker absorbance at 275 nm could be observed for the Triton solutions at higher concentrations. However, even the strong absorbance peak at 224 nm could only be detected for Triton X-100 solutions of a concentration greater than 0.012 mM (as determined for calibration plot). For the supernatant solution analysis, this meant that absorbance peaks were only detected for the Triton modified CB prepared at the highest concentrations, CB_Triton (0.48 mM) and CB_Triton (0.24 mM), which gave estimate supernatant concentrations of 0.11 mM and 0.01 mM (Table 6.5.) From this, surface loadings of 4.1×10^{14} and 2.6×10^{13} molecules/cm², respectively for CB_Triton (0.48

mM) and CB_Triton (0.24 mM), were calculated, demonstrating slightly higher surface loading estimates compared to those determined by TGA.

The absence of the absorption peak is unsurprising for the rest of the modified CB. The concentrations used for the modifications were all below the CMC for Triton (0.24 mM) and therefore it is expected that the majority of surfactant would be adsorbed onto the CB surface. However, the absence of an absorbance peak in the UV-Vis spectra cannot mean Triton X-100 is absent in the supernatant solution, but rather at a concentration below 0.012 mM. Therefore, the Triton concentration present on the CB must be in the range of 0.108 - 0.12 mM for CB_Triton (0.12 mM), 0.06 - 0.072 mM for CB_Triton (0.072 mM) and 0.012 - 0.024 - mM for CB_Triton (0.024 mM). This suggests the surface loadings will be greater than 1.2×10^{14} , 6.6×10^{13} and 1.3×10^{13} molecules/cm² for each of these samples, respectively. These UV-Vis estimated surface loadings are higher than those of 5.6 , 3.6 and 1.2×10^{13} molecules/cm² found by TGA analysis, but the similarity of results between the two analysis methods is a strong indication that the surface modification occurs at this order of magnitude.

XPS

XPS analysis was performed to assess the changed surface chemistry of the modified CB after treatment at different concentrations of Triton X-100 (0.024-0.24 mM). The challenge of the Triton X-100 modification is the absence of an elemental label and as expected the survey scans of the samples only revealed dominant C 1s photoemission peaks at ~285 eV binding energy and O 1s features at ~532 eV binding energy (Figure 6.9). High resolution scans of the carbon and oxygen regions were analysed to determine the relative elemental abundance of each of the samples (Figure 6.9, Table 6.6).

Part II: Physical Nanoparticle Modification Routes

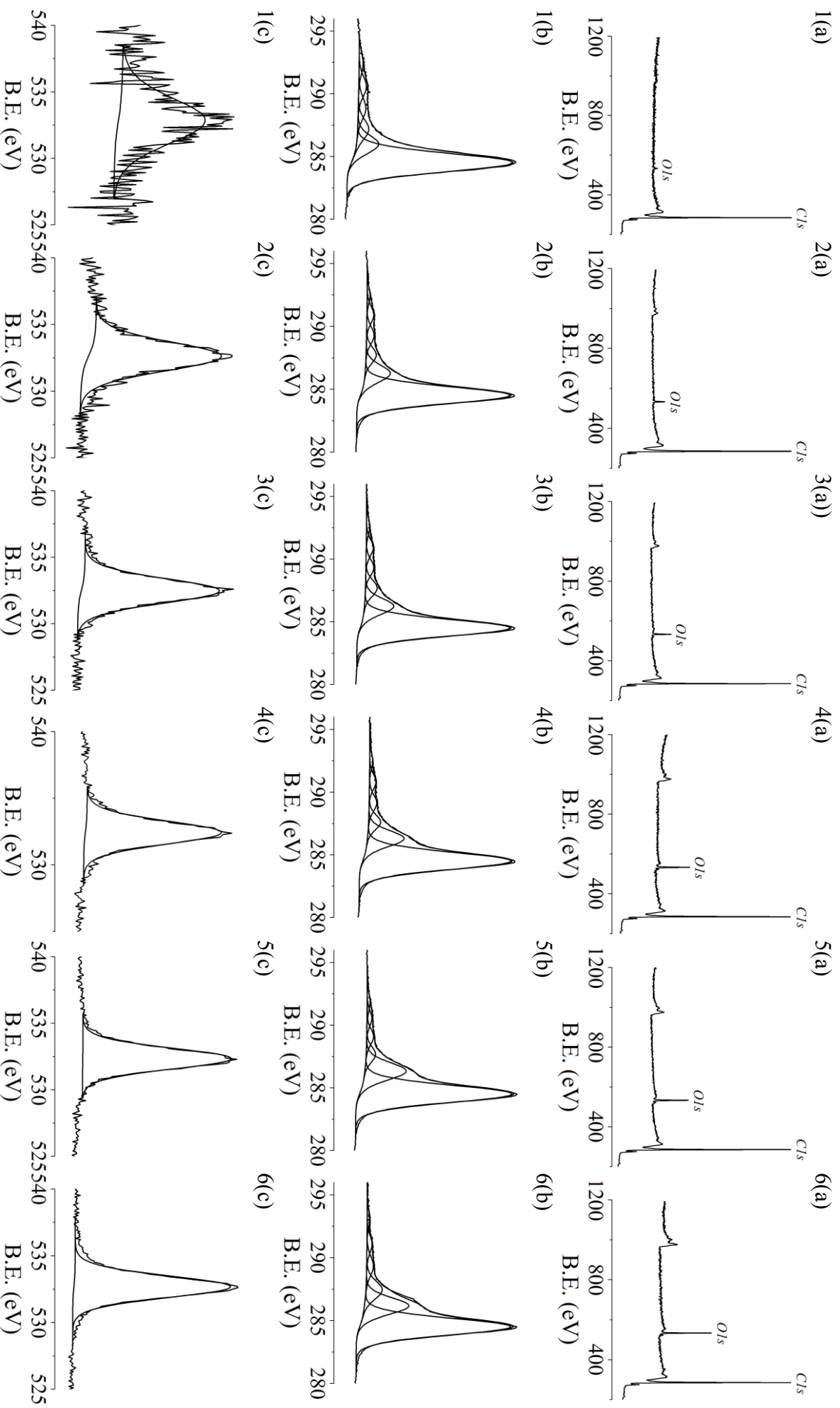


Figure 6.9: XPS (a) wide scan spectra and (b) C 1s and (c) O 1s high resolution spectra of 1. CB_Pristine 2. CB_Triton (0.024 mM), 4. CB_Triton (0.12 mM) 5. CB_Triton (0.24 mM) and 6. CB_Triton (0.48 mM).

Table 6.6: Chemical percentage of the carbon and oxygen content composition of Triton X-100 modified CB determined by XPS analysis.

Sample	XPS (%)	
	C	O
CB_Pristine	98.4	1.6
CB_Triton (0.024 mM)	97.5	2.5
CB_Triton (0.072 mM)	96.6	3.4
CB_Triton (0.12 mM)	93.5	6.5
CB_Triton (0.24 mM)	93.3	6.7
CB_Triton (0.48 mM)	90.9	9.1

An increasing oxygen surface composition, as a function of the concentration of the Triton X-100 solutions used to treat the CB, can be immediately observed in the survey scans of the modified CB samples (Figure 6.9(a)). Additionally, the high resolution scans of the oxygen region reveal the increasing oxygen surface contribution, whereby the oxygen content increased from 1.6 % for pristine CB, to 2.5 % for CB_Triton (0.024 mM), modified at the lowest loading, and increased up to 9.1 % for CB_Triton (0.48 mM), modified at the highest concentration. This result can be attributed to the increasing concentration of the polyethylene oxide chain of the Triton X-100 present on the CB surface.

With regard to the high resolution spectrum of the C 1s region, all the CB samples were devolved into 6 photoelectron peaks of different chemical environments, as before in Chapter 3 and 4. The principal peak was positioned at 284.5 eV (C-C, C-H) and subsequent peaks due to contributions from carbon coordinated to oxygen were at ~286.2 eV (C-O, ± 0.1 eV), ~287.6 eV (C=O, ± 0.1 eV) and ~289.2 eV (COOH, ± 0.1 eV) binding energies. Weak π - π^* features were also observed at ~290.8 eV (π - π^* , ± 0.2 eV) and ~292.5 eV (π - π^* , ± 0.4 eV). Further information extracted from the XPS analysis, including the peak binding energy, charging, FWHM of the analysed XPS spectra, is included in the Appendix, nevertheless, the peak areas for the devolved C 1s peaks for each of the CB samples is presented in Table 6.7.

Table 6.7: The relative peak areas of devolved C 1s peaks in the high resolution XPS spectra of the unmodified and Triton X-100 modified CB.

Sample	C-C/C-H (284.5)	C-O (286.2)	C=O (287.6)	COOH (289.2)	π - π^* (290.8)	π - π^* (292.5)
CB_Pristine	74.4	9.8	5.5	4.2	4.0	2.2
CB_Triton (0.024 mM)	74.0	12.4	4.8	3.8	1.6	1.5
CB_Triton (0.072 mM)	72.3	13.5	5.5	3.7	1.5	1.6
CB_Triton (0.12 mM)	71.0	16.2	5.0	3.5	1.5	1.4
CB_Triton (0.24 mM)	70.7	19.0	3.9	3.0	1.5	1.6
CB_Triton (0.48 mM)	66.4	19.0	7.7	3.4	1.7	1.5

Interestingly, comparison of the C-O contribution (at ~ 286.2 eV) immediately demonstrates a correlation with the CB Triton surface loading. Pristine CB exhibits a C-O contribution of 9.8 %, which is increased to 12.4 % for CB_Triton (0.24 mM), and finally up to 19.0 % for CB_Triton (0.48 mM) modified at the highest loading. This result can also be easily observed in Figure 6.9(b) and is importantly consistent with the increased O 1s contribution at ~ 532.6 (C-O/C=O, ± 0.1 eV) presented earlier. The XPS results therefore establish the successful modification of CB by Triton X-100, with evidence of an increasing surface modification following treatments at higher concentrations of the surfactant solutions.

ATR-IR

The presence of physisorbed Triton X-100 on CB is additionally evident by ATR-IR (Figure 6.10). The CB_Triton samples prepared at higher Triton concentrations of 0.48, 0.24 and 0.12 mM, each display absorbance peaks at ν 1104 cm^{-1} and ν 1250 cm^{-1} corresponding to C-O-C and aryl-O-C vibrations, typically located at 1275-1200 cm^{-1} and 1150-1085 cm^{-1} , respectively.²¹ These peaks correspond to the polyethylene oxide chain functionality of Triton X-100, as indicated by the ATR-IR spectra of the neat Triton X-100 surfactant also included in Figure 6.10. Alternatively, CB_Triton (0.024 mM) and CB_Triton (0.072 mM) prepared at the lowest Triton X-100 concentrations, showed similar functionalities to pristine CB, presumably because the physisorbed surface concentration was below the sensitivity factor of the ATR-IR.

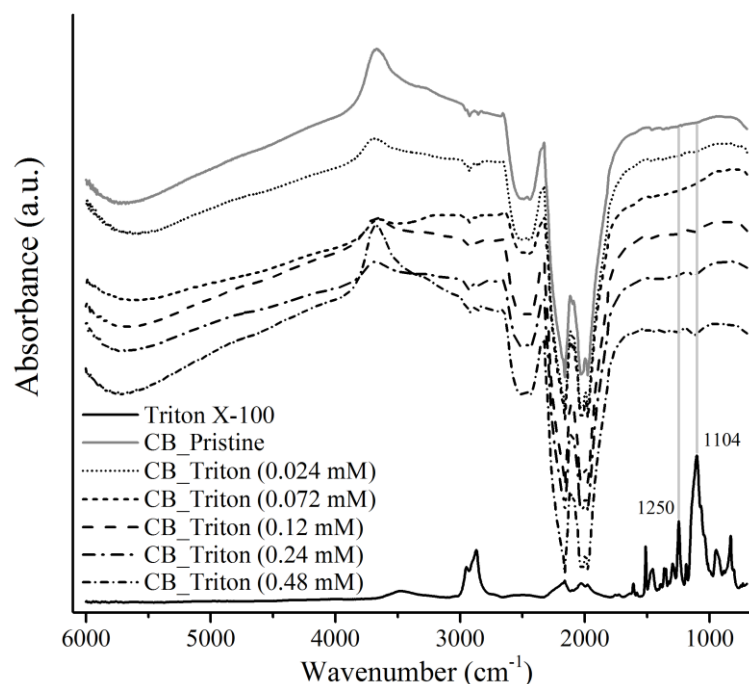


Figure 6.10: ATR-IR spectra of Triton X-100 surfactant (neat) and pristine and modified CB at different loadings of Triton X-100.

Summary - CB Triton X-100 Functionalisation

The surface functionalisation of CB using Triton X-100 proved to be successful following treatment in aqueous solutions at a range of concentrations, 0.024-0.48 mM. Further, all the analysis techniques of the modified CB and the residual supernatant solutions supported the conclusion of an increased surfactant surface loading as a function of the concentration used in the modification procedure. The calculated surface loadings based on the TGA and UV-Vis results ranged from 1.2×10^{13} - 1.2×10^{14} molecules/cm² and 1.3×10^{13} - 4.1×10^{14} molecules/cm², respectively for each technique across the range of surface loadings. Additionally, they are highly comparable to the estimated loading by Chemicalize of 4.9×10^{13} molecules/cm² and 1.6×10^{14} molecules/cm² under the basic assumption of CB modification by the ‘perpendicular’ or ‘parallel’ orientation of the Triton X-100 surfactant.²⁰ It is suggested that orientation of the surface modification might alter as the concentrations increases. Favourable hydrogen bonding interactions between the polyethylene oxide of neighbouring Triton X-100 molecules might be

driving a ‘perpendicular’ type orientation from the CB surface, resulting in a reduced thermal stability, as the interactions of the hydrophobic anchor group with the CB become reduced at higher surface surfactant concentrations.

6.4.2.3. Nanocomposite Analysis

Volume Resistivity

As introduced at the beginning of this Chapter, the aim of this series of functionalised CB by surfactant adsorption is to determine a readily industrially viable technique for the preparation of electrically conductive CB/PP nanocomposites in which the mechanical properties can remain intact. In previous work (Chapter 5), PP nanocomposites were prepared by solvent mixing methods. However, alternatively here lab-scale melt mixing methods have also been employed to prepare the surfactant modified CB/PP nanocomposites as a more comparable protocol to existing industrial nanocomposite manufacturing methods.²² As a primary investigation, the effect of the CB functionalisation by Triton X-100 at different loadings was assessed by preparing CB/PP nanocomposites by melt mixing at the same filler loading of 10 wt. %. This loading was selected because the covalent modified CB_{15b}/PP nanocomposite in Chapter 5 demonstrated good electrical conductivity for this low structure type of CB at the filler addition loading of 10 wt. %. Equally, here the aim is to find a similarly significant improvement to the conductivity following the surfactant functionalisation using Triton X-100 at a low loading filler addition. Accordingly, the volume conductivity was determined from the silver-pasted compression moulded plaques by the 2-probe method of the CB_{Triton} modified PP nanocomposites (Figure 6.11). The raw conductivity data is included in the Appendix.

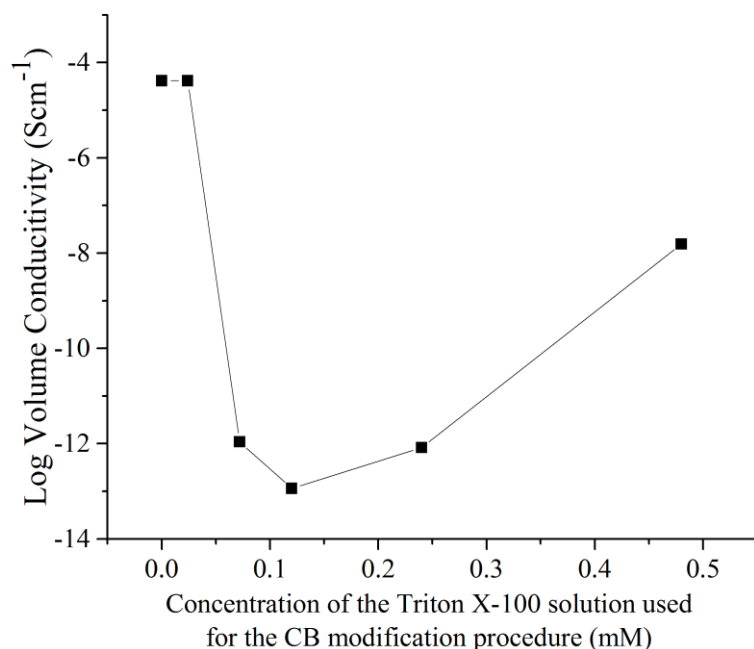


Figure 6.11: Logarithm of the volume electrical conductivity of CB_Pristine and CB_Triton/PP nanocomposites prepared at 10 wt. % by melt mixing methods as a function of Triton X-100 modification loading.

Unfortunately, the conductivity results of the Triton X-100 modified CB/PP nanocomposites at 10 wt. % loading indicate that generally the surface modification leads to a reduced conductivity. However, there is no direct trend observed between high concentrations and low conductivity, as CB_Triton (0.48 mM), with the highest degree of Triton X-100 modification, demonstrated the second highest conductivity of $\sim 1.5 \times 10^{-8} \text{ Scm}^{-1}$. It may be that the optimistic production of the Triton X-100 modified CB/PP nanocomposites at 10 wt. % in fact meant that this set of nanocomposites were produced at the filler concentration at which the percolation threshold is being established. In Chapter 4 the greatest variability in the measured electrical conductivities across the perpendicular sides of the nanocomposite plaques were all either below and or at the percolation threshold. Nevertheless, these results demonstrated the most conductive nanocomposite at $1.5 \times 10^{-5} \text{ Scm}^{-1}$ was PP prepared with CB_Triton (0.024 mM), with the lowest Triton X-100 surface modification.

Discussing the effect Triton X-100, it was selected as an attractive route for CB functionalisation because the extending chains can act as steric stabilisers for the filler particles, thereby hindering agglomerate formation in polymer nanocomposites. Instead, it is possible that at high surface loadings, the surfactant ‘encapsulates’ the conducting CB aggregates, hindering conduction via tunnelling processes between neighbouring CB in the PP matrix. However, this does seem unlikely at the low surface modification loadings used below the CMC. Alternatively, even at very low loadings, the hydrophilic polyethylene oxide chain of Triton X-100 presumably interacts unfavourably with the hydrophobic CB, but equally extension from the CB in the PP matrix in the nanocomposites might also reduce the compatibility of these two components, perhaps surpassing the steric stabilisation separation of the CB aggregates, otherwise leading to the promotion of agglomeration. Last, as discussed in the introduction of the Chapter, there is potential for the formation of a loose network of bridged aggregates, due to hydrogen bonding between the hydrophilic ‘head’ groups of adjacent surfactant modified CB,^{4, 10} which might also be controlling the conductive properties of the nanocomposites. Ultimately, CB modified at the lowest Triton loading, CB_Triton (0.024 mM) exhibited the most promising conductive properties compared to CB modified at higher surfactant concentrations, as well as unmodified CB/PP nanocomposites at 10 wt. % loading. Additionally, a lowered surface CB loading has economic advantages for industrial applications. Therefore, based on this set of results, this modified CB presents the most viable surface functionalisation by Triton X-100 for improved macroscopic properties.

6.4.3. Study C: Investigation of CB_Triton (0.024 mM)/PP Nanocomposites

With CB_Triton (0.024 mM) selected as the most promising Triton X-100 modified CB nanoparticle, PP nanocomposites were prepared at different wt. % addition loadings in

order to fully investigate the changed macroscopic properties following the nano-scale modification. As such, nanocomposites were prepared by lab melt-mixing methods in the interest of further application in industry, but additionally nanocomposites were prepared by solvent mixing methods for comparison purposes with the carbene modified CB work presented in Chapter 5.

Volume Resistivity

The volume electrical percolations curves of CB_Triton (0.024 mM)/PP prepared by lab-scale melt mixing and solvent mixing methods are presented in Figure 6.12 and the raw data can be found in the Appendix.

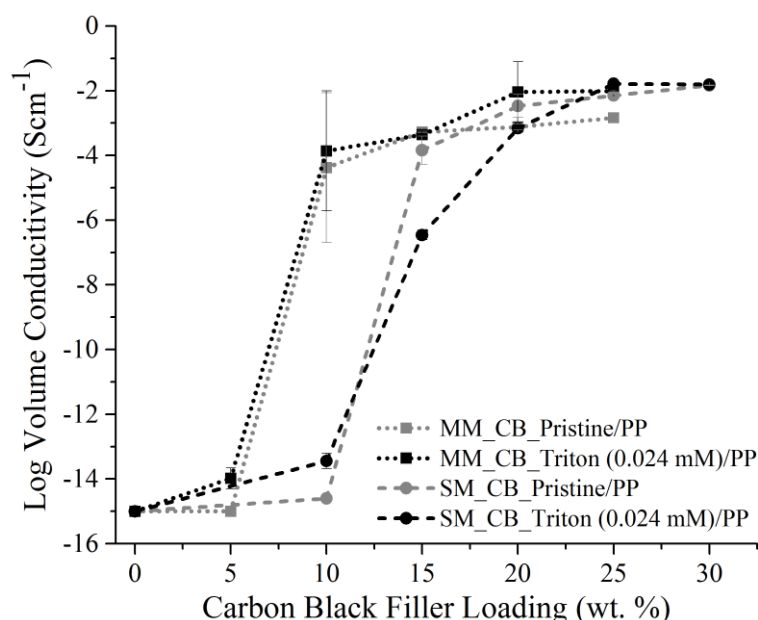


Figure 6.12: Logarithm of the volume electrical conductivity of pristine and CB_Triton (0.024 mM)/PP nanocomposites as a function of CB nanofiller loading. The nanocomposites were prepared by melt mixing (MM) and solvent mixing (SM) methods using CB as received (CB_Pristine) and CB modified by Triton in an aqueous solution at concentration of 0.024 mM (CB_Triton (0.024 mM)). The error bars indicate the error of the measurements taken across the perpendicular sides of the nanocomposite plaque samples.

At first glance, the Triton modified CB/PP nanocomposites demonstrate similar percolation thresholds to the equivalent unmodified CB/PP samples. However, a major difference can be observed between the two processing methods, in which the melt-mix method prepared nanocomposites achieved the percolation threshold, associated by the sharp rise in electrical conductivity, at a lowered required filler concentration of ~10-15

% compared to ~15-20 % wt. by the solvent-mix method. This highlights the importance of the processing conditions of the nanocomposites and the altered macroscopic properties which can result. The solvent mixing method is generally viewed as the better polymer nanocomposite method for good filler dispersion,²³ but this is likely the reason for the increased percolation threshold observed. Alternatively, it appears a better balance between the distribution and dispersion is achieved by the melt mixing method.

Considering the effect of the Triton modification in more detail, the achievement of the percolation threshold is almost identical to the pristine CB/PP nanocomposites prepared by melt mixing. After 15 wt. % loading, however, the Triton modification seems to demonstrate slightly superior conductive properties compared to the unmodified CB. This might be a result of the low degree of surface modification inducing steric stabilisation between the CB aggregates, inhibiting further agglomerate formation in the PP matrix. Additionally, it may be that the modification is reducing the PP viscosity, aiding better dispersion of the CB aggregates in the resulting PP nanocomposite prepared by the melt mixing method, as observed in other nanocomposite systems.²⁴

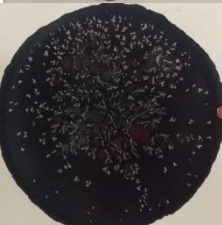
For the nanocomposites prepared by solvent mixing, Triton modified CB/PP almost demonstrates the opposite macroscopic behaviour. Initially, the Triton modified CB indicates an improved conductivity to unmodified CB at 10 wt. % loading. However, as the percolation threshold is approached, conductivity is achieved more slowly for the Triton modified nanocomposites and then finally at 25 and 30 wt. % filler loading, both the modified and unmodified CB/PP nanocomposites display similar conductive properties. The higher percolation threshold of the Triton modified CB/PP nanocomposites might be a result of the surface modification initially hindering the conduction by tunnelling process between the CB aggregates at lower filler loadings. A similar percolation threshold pattern was observed for Triton modified CNTs in an epoxy

matrix.⁶ However, as the filler content increases, and the conductivity networks in the PP matrix form, more similar conductivities between the modified and pristine CB/PP nanocomposites are achieved. Overall, the electrical conductivity results demonstrate similar results for the Triton modified CB and pristine CB by both PP nanocomposites fabrication methods, corroborating with the result in Study B, at 10 wt. %.

Dielectric Analysis

Dielectric analysis demonstrated interesting results in Chapter 5 for the covalent modified CB/PP nanocomposites, providing information about conductivity mechanisms which cannot be determined by DC conductivity measurements. Accordingly, a pristine CB and modified CB_Triton (0.024 mM) solvent mix prepared nanocomposite films (Table 6.8) were prepared at 30 wt. % filler loading, above the percolation threshold, which for reference exhibited DC conductivity values at 1.4×10^{-2} and 1.5×10^{-2} Scm⁻¹, respectively.

Table 6.8: Photos and microscope images of the CB_Pristine and CB_Triton (0.024 mM)/PP nanocomposite film samples (50 μ m) prepared at 30 wt. % filler loading used for dielectric analysis.

Sample	Photo	Microscope Image	
	Film (50 μ m)	$\times 20$	$\times 200$
SM_CB_Pristine /PP 30 wt. %			
SM_CB_Triton (0.024 mM) /PP 30 wt. %			

At this high loading, the pristine CB/PP nanocomposite films display generally visibly good CB dispersion except for a few PP clusters more easily observed in the microscope images. The CB_Triton (0.024 mM)/PP films on the other hand appear to show a larger

degree of PP clusters, and CB agglomeration can also be observed, particularly evident in the $\times 200$ magnification image in Table 6.8.

The resulting dielectric results of the nanocomposite film samples (Figure 6.13) presents the real (ϵ') part and the imaginary (ϵ'') part of the complex permittivity, as a function of frequency, in the range 10 MHz - 10 GHz. The results of PP and the pristine and modified CB/PP nanocomposites at 30 wt. % additionally include a comparison of CB_Pristine/PP at 20 wt. % presented beforehand in Chapter 5.

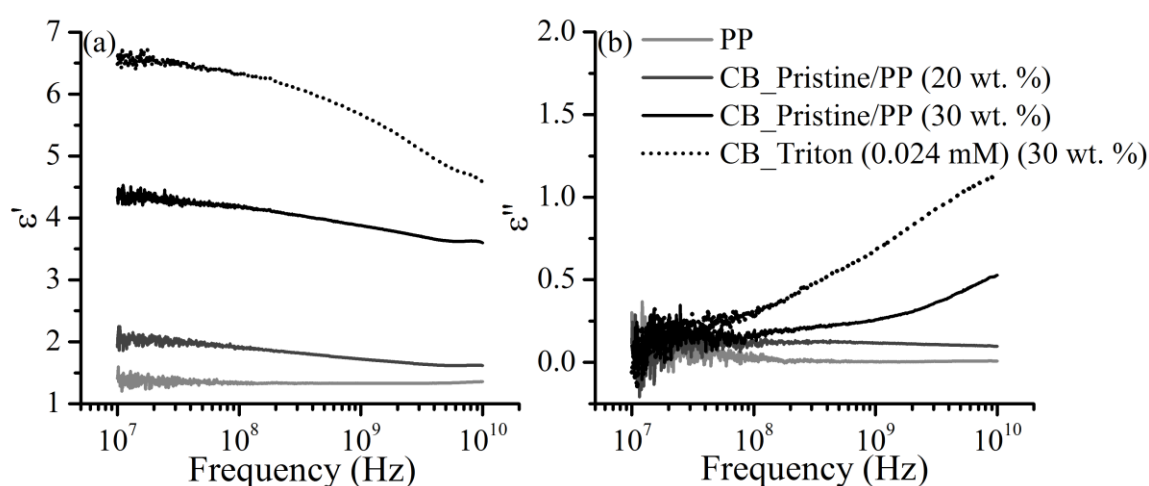


Figure 6.13: (a) Real part (ϵ') and (b) the imaginary part (ϵ'') of the complex permittivity as a function of frequency, averaged over 50 repeat measurements at different points, of pure PP, SM_CB_Pristine/PP at 20 and 30 wt. % loading and SM_CB_Triton (0.024 mM)/PP at 30 wt. % loading nanocomposite films samples (50 μm) in the range 10 MHz - 10 GHz. The same figure, with the error of the repeated measurements displayed, can be found in the Appendix.

The real (ϵ') part, characterises the capacity for electric energy storage,²⁵ and the imaginary (ϵ'') part accounts for the conductive and relaxation effects of the nanocomposite sample,²⁶ as described in more detail in Chapter 5. The PP sample displays a frequency independent response at a value of ~ 1.3 and ~ 0.03 for the real part and the imaginary part of the complex permittivity, respectively. With the addition of CB in the PP nanocomposite films, dielectric relaxation responses as the frequency increases are recorded. SM_CB_Pristine/PP at 20 wt. % displays a low frequency dependent response, initially at ~ 2 and dropping to ~ 1.6 at higher frequencies for the real part of the

complex permittivity. For the imaginary part, an almost flat frequency response is recorded ~ 0.1 , indicating non-conductive behaviour at this frequency. However, at the higher loading of 30 wt. %, SM_CB_Pristine/PP displays an increased real permittivity at a value ~ 4.3 which is reduced to ~ 3.6 at higher frequencies. A resulting dielectric relaxation response can be observed in the imaginary permittivity, starting to peak at ~ 0.5 at the highest frequency recorded of 1×10^{10} Hz. The larger complex permittivity response and frequency dependence for the CP/PP nanocomposite at the higher filler loading at 30 wt. % is, as expected, consistent with an increase in the number of charge carriers present in the sample.

Further, the addition of the Triton CB surface modification leads to an even greater dielectric response, with an increased real permittivity of 6.5 at lower frequency measurements, reduced to 4.7 at the highest frequency recorded. This results in a larger dielectric response in the imaginary permittivity, compared to pristine CB, starting to peak at ~ 1.1 at the highest frequency recorded here of 1×10^{10} Hz. As presented in detail in Chapter 5, the observed frequency dependence upon the dielectric response is a result of the Maxwell-Wagner-Sillars effect, and exposes the inter-filler tunnelling conduction mechanism,²⁷ which is particularly relevant here for the Triton modified films sample. This result therefore reveals that after the nano-scale CB surface modification, there is a changed percolative conduction mechanism, indicating favourable, altered CB-CB and CB-PP interfacial interactions following the physisorption modifications. It has been reported that hydrogen bonding between the hydrophilic ‘head’ groups of the surfactant modification can facilitate the ‘bridging’ of adjacent nanofillers in the polymer matrix, forming a loose network.^{4, 10} This might explain the improved complex permittivity properties observed following the Triton X-100 modification, in comparison, the pristine CB/PP nanocomposites both which displayed similar DC conductivities.

Lastly, the variance of the repeat dielectric measurements (50) at different points on the nanocomposite films can provide an indication of the dispersion and distribution of the CB (Figure 6.14). Interestingly, the results demonstrate a slightly increased measurement reproducibility for the unmodified CB film samples compared to the Triton modified sample. A result which is perhaps unsurprising considering the higher level of PP clusters and CB agglomeration visible in the CB_Triton (0.024 mM) film (Table 6.8).

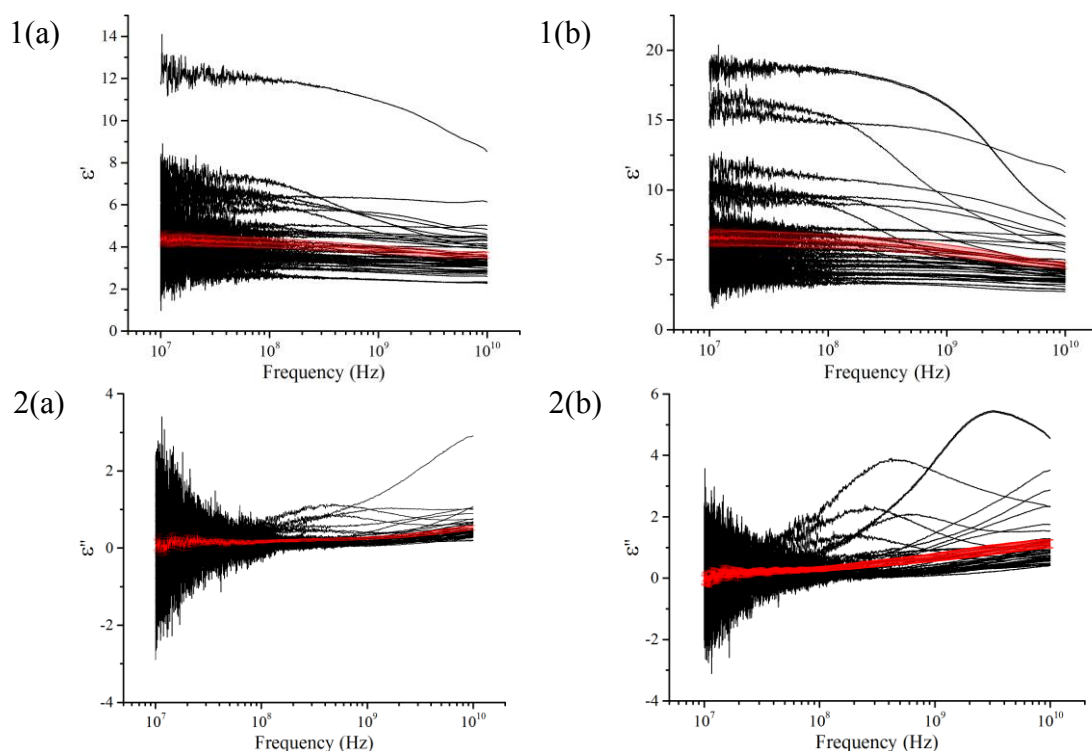


Figure 6.14: Repeat measurements of 1. the real part ϵ' and 2. the imaginary part ϵ'' of the complex permittivity of (a) SM_CB_Pristine/PP and (b) SM_CB_Triton (0.024 mM)/PP at 30 % wt. loading nanocomposite film samples (50 μm) with the average and the calculated error displayed in red. The repeat measurement data of PP and CB_Pristine/PP at 20 wt. % loading can be found in Chapter 5.

Morphological Characterisation

TEM micrographs of the Triton modified CB/PP nanocomposites thin films at 20 wt. % loading, prepared by the solvent mixing, (Figure 6.15) provides further visual indication of the altered dispersion of the CB nanofiller in comparison to pristine CB, also presented in Chapter 5.

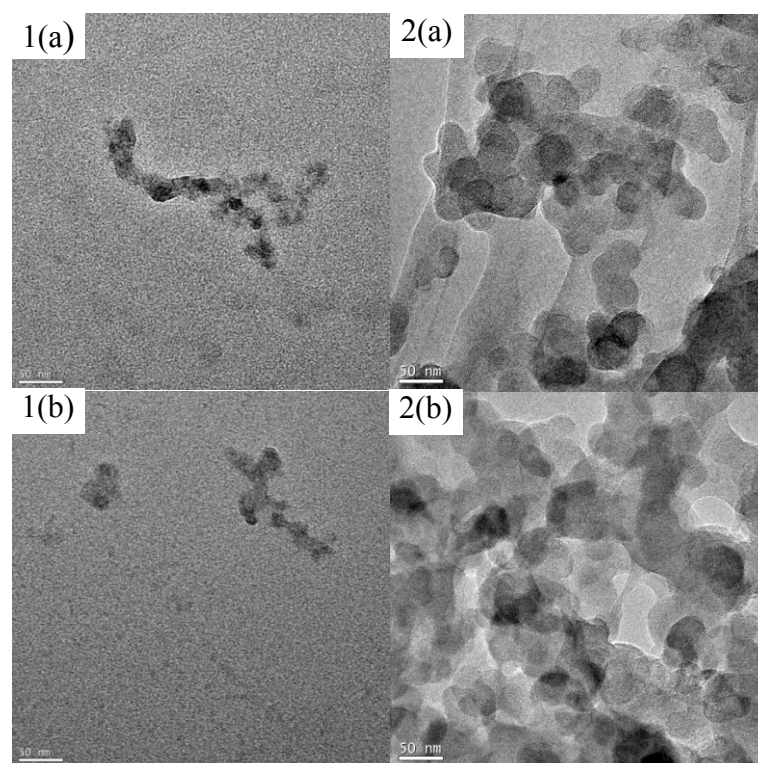


Figure 6.15. TEM micrographs for 1. SM_CB_Pristine/PP and 2. SM_CB_Triton (0.024 mM)/PP nanocomposites at a loading of 20 wt. % at 50 nm.

The TEM images of the Triton modified CB embedded in PP, compared to pristine CB, indicate fewer isolated CB aggregates but rather large agglomerates. This result conforms with the visible dispersion of the films prepared at the higher loading of 30 % (Table 6.8) as well as the reproducibility of the repeat dielectric measurements (Figure 6.14). This result suggests poor filler-polymer compatibilities or equally the unhindered attractive filler-filler interactions, following the Triton X-100 modification. Further, the agglomeration displayed in the TEM images (Figure 5.15(2a-b)) might explain the slightly lowered DC conductivity results at 20 wt. % of the Triton modified CB/PP

solvent mixed nanocomposites, compared to pristine CB. This said, the dielectric analysis results at a higher loading (30 wt. %) did also demonstrate that the low surface loading of Triton X-100 to CB directed an improved inter-filler tunnelling conduction mechanism compared to pristine CB. Therefore, the TEM image could be showing the formation of ‘soft agglomeration’ of the modified CB in the PP matrix, as a result of the bridging between the adjacent modified CB,^{4, 10} which could be contributing to the modified connectivity observed by dielectric analysis.

Thermal Analysis: STA and DMA

Due to the similarly high filler loadings required to achieve good conductivity for the Triton modified CB, compared to unmodified CB, the assessment of the thermal and mechanical properties of the nanocomposites was especially important for these samples.

6.4.3.1. STA Thermal Analysis

Thermal analysis experiments of the solvent and melt-mix prepared nanocomposites were performed to evaluate the effect of the Triton X-100 modification upon the melting, crystallisation and decomposition behaviour. Accordingly, the key data, extracted from the DSC, TGA and DTG thermal analysis curves, are reported in Table 6.9 and the accompanying raw data can be found in the Appendix.

The degree of crystallinity (X_C) was calculated by the same method as used in Chapter 5 by:

$$X_C = \frac{H_m}{(1 - x)H_0} \times 100 \quad \text{(Equation 6.1)}$$

where H_m is the sample melting enthalpy, as measured by DSC, H_0 is the melting enthalpy of 100 % crystalline PP, which is reported to be 207.1 J/g,^{28,29} and X_C is the weight fraction of CB present in the nanocomposite.³⁰

Table 6.9: Extracted DSC, TGA and DTG data from thermal analysis runs of pristine and modified CB_Triton (0.024 mM)/PP nanocomposites.

Sample	CB Loading (Wt. %)	DSC					χ_c^f (%)	TGA		DTG
		T_{oc}^a (°C)	T_{pc}^b (°C)	T_{om}^c (°C)	T_{pm}^d (°C)	ΔH_m^e (J/g)		T_{pd}^g (°C)	T_{od}^h (°C)	T_{pd}^i (°C)
PP_Pristine ^j	0	121.1	116.5	150.8	163.0	77.0	37.2	470.9	444.6	468.5
S.D. PP_Pristine	0	0.0	0.1	0.5	0.1	0.6	0.3	1.1	0.7	0.2
SM_PP_Processed ^k	0	127.6	122.9	149.1	163.2	71.1	34.3	474.0	446.3	472.3
S.D. PP_Processed	0	1.7	1.9	1.8	0.7	0.7	0.3	0.8	2.1	1.0
MM_PP_Processed	0	127.9	121.4	135.2	160.7	60.2	29.1	466.7	433.0	465.0
SM_CB_Pristine/PP	10	128.9	124.1	145.6	161.9	68.0	36.5	475.9	449.2	475.1
	15	125.1	119.9	149.3	164.2	62.7	35.6	477.3	450.5	475.7
	20	132.5	125.5	146.7	165.5	59.4	35.9	477.7	456.4	477.2
	25	131.5	123.8	146.8	165.1	60.0	38.6	476.1	458.9	476.1
	30	133.8	126.6	147.6	166.0	59.2	40.8	484.5	464.9	483.2
SM_CB_Triton (0.024mM)/PP	10	128.3	121.7	148.4	164.5	59.8	32.1	476.4	449.3	472.7
	15	127.1	121.3	150.6	164.5	57.8	32.8	477.3	447.2	472.5
	20	127.5	122.4	149.5	163.6	55.2	36.2	474.5	450.3	472.2
	25	128.3	121.2	147.4	166.6	52.5	33.8	475.3	454.2	473.1
	30	129.0	122.7	147.9	164.6	47.0	32.4	478.6	452.7	476.7
MM_CB_Pristine/PP	5	129.7	124.2	143.3	161.8	64.6	32.8	469.2	437.6	466.4
	10	134.6	129.3	147.5	166.3	71.8	38.5	476.5	456.4	474.2
	15	128.9	122.0	147.5	166.7	58.9	33.4	479.6	457.2	477.0
	20	130.2	119.0	145.9	162.7	61.2	36.9	472.1	439.7	469.0
	25	128.7	117.8	142.5	161.7	56.3	36.3	472.7	437.4	470.1
MM_CB_Triton (0.024 mM)/PP	5	126.8	119.2	139.8	157.2	54.7	27.8	467.0	427.2	464.5
	10	134.9	129.6	147.7	166.3	71.5	38.3	476.4	450.6	473.3
	15	129.4	122.8	146.6	167.1	59.0	33.5	476.3	451.9	474.0
	20	129.3	123.8	147.9	165.1	58.1	35.1	479.8	458.5	477.2
	25	130.3	119.7	145.8	163.0	58.4	37.6	471.9	438.7	469.2

^a T_{oc} , onset crystallisation temperature.^b T_{pc} , peak crystallisation temperature.^c T_{om} , onset melting temperature (second melting cycle).^d T_{pm} , peak melting temperature (second melting cycle).^e ΔH_m , enthalpy of melting (second melting cycle).^f χ_c , is the degree of crystallinity.^g T_{pd} , peak decomposition temperature (DSC).^h T_{pd} , onset decomposition temperature (TGA).ⁱ T_{pd} , peak decomposition temperature (DTG).^j Average of three repeat measurements.

The thermal analysis results for the pristine and Triton X-100 modified CB/PP nanocomposites prepared by both production methods generally demonstrate similar results. The most interesting result is revealed by the decomposition profiles of the nanocomposites at higher loadings. As the filler content increases, it is expected that the decomposition temperature will increase as the dispersed nanofiller acts as a barrier, shielding the PP matrix from the degradation products.³¹ This is observed for both the unmodified and modified CB prepared by the solvent mixing method. However, for the melt-mixed nanocomposite samples prepared using pristine CB, the decomposition temperature appears to peak at 15 wt. % filler addition at ~480 °C (T_{pd} – DSC) and then at

20-25 wt. % filler loading reduces to ~ 472 °C (T_{pd} – DSC). This result compared to the Triton modified CB/PP nanocomposite suggests improved thermal stability after the Triton modification, as the decomposition temperature peaks to ~ 480 °C (T_{pd} – DSC) at 20 wt. % addition and is only reduced to ~ 472 °C (T_{pd} – DSC) at 25 wt. % addition. Equally, the rate of the decomposition is shifted by ~ 8 °C (T_{pd} – DTG) for the Triton modified CB/PP nanocomposite at 25 wt. % compared to unmodified CB. The improvement of the decomposition profile as a function of the filler addition for the Triton modified nanocomposite sample presents an indication of the preservation of the mechanical properties at higher loading filler additions. Alternatively, the abrupt shift of the degradation temperatures of the pristine CB/PP nanocomposite suggests a reduced CB-PP compatibility and the likelihood that the critical filler concentration has been reached, indicating the failure of the mechanical properties of this nanocomposite at this high loading.²²

Considering the rest of the DSC data in more detail, it can be observed that the presence of pristine or Triton modified CB generally results in raised onset (T_{oc}) and peak (T_c) crystallisation values indicative of the accelerated nucleation efficiency of the nanofiller in the PP matrix,³² as observed in Chapter 5. That said there was no clear correlation of the T_{oc} and T_{pc} values as a function of filler loading. Solvent prepared Triton X-100 modified CB nanocomposites displayed a generally lowered χ_c , possibly an indication of greater agglomeration in the system system.³³ Conversely, Triton modified CB nanocomposite prepared by melt-mixing displayed improved χ_c , compared to pristine CB/PP nanocomposites prepared by both methods, in agreement with the results of Triton modified CNT/PP nanocomposites in the literature,⁴ and suggests improved compatibilisation with the PP matrix after functionalisation.

Additionally, generally improved peak melting temperatures (T_{pm}) were observed following the addition of the CB nanofiller. This is attributed to the nucleating effect of the CB nanofiller – discussed above – resulting in the formation of smaller crystallites and a decreased lamellar thickness in the PP matrix.³³ However, no significant trend concerning the effect of the modification nor the filler loading can be established for the T_{pm} . Alternatively, the onset melting temperatures (T_{om}) were generally reduced at lower nanofiller additions compared to pristine PP and solvent mixed processed PP. However, at higher filler loadings, the Triton X-100 functionalisation seems to demonstrate improved T_{om} compared to the equivalent unmodified CB/PP nanocomposites, potentially an indication of improved thermal stability by more effective shielding of the modified CB.³¹

Overall, the STA thermal analysis presents suggestive evidence of improved CB/PP nanocomposite thermal properties following the Triton X-100 CB surface modification, in particular for the melt-mix prepared samples.

6.4.3.2. DMA

Dynamic Mechanical Analysis (DMA) was used in order to see if the Triton X-100 CB modification directed improved mechanical properties. Accordingly, the storage modulus (E') as a function of temperature of solvent mix prepared CB/PP nanocomposites, with and without Triton X-100 surfactant treatment, at 15 and 25 wt. % filler addition (close to the percolations threshold) are presented in Figure 6.16, with key data included in Table 6.10.

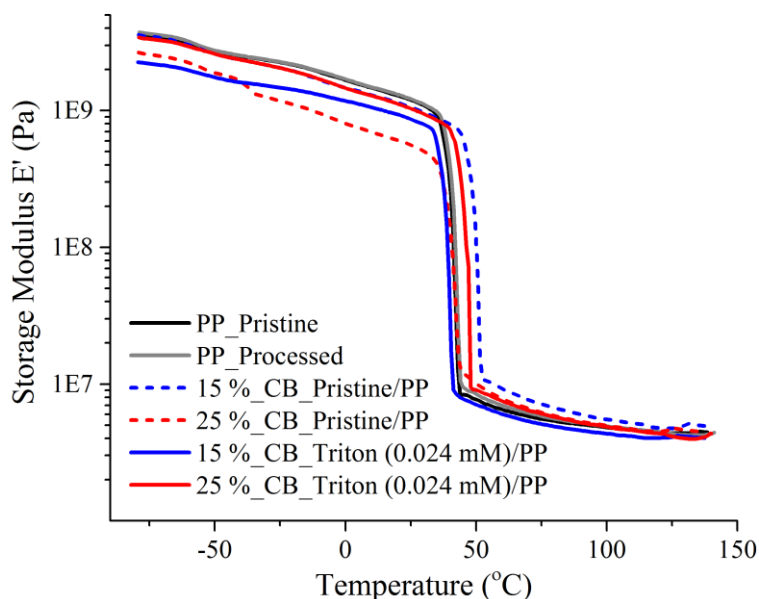


Figure 6.16: Storage modulus (E') (measured at 1 Hz at a heating rate of 5 °C/min) as a function of temperature for PP and pristine and Triton X-100 modified CB/PP nanocomposites, at 15 and at 25 wt. % loadings, prepared by solvent mixing methods before pressing into films (0.25 mm).

Table 6.10: Extracted DMA data including α and β and relaxation peak data, as determined from the Tan δ curves, and the storage modulus (E') at -70 °C.

Sample	Tan δ				Storage E'
	Relaxation γ		Relaxation β		At -70 °C
	(°C)	Height	(°C)	Height	(Pa)
PP_Pristine	-56.6	0.041	-5.6	0.044	3.5×10^9
PP_Processed	-56.5	0.041	-5.3	0.045	3.5×10^9
15 %_CB_Pristine/PP	-56.9	0.046	-10.3	0.056	3.4×10^9
25 %_CB_Pristine/PP	-58.0	0.059	-7.0	0.087	2.5×10^9
15 %_CB_Triton (0.024 mM)/PP	-53.0	0.052	-8.2	0.071	2.2×10^9
25 %_CB_Triton (0.024 mM)/PP	-55.0	0.052	-7.8	0.065	3.3×10^9

As presented in Chapter 5, the major transition resulting in a substantial reduction in the storage modulus E' normally occurs close to the T_m of the polymer samples, expected at ~150 °C according to DSC analysis for PP. However, all the samples tested in this set of analysis displayed this transition at the lowered temperature of ~40-50 °C compared to the transitions in the temperature range of ~100-150 °C for the DMA samples set reported in Chapter 5. This result cannot be attributed to CB addition or the Triton modification because the repeated pristine and processed PP samples also exhibited the low temperature transition (repeated experimental data is included in the Appendix). Otherwise, it is likely that the lowered T_m in this data is because of the different DMA

instruments used, as this set of samples were tested on a Mettler DMA 1, compared to a PerkinElmer® DMA 8000 used beforehand (Chapter 5), although the same running conditions were used. Nonetheless, these results can provide a relative comparison for this sample set to permit evaluation of the effect of Triton, but the T_m will not form part of the analysis discussion.

Overall, it can be observed that the addition of the CB nanofiller, whether modified or pristine, has resulted in a slight decrease in the storage modulus at lower temperatures compared to PP (pristine and processed) which displayed an E' of 3.5×10^9 Pa. This indicates that the CB filler additive did not add any reinforcing effects to the PP.³⁴ Nevertheless, the high loading content of these nanocomposite samples (15 and 25 wt. %) means it is unsurprising that the critical content, at which the nanofiller can contribute a strengthening effect has been surpassed and instead the tendency of the CB to aggregate at these loadings has compromised the mechanical properties of the nanocomposite.²² Unfortunately, the Triton modification at 15 % wt. loading appears to have lowered the storage modulus to 2.2×10^9 Pa, compared to the pristine nanocomposite, which alternatively exhibited a similar storage modulus close to the unmodified PP at 3.4×10^9 Pa. Inversely, at the higher filler loading (25 wt. %), the Triton X-100 sample demonstrates a superior storage modulus, also close to PP, at 3.3×10^9 Pa, compared to 2.5×10^9 Pa for the unmodified CB/PP sample. This result suggests that at the higher filler concentration of 25 wt. %, the Triton X-100 modification improves the CB-PP interfacial interactions, concomitant with an improved stress transfer at the interface.³⁵ The fact that this was not demonstrated at the lower loading at 15 wt. % for the Triton modified CB/PP nanocomposite might be because the efficiency of the stress transfer was reduced at this loading, as it is below the critical concentration at which three-dimensional filler networks are formed in the filler matrix as indicated by the electrical

conductivity percolation curves previously discussed. However, without repeated sample analysis, this cannot be confirmed here.

Table 6.10 and Figure 6.17 display evidence of the damping factor ($\tan \delta$) of the sample set and as determined from the peak temperature in the $\tan \delta$ curves, two of the expected relaxations for PP can be observed at ~ -55 °C (γ), attributed to the short range motions of chain segments in the amorphous regions and at ~ -5 °C (β), due to the glass-rubber transition.³¹

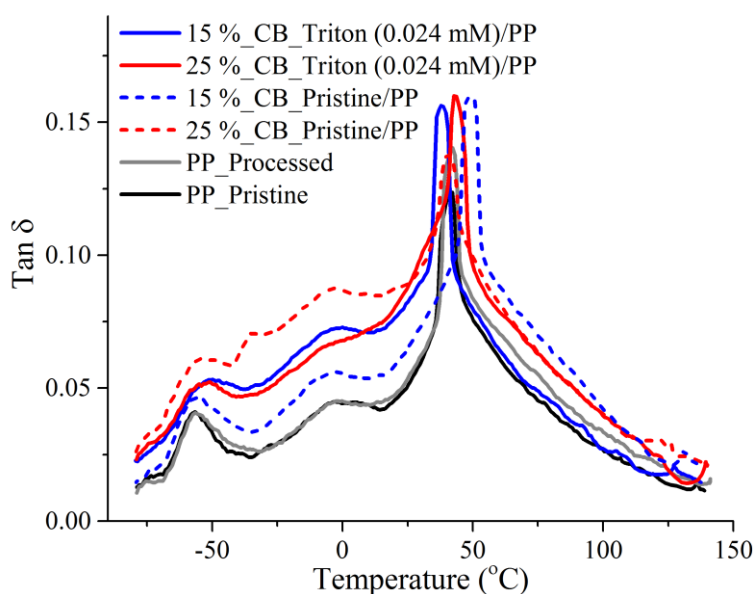


Figure 6.17: $\tan \delta$ (measured at 1 Hz and heating rate 5 °C/min) as a function of temperature for PP and pristine and Triton X-100 modified CB/PP nanocomposites, at 15 and at 25 wt. % loadings, prepared by solvent mixing methods before pressing into films (0.25 mm).

Unfortunately, the transition usually found at ~ 65 °C (α), due to motions of the crystallites in the interphase regions, is dominated by the lowered T_m transition of this DMA sample set. Nonetheless, below ~ 20 °C, the $\tan \delta$ curves display excellent reproducibility of the pristine and processed PP. Alternatively, for the Triton X-100 modified and pristine CB/PP nanocomposite, differences are revealed in the $\tan \delta$ curves exposing the effects of the filler addition and the functionalisation upon both the amorphous and crystalline regions of the PP matrix. First, a small increase of the γ relation peak for the Triton-modified CB/PP samples (compared to the PP samples)

indicates a reduced polymer chain mobility, suggesting improved CB-PP interfacial interactions. Alternatively, the pristine CB/PP nanocomposite samples both displayed lowered γ relation peaks compared to PP, indicating the opposite effect. However, the β relaxation peaks demonstrated no clear effect of modification, but the addition of CB resulted in reduced T_g temperatures compared to the PP samples, consistent with the lowered χ_c as observed in the DSC results. Generally, an increased β relaxation peak temperature is expected (as observed for the γ relation peaks) concomitant with the immobilised polymer in the interfacial region of the CB particles.³⁶ However, lowered T_g upon filler addition to PP has also been reported, and it was suggested that the obstruction to the polymer chains, as a result of the presence of the filler in the polymer matrix, can actually direct an increase of the free volume, permitting polymer movement.³⁷ Further, perhaps the increased filler addition from 15 to 25 %, reduced this free volume effect in these results; both pristine and modified CB demonstrated an increased T_g temperature closer to the PP value at the higher filler loading. Additionally, the increase in the $\tan \delta$ value for all the nanocomposites, compared to PP, also indicates a greater degree of polymer movement with an increased energy dissipation of the system.³⁶ One last point, the broadening of Triton modified CB/PP peaks denotes a wider range of relaxations which could be suggestive of a greater degree of CB-PP interactions.³⁸

The DMA nanocomposites results of this small sample set, suggests that the Triton modification of CB leads to improved interaction with the PP matrix, likely as a result of the reduced surface tension of the CB after the modification.

6.5. Concluding Remarking

In this Chapter, the modification of CB by physisorption of the surfactant Triton X-100 was investigated for application in PP nanocomposites, with the following conclusions:

- The functionalisation protocol of CB by the treatment of Triton X-100 was developed in a number of experiments using surfactant solutions prepared at different concentrations (0.024-0.48 mM), in aqueous and organic media (toluene, chloroform and m-xylene), at different sonication times (1-2 hrs) and two CB/solvent wt. % additions were used (0.15-0.3 %). Accordingly, an optimised CB treatment protocol at 0.024 mM(aq) at 0.3 % CB addition with sonication for 1 hr was used for the functionalisation of CB for PP nanocomposites.
- The CB surface functionalisation by Triton X-100 was confirmed by thermal analysis TGA wt. loss data, indicating the loss of the modification in accordance to the treatment at the range of solution concentrations (0.024-0.48 mM) with evaporation temperatures of 354.2-306.1 °C presenting calculated surface loadings of 1.2×10^{13} - 1.2×10^{14} molecules/cm². This result correlated with the increase oxygen content detected by XPS from 2.5-9.1 %, and is supported by BET and ATR-IR and UV-Vis analysis.
- CB/PP nanocomposites were prepared using CB modified at different Triton X-100 loadings by melting mixing at 10 % wt. loading. Unfortunately, the electrical conductivity was generally lowered following the CB treatment by Triton X-100, with only the CB modified at the lowest Triton X-100 loading, prepared at 0.024 mM, displaying a comparable conductivity to the pristine CB/PP at 1.5×10^{-5} Scm⁻¹.
- Accordingly, a series of the CB/PP nanocomposites were prepared at 5-30 wt. % loading by solvent and melt mixing methods comparing pristine CB and Triton X-100 modified CB. The electrical conductivity percolation curves demonstrated a

lowered percolation threshold for the nanocomposites prepared by melt mixing, compared to solvent mixing, exposing the different control of the CB dispersion and distribution capabilities by the two preparation methods. After Triton X-100 modification, the percolation threshold generally remained unchanged compared to unmodified CB. Nevertheless, it was observed that for the melt-mix prepared nanocomposites, higher levels of conductivity were realised at the higher filler loadings following the modification pre-treatment. Alternatively, the Triton X-100 modified CB/PP samples prepared by solvent mixing achieved the percolation threshold more gradually than the Pristine CB/PP samples, but at high loadings (25 wt. %) similar conductivities were achieved.

- Thermal analysis was performed on all the prepared nanocomposites and TEM, dielectric analysis and DMA measurements were made for selected solvent prepared nanocomposites at higher filler loadings (15-30 wt. %). The major difference was observed in the dielectric analysis, in which the advanced complex permittivity after functionalisation indicated improved connectivity between the CB nanofillers at 30 % loading. Additionally, DMA and STA indicated improved mechanical and thermal properties for the Triton X-100 modified CB/PP samples at the high filler loadings. Overall, these results present evidence that the surfactant modification improves the compatibility between the CB and PP. This could be possibly explained by an improved filler network at higher loadings due to ‘soft agglomeration’ in the PP matrix as a result of CB bridging between hydrophilic polar ‘head’ group present on adjacent modified CB.

To conclude, the preparation of CB modified using Triton X-100 demonstrated effective functionalisation of the nanocarbon. Further, the Triton X-100 modification to CB presented promising macroscopic property improvements to the PP nanocomposites.

6.6. References

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7. Optimised ACB Surfactant Functionalisation for PP Nanocomposites

7.1. Introduction

Functionalisation by the physisorption of Triton X-100 to nanocarbon fillers presents a simple, inexpensive and effective modification approach for improved nanocomposite properties.^{1, 2} Results in the previous Chapter 6 demonstrated that CB modified at low surface loadings of Triton X-100 (1.2×10^{13} molecules/cm² – TGA) present similar electrical conductivity properties to PP nanocomposites prepared with unmodified CB. However, improved thermal, mechanical and promising dielectric permittivity properties at high filler loadings suggested improved CB-PP compatibility as a result of the physisorbed non-ionic surfactant. This is a significant result, as typically nanocomposites reach a critical concentration at which point the intrinsic polymer mechanical properties begin to breakdown, due to the formation of super-agglomerates at higher filler loadings.³ As such, this Chapter presents further optimisation of this surfactant modification in order to determine if this simpler approach, compared to the covalent work presented in Chapters 3-5, could be viable for application in industry.

Two major procedure changes have been made in this section of work. First, the CB, used in Chapter 6 for Triton X-100, has been replaced with ACB, acetylene black, the same nanomaterial used in some of the covalent modification work in Chapter 4. ACB is a subtype of carbon black with a higher structure and crystallinity, prepared by the decomposition of acetylene gas,^{4, 5} presenting an opportunity to test the Triton X-100 functionalisation and ACB/PP nanocomposite fabrication with a higher quality carbon-based nanomaterial. Second, the Triton X-100 modification protocol will be performed in combination with a granulation procedure, typically in use in the manufacture of Carbon Blacks. Wet or dry granulation, without or without water as the binding agent, is used to

convert the high volume of low density, directly produced Carbon Black powder into granules, which can be more easily packed and transported.⁶ Since this granulation process is already in place in the production line of ACB, it presents an excellent opportunity to see if a Triton X-100(aq) solution, instead of water as the binder, can be used in order to produce the modified ACB.

7.1.1. Aims of the Project

This Chapter presents the optimisation of the surface functionalisation of ACB by Triton X-100 combined with a granulation procedure and assessment of the resulting properties of the ACB/PP nanocomposites. The key aims of this work include:

- To successfully translate the lab scale Triton X-100 surface modification of CB used in Chapter 6 to ACB and to further develop it for combination with a granulation procedure.
- To identify the presence and establish the degree of Triton X-100 surface modification on the dried ACB powder and granules prepared by both lab-scale and industry scale procedures.
- To compare the effect of the Triton X-100 surfactant functionalisation, prepared at lab-scale and by the granulation procedure for ACB/PP nanocomposites.

Ultimately, the aim is to determine the viability of this simple nanocarbon modification approach in industry for application in polymer nanocomposites with superior properties.

7.2. Experimental Details

7.2.1. Materials

Acetylene Black (ACB, AB50P) and commercial grade polypropylene (PP, 2440TC polypropylene copolymer with ethylene as the co-monomer, MFI 55 g/10 min) was provided by IRPC Ltd., Thailand. Triton X-100 ($C_{14}H_{22}O(C_2H_4O)_{9-10}$) was purchased from Sigma Aldrich Inc. and solutions for the lab-scale modification protocol were prepared using ultrapure water ($>18\text{ M}\Omega\text{cm}$, Millipore Water systems).

7.2.2. Preparation of Triton X-100 Modified ACB

7.2.2.1. Preparation of Triton X-100 Modified ACB-Lab Scale

The same functionalisation protocol used in Chapter 6 was used to modify the ACB in this work. A Triton X-100 aqueous solution (100 mL) and ACB water dispersion (600 mg, 100 mL) were each sonicated for 10 min. After combining, the ACB/Triton aqueous dispersion (600 mg, 200 mL, 0.024 mM) was sonicated for 1 hr in an ultrasonic bath and left to settle for 24 hrs. The dispersion was filtered using a Whatman™ Glass Vacuum Membrane Filter and the modified ACB dried in an oven at 80 °C overnight.

7.2.2.2. Preparation of Triton X-100 Modified ACB-Industrial Scale (500g)

The functionalisation approach for ACB using Triton X-100 was scaled up from lab production of 600 mg at Oxford to 500 g at IRPC Ltd. where ACB is produced, in combination with a wet granulation method. The protocol for the granulation procedure includes combination of ACB to water at 45:55 w/w %, followed by stirring in a high speed mixer at 1,100 rpm for 10-15 min. After this, the granulated product is dried for 6-10 hrs at a temperature of 150 °C. This protocol was adapted at IRPC for the functionalisation of ACB (500 g) using an aqueous Triton X-100 solution (611.1 g, 0.024 mM) as the binder instead of water. Accordingly, the Triton X-100 modified ACB

granulated sample along with a processed granulated ACB sample – in which only water was used as the binder – were sent to Oxford (Figure 7.1).



Figure 7.1: Processed ACB and Triton X-100 modified ACB by the granulation method at 500g scale.

7.2.3. Characterisation of the Triton X-100 Modified ACB

The pristine, processed (granulated) and Triton X-100 modified ACB nanoparticles prepared at lab-scale (600 mg) and by the adapted granulation procedure (500 g) were analysed by BET, TGA and XPS surface analysis methods, the experimental protocols are detailed in Chapter 2. For reference, the samples are labelled as follows:

- ACB_Pristine (Powder): ACB powder as produced from IRPC;
- ACB_Processed (Granulated): Granulated ACB, without surfactant addition;
- ACB_Triton (Powder): Triton X-100 modified ACB, lab-scale protocol (600 mg);
- ACB_Triton (Granulated): Triton modified ACB, industry-scale (500 g) by the granulation protocol.

7.2.4. Preparation of ACB Based PP Nanocomposites

PP pellets (~0.5 g) were clipped and pristine, granulated processed or Triton-X100 modified ACB at different wt. % of PP (2, 2.5, 3, 3.5, 5 and 7 %), were dry mixed together in a flat bottom test tube (1 min) prior to positioning in the melt mixing apparatus. The sample was then heated and stirred at a sequential temperature program of:

180 °C-15 min, 190 °C-5 min, 200 °C-10 min, after which the sample was stirred at increasing speeds of 50-300 rpm for a further 15 min at 200 °C. After 45 min in the melt mixing equipment the sample was removed and left to cool before clipping to nanocomposites pieces $\sim 1 \times 1 \times 1 \text{ mm}^3$.

The resulting nanocomposite sample was then used to prepare plaque samples ($1 \times 1 \times 0.1 \text{ cm}^3$) for conductivity measurements, as presented in Chapter 5. Nanocomposite films samples (250 μm) were prepared for DMA, by the same procedure as detailed in Chapter 6, the experiments were conducted using a PerkinElmer[®] DMA 8000. The procedures used for the DMA and conductivity analysis are detailed in Chapter 2.

7.3. Results and Discussion

7.3.1.1. Modified ACB Characterisation

The ACB samples, pristine, processed and Triton modified at lab-scale and by granulation were analysed by BET, XPS and TGA to evaluate the success of the surface functionalisation.

BET

BET analysis was conducted in order to evaluate changes to the ACB surface area following surfactant functionalisation. Additionally, it provided a useful method to assess the effect of the granulation process on the ACB properties, a processing step which could also alter the nanocomposite properties. Table 7.1 summarises the BET measurements, while the adsorption and desorption isotherms, as well as the raw data of the repeated measurements are included in the Appendix.

Table 7.1: BET summary data of pristine ACB, granulated pristine ACB and Triton modified ACB powder and granulated samples.

Sample	BET Surface Area (m ² /g)	t-Plot External Surface Area (m ² /g)	t-Plot Micropore Area (Å)	BJH Adsorption Average Pore Diameter (Å)	BJH Desorption Average Pore Diameter (Å)
ACB_Pristine (Powder) ^a	79.8 (0.1) ^b	73.1 (0.3)	6.7 (0.3)	73.1 (0.3)	122.8 (0.9)
ACB_Processed (Granulated) ^a	77.7 (0.3)	72.7 (0.1)	4.9 (0.2)	144.6 (0.6)	142.0 (0.7)
ACB_Triton (Powder)	51.9	47.4	4.6	149.5	160.5
ACB_Triton (Granulated) ^a	44.0 (0.3)	51.7 (0.1)	-	183.4 (7.5)	196.6 (4.5)

^a Average of 3 repeat BET measurements.

^b Standard deviation has been included for repeated measurements in brackets.

Overall, the BET results indicate that functionalisation by the Triton X-100 surfactant results in a reduced surface area of the ACB, as observed for the modified CB samples in Chapter 6. Again, this suggests that the surfactant molecules present on the ACB surface are inhibiting nitrogen adsorption onto the pores. Additionally, following the granulation procedure, processed ACB demonstrated only a small reduction of the surface area of ~2 m²/g compared to pristine ACB powder. Therefore, the greater surface area reduction of the Triton modified ACB by the granulation process presents an early indication of a higher surfactant surface loading.

XPS

The elemental surface concentration of the samples was determined using X-ray photoelectron spectroscopy (XPS) to provide evidence of the successful surfactant functionalisation onto ACB. The main features present in the survey scan for the ACB blank samples and Triton X-100 modified ACB samples were dominant C 1s photoelectron peaks at ~285 eV binding energy and a small O 1s peak at ~532 eV binding energy (Figure 7.2). The survey scan of pristine ACB has not been included here, as it was presented in Chapter 5, however for reference pristine ACB displayed an equivalent surface composition to unmodified ACB after the granulation in water which is presented in Figure 7.2(a).

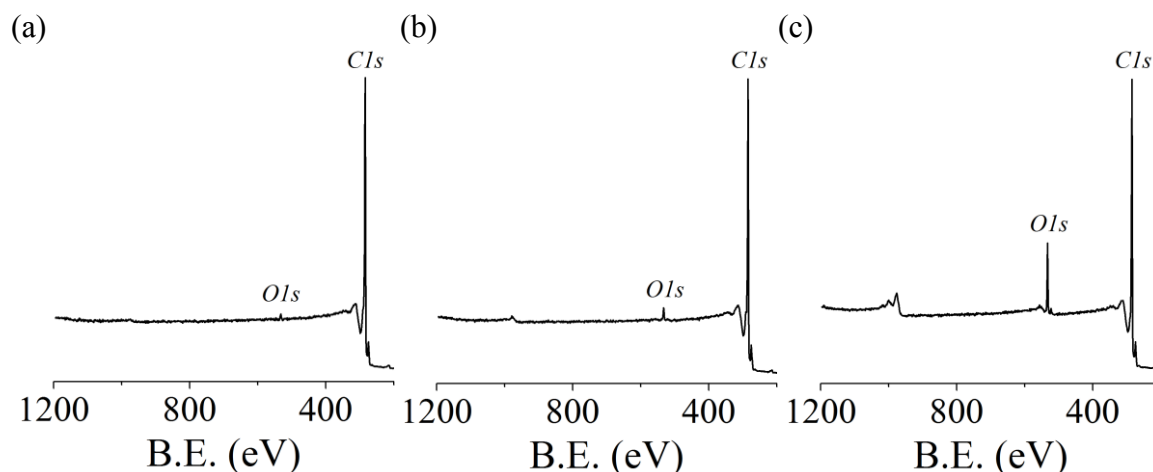


Figure 7.2: XPS survey scans of (a) ACB_Processed (Granulated) (b) ACB_Triton (Powder) and (c) ACB_Triton (Granulated) samples.

High-resolution scans permitted an evaluation of the relative abundance percentages of carbon and oxygen content present on the blank and surfactant modified ACB samples (Table 7.2).

Table 7.2: Chemical percentage of the carbon and oxygen surface composition of pristine and processed ACB and Triton X-100 modified ACB samples, determined by XPS analysis.

Sample	XPS (%)	
	C	O
ACB_Pristine (Powder) ^a	99.5	0.5
ACB_Processed (Granulated)	99.0	1.0
ACB_Triton (Powder)	98.1	1.9
ACB_Triton (Granulated)	92.5	7.5

The increased oxygen content of the modified ACB samples of 1.9 % and 7.5 %, prepared at lab-scale and by the granulation method, respectively, compared to 0.5-1 % for the blank ACB samples, indicates successful surface modification: polyethylene oxide chains of Triton X-100 are now detected on the CB surface. The result is consistent with the XPS analysis performed in Chapter 6. Further, the higher oxygen content of the granulated Triton-modified ACB suggests a higher surfactant surface loading, correlating with the reduced BET surface area for this sample.

Additional details, including the sample binding energies, charging, FWHM values and relative peak areas of the C 1s deconvoluted peaks are included in the Appendix. In summary,

the high resolution spectra of the C 1s region of all the ACB samples were deconvoluted into 6 photoelectron peaks of different chemical environments, as used in the XPS characterisation for all the carbon-based nanoparticles in this thesis. As before, the principal peak was positioned at 284.5 eV (C-C, C-H) and subsequent peaks due to contributions from carbon coordinated to oxygen were at ~286.0 eV (C-O, ± 0.1 eV), ~287.3 eV (C=O, ± 0.1 eV) and ~288.8 eV (COOH, ± 0.2 eV) binding energies. Weak π - π^* features were also observed at ~290.5 eV (π - π^* , ± 0.1 eV) and ~291.9 eV (π - π^* , ± 0.2 eV). Additionally, the relative percentage composition of the C-O contribution peak at ~286.0 eV increased after the addition of Triton X-100 to the ACB surface. For the ACB powder samples, the C-O contribution increased a small amount from 11.0 % to 11.7 %, before and after modification, respectively. For the granulated ACB samples, the difference was more substantial, whereby an increase in the C-O contribution from 12.3 % to 17.2 % was observed before and after modification, respectively. This result is in agreement with the increased surface oxygen detected for these modified samples, and is consistent with the XPS characterisation in Chapter 6.

Thermal Analysis

Thermogravimetric analysis of the ACB samples was used to confirm the Triton X-100 surfactant modification and to determine the degree of surface loading. For both modified ACB samples, powder and granulated, one step weight losses of 1.0 % and 8.2 % were observed in the temperature range of 150-500 °C, respectively, attributed to the evaporation of the physisorbed Triton X-100 (Figure 7.3). The extrapolated onset temperatures indicate a lowered thermal stability for the granulated modified ACB at ~284.7 °C, compared to ~324.1 °C for the lab-scale powder modified ACB. This result is consistent with the greater weight loss detected for this sample. A reduced thermal stability as a function of the Triton X-100 surface loading was observed in Chapter 6.

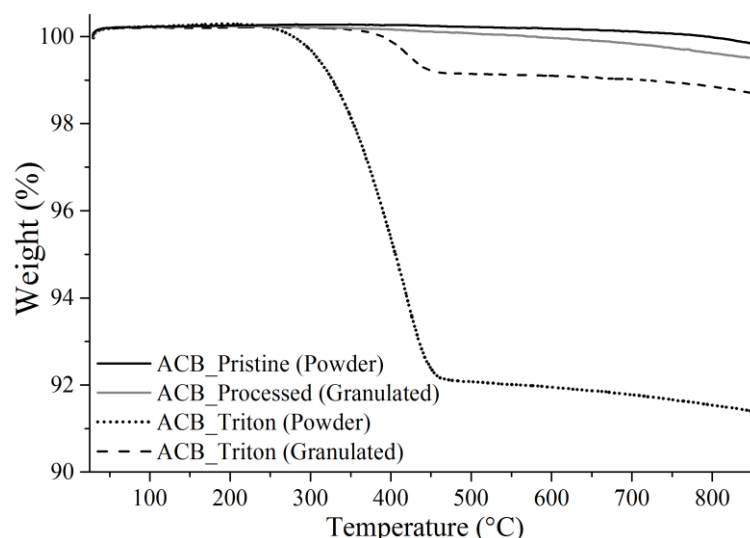


Figure 7.3: Thermogravimetric analysis of pristine ACB, processed ACB by granulation and Triton modified ACB powder and granulated samples, under nitrogen flow.

Table 7.3 displays the weight loss data, as detected by TGA, in the temperature range of the surfactant removal, and the resulting surface loading is estimated at 1.30×10^{13} and 1.07×10^{14} molecules/cm² for the lab-scale modified and granulated ACB, respectively. This result is consistent with the surface loading and Chemicalize⁷ estimates presented in Chapter 6.

Table 7.3: Thermogravimetric analysis weight loss data, calculated surface loading and extrapolated onset decomposition temperature of pristine ACB, processed ACB by granulation and Triton modified ACB powder and granulated samples.

Sample	TGA Weight Loss (%)			Surface Loading ^a		Onset Temp. (°C)
	30-150 °C	150-500 °C	Sample Wt. Loss due to the Mod. (g)	Moles /g	Molecules /cm ²	
ACB_Pristine (Powder) ^a	+0.2	0.1				
ACB_Processed (Granulated)	+0.2	0.2				
ACB_Triton (Powder)	0.1	1.0	1.23×10^{-4}	1.72×10^{-5}	1.30×10^{13}	284.7
ACB_Triton (Granulated)	0.2	8.2	9.94×10^{-5}	1.42×10^{-4}	1.07×10^{14}	324.1

^a The TGA surface loading calculations were the same as used in Chapter 6, in which the measured decomposition temperature range was 150-500 °C.

^b Assumes monolayer surface coverage of the experimentally determined BET surface areas of ACB_Pristine (79.8 m²/g).

7.3.1.2. ACB Characterisation Summary

The BET, XPS and TGA results demonstrate the successful surface functionalisation of the ACB nanoparticles after treatment with Triton X-100 at lab-scale and by granulation

methods. Further, the modified ACB by granulation presents a higher surface loading compared to the lab-scale modified ACB.

7.3.1.3. Nanocomposite Analysis

PP nanocomposites with Triton X-100 modified ACB powder and granules, and processed ACB granules were prepared by melt mixing methods at a range of filler loading 2-7 wt. % in order to produce electrical conductivity percolation curves. Additionally, pristine ACB/PP nanocomposites (2-9 wt. %) were prepared and the volume conductivities determined by Dr Emina Hadzifejzovic, and are included in this section as a comparison unmodified ACB powder. Selected nanocomposite samples analysed by DMA, are also presented in this section of work.

Volume Resistivity - Conductivity Percolation Curve

Figure 7.4 demonstrates the effect of the granulation and the Triton X-100 ACB surface modification upon the electrical volume conductivity of the ACB/PP nanocomposites. The raw data of the conductivity measurements are included in the Appendix.

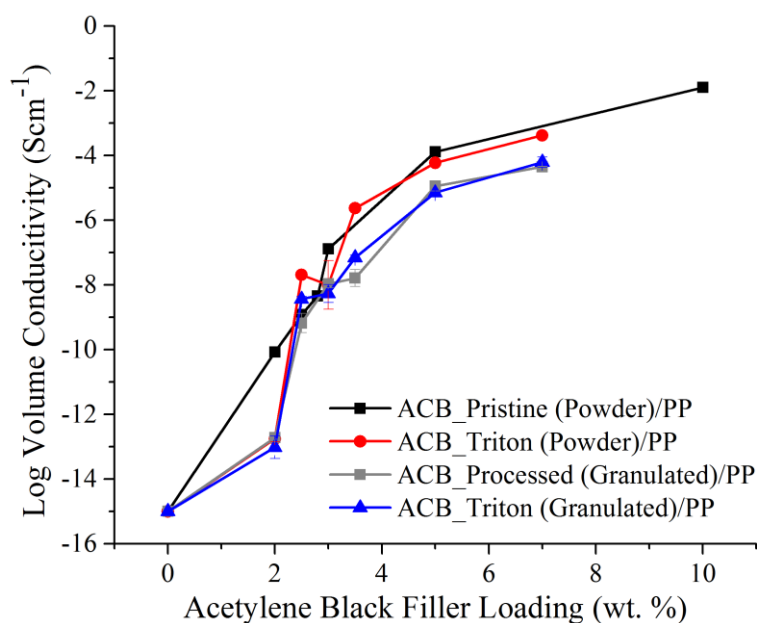


Figure 7.4: Logarithm of the volume conductivity as a function of ACB filler loading of PP nanocomposites prepared with pristine ACB, granulated pristine ACB and Triton modified ACB powder and granulated samples. The percolation curve for ACB_Pristine/PP nanocomposites was prepared by Dr Emina Hadzifejzovic.

The first result is the dramatic reduction of the percolation threshold exhibited for all the ACB/PP composites at ~2.5-5 wt. % compared to the percolation thresholds ~10-20 wt. % for the CB/PP nanocomposites presented in Chapters 5 and 6. This result exposes the impact upon the conductivity results of the different Carbon Black nanoparticles types, CB and ACB, despite their relatively similar BET surface areas of 75.2 m/g² and 79.8 m/g², and surface oxygen content, found at ~3 % and ~1 % by XPS, respectively. Instead, it is more likely that the more efficient high structure type of ACB, compared to low structure CB, directed the major decrease in the percolation threshold for the ACB/PP nanocomposites observed here.⁸⁻¹⁰

Commenting further on the differences between the ACB/PP samples, the percolation curves demonstrate no major shifts of the percolation threshold, and generally similar trends of increasing conductivity with increasing filler loadings. Nonetheless, lowered volume conductivities are evident following the ACB granulation. This is an expected outcome considering the greater challenge of mixing ACB granules compared to fine ACB powder. Additionally, it can be observed that the Triton modification of the ACB granules upon the conductivity results has had no obvious effect. Alternatively, for the powder ACB/PP nanocomposites, an increased conductivity at 2 % loading of $\sim 8 \times 10^{-11}$ Scm⁻¹ for pristine ACB is observed, compared to $\sim 2 \times 10^{-13}$ Scm⁻¹ for the Triton modified ACB/PP nanocomposite. This could be an indication of the Triton X-100 surface modification hindering the conduction by tunnelling processes between the ACB aggregates at this low filler loading, consistent with the CB/PP nanocomposite conductivity results presented in Chapter 6.

Overall, these results are encouraging, as the conductivities of the nanocomposites using blank, granulated and modified ACB are all in the same range of electrical conductivities.

Thermal Analysis: DMA

Dynamic Mechanical Analysis (DMA) was conducted in order to determine if the Triton X-100 modification of this higher quality ACB nanocarbon can improve the mechanical properties of the resulting PP nanocomposites. Therefore, PP nanocomposites, at 3 % and at 5 wt. % filler loadings of pristine and lab-scale Triton modified ACB (powder) were prepared for testing. Figure 7.5 presents the storage modulus (E') as a function of temperature, extracted data is included in Table 7.4.

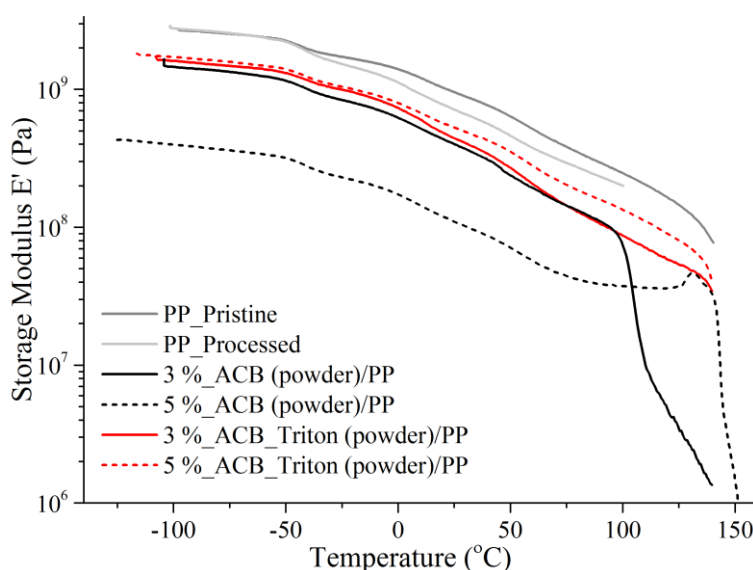


Figure 7.5: Storage modulus (E') (measured at 1 Hz at a heating rate of 5 °C/min) as a function of temperature for PP and pristine and Triton X-100 modified ACB/PP nanocomposites, at 3 and 5 wt. % loadings, prepared by melt mixing methods before pressing into films (0.25 mm).

Table 7.4: Extracted DMA data including α and β relaxation peak data, as determined from the Tan δ curves, and the storage modulus (E') at -70 °C.

Sample	Tan δ				storage E'
	Relaxation γ		Relaxation β		At -70 °C
	(°C)	Height	(°C)	Height	(Pa)
PP_Pristine	-42.4	0.048	10.6	0.063	2.5×10^9
PP_Processed	-41.5	0.058	10.6	0.082	2.5×10^9
3 %_ACB_Pristine/PP	-40.1	0.089	7.7	0.101	1.3×10^9
5 %_ACB_Pristine/PP	-40.0	0.061	10.3	0.080	3.6×10^8
3 %_ACB_Triton (0.024 mM)/PP	-39.3	0.074	11.4	0.110	1.5×10^9
5 %_ACB_Triton (0.024 mM)/PP	-40.0	0.061	8.2	0.074	1.6×10^9

The DMA data displays the expected for result PP, whereby three relaxations at ~ -40 °C (γ), ~ 10 °C (β) and ~ 65 (α) °C and the major transition, T_m , ~ 110 - 150 °C, can be observed, as previously discussed in detail in Chapters 5 and 6. The onset temperatures of the melt transitions cannot provide any significant results due to the variation between the PP control samples. However, the E' values at -70 °C indicate that addition of the ACB nanofiller reduces the storage modulus from that of 2.5×10^9 Pa observed for both pristine and processed PP. Nevertheless, the Triton modification to ACB seems to have reduced the degradation of the storage modulus of the polymer nanocomposites. At 3 % filler loading, with the addition of Triton X-100 modified ACB, the storage modulus was only reduced to 1.5×10^9 Pa, compared to pristine ACB, in which a further decrease to 1.3×10^9 Pa was observed. Then, at the increased filler loading of 5 %, pristine ACB filler displayed the most significant reduction in the storage modulus of 3.6×10^8 Pa whereas for Triton modified ACB/PP, a high storage modulus of 1.6×10^9 Pa was observed. This suggests that the Triton modification facilitates good compatibility between the CB with PP and consequently an improved filler network structure in the PP matrix,¹¹ enabling the polymer storage modulus properties to remain intact, despite the increasing nano-filler content.

Figure 7.6 displays the damping factor ($\tan \delta$), and Table 7.4 the summary data, of the ACB/PP nanocomposite samples.

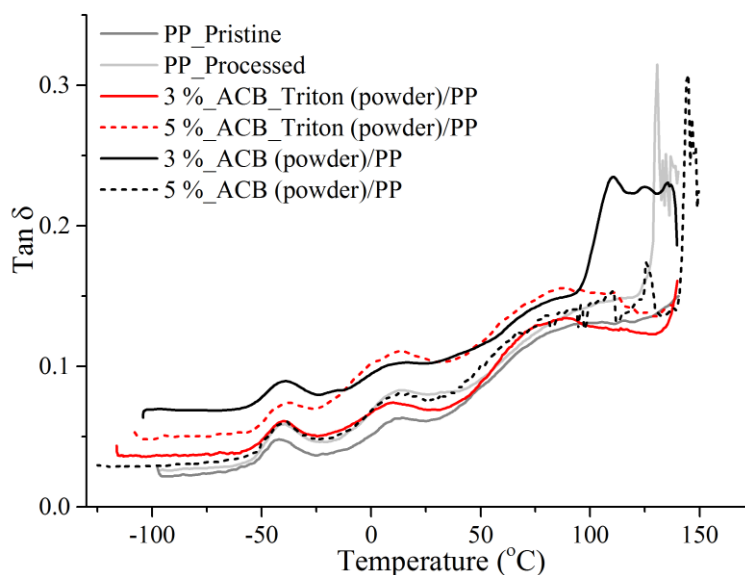


Figure 7.6: Tan δ (measured at 1 Hz and heating rate 5 °C/min) as a function of temperature for PP and pristine and Triton X-100 modified ACB/PP nanocomposite samples, at 3 and 5 wt. % loadings, prepared by melt mixing methods before pressing into films (0.25 mm).

Unfortunately, evaluation of the Tan δ peaks does not indicate any major changes after the ACB filler addition to PP or the Triton X-100 modification. A small increase for all γ relaxations – attributed to the restriction of the short-range motions of chain segments in the amorphous regions¹² – can be observed for all the ACB/PP nanocomposite samples at ~ -40 °C, compared to ~ -42 °C for the PP samples. This indicates a reduced polymer chain mobility as a result of the addition of ACB to PP, as expected.¹³ The value of the β relaxations (glass-rubber transition T_g) demonstrates some changes following the addition of pristine and modified ACB, however there is no clear contribution towards these changes, either as function of ACB loading or the Triton X-100 modification. Generally, an increase in the damping factor upon filler addition compared to PP is also observed for the four samples, in a similar result as presented in Chapter 6. Ultimately, the DMA results of the small selection of ACB/PP samples demonstrate the encouraging results which show that the mechanical properties at higher filler loadings are enhanced by the Triton X-100 modification treatment.

7.4. Concluding Remarks

In this work, a lab-scale and a granulation modification protocol using the Triton X-100 investigated the functionalisation of the higher quality Carbon Black, acetylene black, for application in PP nanocomposites. Accordingly, the following conclusions have been made:

- The CB modification procedure, optimised in Chapter 6, was successfully translated to ACB, both at lab-scale (600 mg) and by granulation (500 g) at IRPC Ltd.. Successful functionalisation by the two protocols was confirmed by lowered surface areas (BET), increased oxygen surface content of 2 % and 8 % (XPS) and the decomposition of the physisorbed modification at 285 °C and 324 °C, presenting surface loadings of 1.3×10^{13} and 1.1×10^{14} molecules/cm² (TGA) at lab-scale and by granulation, respectively. The granulation process therefore demonstrated an increased surface loading compared to the lab-scale modification.
- A series of PP nanocomposites were prepared by melt mixing at low filler additions, 2 -10 wt. %, of blank and surfactant modified ACB, compared to 5-25 wt. % used for CB/PP nanocomposites in previous work, due to the lowered percolation threshold of the high structure ACB nanofiller.
- Comparable electrical conductivity for the modified, granulated and blank ACB/PP nanocomposite samples was observed, with a percolation threshold at ~2.5 - 3.5 wt. %, although a slight reduction in electrical conductivity was demonstrated following the granulation procedure. DMA on powder ACB/PP nanocomposites prepared at 3 % and 5 wt. % loadings demonstrated improved storage moduli with the addition of Triton X-100, supporting the results in Chapter 6, which also suggested improved nanocomposite mechanical properties at high filler loadings following the surfactant modification.

Finally, this work demonstrates a simple and viable Triton X-100 nanofiller modification for industrial scale-up and proposes an opportunity to produce nanocomposites at high filler loadings whilst preserving the original polymer mechanical properties.

7.5. References

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8. Part I and Part II Summary, Conclusions and Outlook

8.1. Summary

This thesis set out to establish the extent to which the mechanical, electrical and thermal macroscopic properties of PP nanocomposites could be improved by simple, tailored covalent and non-covalent nano-scale modifications of various nanofillers. Each project consisted of four main steps towards the production of the polymer nanocomposites:

1. Nanoparticle functionalisation;
2. Characterisation of the nanoparticles;
3. In house preparation methods of the solvent and melt-mixed PP nanocomposites;
4. Evaluation of the resulting nanocomposite properties.

Accordingly, in order to summarise the work in this thesis, the combined accomplishments for each of the different routes (both covalent and non-covalent) are detailed below.

8.1.1. Nanoparticle Functionalisation

Covalent and non-covalent functionalisation methods were used to modify a series of nanofillers in order to tailor their surface chemistries to PP and to inhibit nanofiller agglomeration by incorporation of sterically stabilising groups (Figure 8.1).

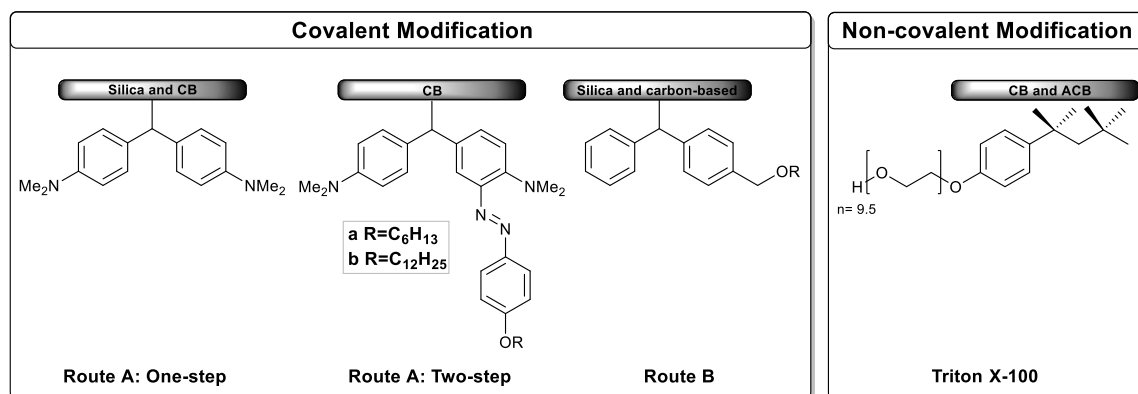


Figure 8.1: Schematic showing the covalent and non-covalent functionalisation routes used for silica and carbon-based nanofillers in this work.

- The first covalent modification procedure, Study A, optimised the published two step method to prepare *bis*(dimethylamino)diaryl diazo from the equivalent benzophenone¹ for the insertion of hydrophobic N-label functionality to CB and silica nanofillers in repeated procedures. Additionally, for one of the pre-modified CB samples, the surface was further manipulated by secondary azo-coupling reactions using selectively prepared diazonium salts tethered in sterically stabilising hexyl and dodecyl hydrocarbon chains.
- In the second covalent investigation, Study B, a more direct one-step modification approach was developed to optimise the introduction of hydrophobic steric stabilising functionality to the nanofiller surface. For this tailored precursor diaryldiazo compounds terminated in hydrocarbon chains of variable length (hexyl or dodecyl) were prepared in a four-stage synthesis procedure. Accordingly, nanosilica, microsilica, CB, ACB and CNT were all modified by the hexyl terminated diaryl complex. CB and nanosilica were also modified by the dodecyl terminated complex. In addition to performed modification reactions, the carbene decomposition reaction was investigated by thermal analysis (TGA-DSC) of the diazo-coated nanofillers. Significantly, the loss of nitrogen upon generation of the carbene species was recorded at a peak rate temperature of 126 °C for both ACB and CB.
- The non-covalent modification approach used the physisorption of Triton X-100 for CB and ACB to insert the sterically stabilising polyethylene oxide chains of the ‘tail’ group to the nanofiller surfaces. The functionalisation protocol for CB was optimised in a number of experiments in which the main investigation, Study B, evaluated the treatment of CB at a range of concentrations (0.024-0.48 mM)(aq). The final Triton X-100 protocol used 0.024 mM(aq) for a 0.3 wt % addition of CB and ACB, prepared

at lab scale (600 mg) and additionally, ACB was modified in combination with a granulation procedure (500 g) at IRPC, where ACB is produced.

8.1.2. Nanofiller Characterisation

Extensive surface analysis using BET, XPS, STA (TGA-DSC), CHN, ATR-IR and SSNMR methods established the success of the covalent and non-covalent nanofiller functionalisation procedures. In particular, a combination of TGA, CHN and UV-Vis results were used to estimate the surface loadings of the various functionalised nanofillers in the range of 10^{12} - 10^{14} molecules/cm². Additionally, SSNMR was used for the first time to analyse the diaryl carbene modification to microsilica and nanosilica.

- In Study A, the N-label functionality of the modification provided direct evidence of the carbene insertion reaction to the silica and CB nanoparticle surfaces, this was confirmed by XPS and supported by the results of CHN analysis. Further, estimated surface loadings at a range of the $\sim 10^{12}$ - 10^{14} molecules/cm² were calculated from TGA and CHN analysis. SSNMR analysis of the nanosilica identified the presence of the modifier by assignment of the benzene ring and the dimethyl amino groups. However, contamination of the nanofillers during the modification procedure was evident in the XPS, thermal analysis and SSNMR analysis, possibly by result of metal chelation to the dimethyl amino groups at the functionalised surface. Additionally, the success of the second step azo-coupling to the CB was immediately apparent due to the two-step weight loss in the TGA thermogram, a result also supported by the increased oxygen content as detected by XPS. Moreover, it was the only sample to display evidence of covalent functionalisation by ATR-IR.
- In Study B, it proved more challenging to establish the presence of the covalent modification due to the absence of the nitrogen label. Nonetheless, TGA analysis demonstrated surface loadings in the range of $\sim 10^{12}$ - 10^{13} molecules/cm² for the

modified nanofillers. Meanwhile, SSNMR analysis demonstrated successful surface modification by the identification of the aromatic rings, ether group and hydrocarbon chains present for all the microsilica and the nanosilica samples. Importantly, the purity of the surface modification of all the nanofillers, especially in comparison with the results in Study A, was evident from XPS and CHN analyses.

- For the non-covalent Triton X-100 functionalisation to CB, the surface loadings were established at $\sim 10^{13}$ - 10^{14} molecules/cm², and varied in accordance to the treatment concentration. Additionally, TGA revealed a reduction in the decomposition temperatures of the Triton X-100 modification (from ~ 354 - 306 °C) as the surfactant surface concentration increased, possibly an indication of altered conformation at the CB surface. Additional surface analysis by XPS identified the altered oxygen content at the surface (~ 3 - 9 %) as a function of loading, supported by reduced BET surface areas, as well as by ATR-IR and UV-Vis analysis for the samples modified with high Triton X-100 surface concentrations. Finally, ACB modified by Triton X-100 at lab scale (600 mg) and by granulation (500 g) also demonstrated successful surface functionalisation, for which granulated ACB demonstrated a higher surface loading. TGA established surface loadings in the range $\sim 10^{13}$ - 10^{14} molecules/cm², XPS analysis demonstrated an increased oxygen surface content (2-8 %) and BET measurement indicated lowered surface areas following the Triton X-100 modification to ACB.

8.1.3. Nanocomposite Fabrication

PP nanocomposites using the functionalised nanofillers and control unmodified samples were prepared by developed solvent and melt-mixing methods and equipment, and further processed into films and plaques for analysis.

- In this work, each step of the nanocomposite preparation was carefully planned and optimised. In some instances, the equipment was specifically designed and produced (melt-mixing and plaque preparations) so that lab scale nanocomposite samples could be prepared.
- Accordingly, PP nanocomposites were prepared by solvent mixing methods using the covalent modified nanofillers prepared in Study B. Microsilica/PP and nanosilica/PP nanocomposites were prepared at a range of loading of 1-10 wt. % and CB/PP nanocomposites at 5-30 wt. % nanofiller loadings.
- For the non-covalent modified nanofillers, PP nanocomposites were prepared by both solvent and meltmixing methods. First, in Study B, PP nanocomposites of CB, modified at different Triton X-100 surface loadings, were prepared at 10 wt. % loading by melt-mixing. Following the selection of CB modified at the lowest Triton X-100 loading (prepared at 0.024 mM), nanocomposites were prepared by both mixing methods at 5-30 wt. % filler loadings. Finally, PP nanocomposites with ACB modified by Triton X-100 at lab scale and by granulation were prepared by meltmixing methods at 2-10 wt. % loadings.

8.1.4. Nanocomposite Characterisation

The prepared PP nanocomposites were analysed by a range of techniques to evaluate the changed macroscopic properties following the various surface functionalisation approaches performed to the different nanomaterial types. Characterisation methods included thermal analysis (TGA, DSC, DMA), DC conductivity, dielectric analysis and morphological analysis (TEM and visual analysis of the nanocomposite thin films.) Unfortunately, the silica nanocomposites demonstrated no significant evidence of changed mechanical or thermal properties following the performed carbene nanofiller modifications. The CB nanocomposites on the other hand demonstrated definitive

macroscopic differences following the nano-scale functionalisations. The dodecyl terminated covalent modified CB demonstrated a lowered electrical percolation threshold and improved CB dispersion in the PP. Alternatively, for the non-covalent Triton modification, no percolation threshold shift was observed, however DMA measurement indicated retained mechanical properties of the nanocomposites prepared at higher filler loadings.

- The silica nanocomposites were predominantly investigated by thermal analysis techniques in order to ascertain whether the sterically stabilising hexyl and dodecyl terminated diaryl complex inserted onto the surface resulted in improved thermal and mechanical properties. Unfortunately, no significant evidence demonstrated any changes to the macroscopic PP properties after modification to either the nanosilica or microsilica. It may be that the developed solvent mixing method was inadequate for Si/PP nanocomposites and therefore the effective evaluation of the surface functionalisation was hindered by the super agglomeration of the silica in the PP. This would explain the unexpected similarity of the microsilica and nanosilica PP nanocomposite results. Otherwise, the analysis methods may not have been sensitive enough, or it may be that the low surface loading or extent of the introduced functionality was inadequate to effectively improve the dispersion in the PP nanocomposites.
- For the nanocomposites prepared using CB, the effect of the covalent and non-covalent functionalisation approaches could be more easily determined, compared to the silica nanocomposites. This is because the DC conductivity and dielectric analysis methods permitted evaluation of the 3D nanofiller structure and its connectivity within the PP matrix. The covalent modified CB/PP nanocomposites demonstrated contrasting results, in which the hexyl terminated diaryl

functionalisation led to a reduction in the conductivity and thermal analysis, while the TEM images indicated greater agglomeration compared to the unmodified CB/PP nanocomposites. Alternatively, the diaryl functionalisation terminated in the dodecyl hydrocarbon chain displayed a substantial improvement to the nanocomposite properties compared to unmodified CB. Enhanced dielectric and electrical properties were observed, in which the electrical percolation threshold was reduced to ~10 wt. % filler addition, almost half the required filler loading to achieve conductivity for unmodified CB/PP nanocomposites. These results correlated with the visibly improved dispersion of CB aggregates and reduced CB agglomerate formation in the prepared thin films (15 μm) and the TEM images. Finally, thermal analysis illustrated increased crystallisation temperatures following the CB modification, indicating an increased number of nucleation sites owing to separated and dispersed CB aggregates present in the nanocomposite. This is an important result for this carbene modified CB/PP nanocomposite - it demonstrates that this functionalisation procedure permits attainment of the important electrical conductivity properties – amongst others – at a lowered nanofiller addition, which is crucial for the preservation of the innate attractive mechanical properties of PP.

- For the non-covalent work, the effect of the CB Triton X-100 modification at different surface loadings was evaluated by DC electrical conductivity, in which the CB modified at the lowest Triton X-100 concentration proved to be the most promising candidate. Next, DC conductivity results at a range of filler loadings demonstrated generally similar electrical percolation thresholds following the Triton X-100 functionalisation compared to unmodified CB prepared PP nanocomposites. In fact, in this work, the more interesting result was presented by the different percolation thresholds according to the processing methods. A lowered percolation

threshold was recorded for the melt mixing method (~10-15 wt. %) compared to the solvent mix prepared nanocomposites (~15-20 wt. %), exposing the dependence of the dispersion and distribution state of the nanofiller upon the processing methods. With regard to the effect of the Triton modification, the dielectric and thermal analysis results nonetheless presented evidence of improved connectivity between the CB aggregates following the Triton X-100 modifications, especially at higher filler loadings. This is possibly as result of the modified CB forming a loss network in the nanocomposite influenced by the modification.

- The ACB nanocomposites presented another dramatic shift in the electrical DC conductivity percolation threshold results, which was reduced to ~2.5-3.5 wt. %. This was because of the higher quality, high structure of the ACB, compared to more commonly manufactured lower quality, low structure furnace CB, which has otherwise been used in this work. Interestingly in these results, it should be noted that the slightly different surface loadings of the Triton modification present on the ACB – prepared at lab scale and by the granulation procedure – demonstrated comparable conductivity results to the equivalent blank samples. The granulation process did however result in a small reduction to the DC conductivity for both the unmodified and Triton modified ACB/PP samples, although it was not a significant reduction as the percolation threshold was not altered. Lastly, DMA analysis of ACB/PP nanocomposites at 3 and 5 wt. % additions suggested the Triton X-100 modification demonstrated retained mechanical nanocomposite properties at the higher nanofiller loading of 5 %, compared to unmodified ACB. This is an important result. Relatively high nanofiller loadings may be required to achieve good electrical conductivity for the Triton modified CB and ACB, comparable to the unmodified samples, however

the DMA results indicate that the Triton modification proposes nanocomposites with retained mechanical properties at these higher nanofiller loadings.

8.2. Conclusions

Ultimately, the high volume of data presented herein demonstrates a range of versatile methods which can be effectively used to manipulate the surfaces of nanofillers of varying properties and sizes. The work in this thesis presents the extension of the carbene modification technology, previously used to modify silica gel^{1, 2} and carbon nanotubes,³ and now successful functionalisation has been established for silica nanoparticles and Carbon Black nanoparticles (furnace Carbon Black (CB) and acetylene black (ACB)). Additionally, modification of the CBs (CB and ACB) by the physisorption of Triton X-100 was extensively studied, and although previously investigated to improve solvent dispersion of carbon-based nanofillers,^{4, 5} this work develops the understanding of the extent of the surface modification to the CBs tested in a series of different parameters. Further, advancements of the surface analysis techniques use to characterise the covalent and non-covalent modified nanofillers, in particular thermal analysis (TGA-DSC) and SSNMR, provided extensive new evidence to demonstrate the success of these functionalisation procedures.

Next, the carbene modification of silica and CB nanofillers was tested for the application in nanocomposites for the first time. Triton X-100 modified nanofillers have previously been used in the production of nanocomposites,^{6, 7} however the modification of the nanofiller by granulation and the use of this functionalisation approach for a CB/PP nanocomposite system has not been previously investigated. Unfortunately, the effects remain inconclusive for the silica nanocomposites. However, after functionalisation of the carbon-based nanofillers, the advancement of the nanocomposite properties was demonstrated by the altered electrical conductivity, mechanical and thermal stability

performance of the resulting materials. Comparing the results of the covalent modification to the non-covalent approach, overall the former demonstrated the more substantial improvement to the nanocomposite properties, by the improved dispersion and the reduced filler loading required for the achievement of good electrical conductivity. Nevertheless, the surfactant approach demonstrates the advantages of a simpler, more industrially viable functionalisation method, with the potential of improved mechanical properties for nanocomposites prepared at high filler loadings – an important prospect in this technology.

8.3. Outlook

It can be considered that the results presented in this thesis offer a proof-of-principle, demonstrating the influence of the different nano-scale functionalisations upon the final properties of the polymer nanocomposites. However, further investigations are required to understand more clearly the effects of each of the surface modifications upon the final nanocomposite properties. In particular, to understand the effect of the hexyl termination compared to the dodecyl termination for the CB/PP nanocomposites prepared by covalent methods. For the non-covalent modification, more extensive analysis is required to understand the effect of the Triton X-100 modification upon the mechanical properties of the CB and ACB/PP nanocomposites. Nonetheless, the influence of the relatively simple modification methods developed in this work has been clearly demonstrated, and reveals the opportunity for further specialisation of nanofiller surfaces in the pursuit of the multifunctional polymer nanocomposites. For example, these same underlying functionalisation routes could be applied to a number of different nanofillers such as inorganic (TiO_2 or MgO) or carbon-based (graphene, nano diamond, nano-onions) nanofillers, amongst others. Another pathway of subsequent research would be to use mixed nanocomposite systems for the production of advanced materials. This has been

used in some studies already. In one study, for example, the combination of CNT and CB nanofillers at lower filler additions demonstrated nanocomposites with excellent electrical conductivity and balanced mechanical properties.⁸ In this content, the versatile carbene and surfactant functionalisation procedures could be used to tailor the surfaces of nanofillers of different innate chemistries, sizes and aspect ratios in order facilitate good synergy between them, as well as for improved compatibility with a chosen polymer matrix, offering another interesting direction in this rapidly advancing interdisciplinary field.

8.4. References

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Appendix 1 - Organic Experimental

1.1. General Procedures and Equipment

Reactions were carried out in oven dried flasks. Anhydrous reactions were conducted in an inert atmosphere, under nitrogen when indicated. Dry THF was obtained by passage through dry alumina column.¹⁸ Water refers to purified de-ionised water by an Elix® UV-10 system. Standard solvents were used as received, analytic or HPLC grade, without prior purification. 'Petrol' refers to petroleum ether with boiling point 40-60 °C. Solvents were evaporated at 40 °C and below at reduced pressure using a Buchi Rotavapor R-210 with a Vacuubrand CVC2 pump and pressure control system.

Sodium hydride used was 60 % dispersion in mineral oil and *N*-Bromosuccinimide (NBS) was recrystallised before use.¹ All other reagents used were sourced from Alfa Aesar Chemicals Ltd., Sigma-Aldrich Chemicals and Lancaster Chemicals Ltd. Microsilica (Si_MP) was purchased as Merck Geduran Si 60 silica gel (0.040-0.063 mm) and nanosilica (Si_NP, 10-20 nm, density 2.2-2.6 g/mL) from Sigma-Aldrich. Commercial Monarch® Carbon Black (CB, M 430, 27 ± 10 nm, density 1.1 - 1.9 g/cm³) was supplied by Cabot Corporation (Billerica, MA, USA) and Acetylene Black (ACB, AB50P) was provided by IRPC Ltd., Thailand. Multi-walled Carbon Nanotube powder (CNT, diameter 80-85 nm, length 10-15 µm) was sourced from the graphene supermarket.

Temperatures below 25 °C were achieved using cooling baths: ice/water for 0 °C, ice/NaCl/water for -5 °C and acetone/CO₂(s) for -78 °C. Thin layer chromatography (TLC) was used to follow reactions and purifications where possible using Merck aluminium foil backed sheets pre-coated with 0.2 mm Kieselgel 60 F₂₅₄ silica gel. Plates were visualised using UV fluorescence (λ_{max} 254 nm) or with staining using a 5 % solution of phosphomolybdic acid in ethanol or aqueous solutions of KMnO₄, followed by heating.²⁰

Flash column chromatography was performed with Merck Geduran Si 60 silica gel (0.040-0.063 mm) on a glass column.

Melting points (mp) were recorded with a Stuart Scientific SMP1 melting point apparatus using open capillaries and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometers as neat samples and characteristic peak reported in wavenumbers (cm^{-1}). NMR spectra were recorded on Bruker DPX200 (200 MHz) and AVN400 (400 MHz) spectrometers. Chemical shifts (δ_{H} , δ_{C}) are reported in parts per million (ppm) and coupling constants, J , are in hertz, Hz. Low resolution mass spectra (m/z) were recorded with a Fisons Platform spectrometer by electrospray ionisation (ESI). Accurate high resolution mass spectra were obtained using a Bruker microTOF; m/z values are reported in Daltons.

1.2. Covalent Modification Protocols

1.2.1. Carbene Precursor Synthetic Methods

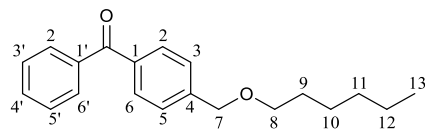
All the reactions were performed in air unless otherwise stated and general procedures indicated where possible.

1.2.1.1. General Method (I): Ether Formation²

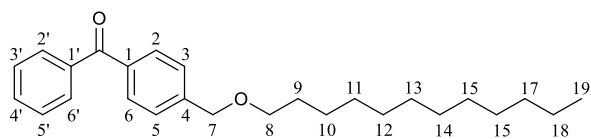
These reactions were performed under nitrogen. A solution of the alcohol (1 eq) in dry THF (15 mL) was added to a stirring solution of NaH in dry THF (15 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was left to stir whilst warming slowly to room temperature. 4-Bromomethylbenzophenone **11** (1 eq) in a solution of dry THF (15 mL) was then added at $0\text{ }^{\circ}\text{C}$. The mixture was left stirring at room temperature until completion of the reaction, as observed by TLC analysis. Excess THF was removed *in vacuo*, the residue redissolved in DCM and the reaction quenched with NaHCO_3 solution (sat.). The organic phase was extracted and then washed with water ($2 \times 15\text{ mL}$). The resultant organic fraction was dried over MgSO_4 , filtered and

concentrated *in vacuo* to give the crude products as oils. Purification of the crude products was conducted via silica column chromatography.

4-(Hexoxyl) methyl benzophenone (**12a**)



4-Bromomethylbenzophenone³ **11** (1 g, 3.6 mmol) and hexanol were reacted together with NaH (0.25 g, 7.3 mmol) under conditions in general method **I**. After stirring at room temperature for 72 hrs, the reaction was worked up to give a yellow oil (1.08 g). Purification *via* silica column chromatography (eluent 310:1 petrol: EtOAc) gave **12a** as a colourless oil (0.60 g, 56 %); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 2929, 2857 (C-H str.), 1657 (C=O), 1609 (Ar C=C), 1447, 1308, 1275 (Ar C-O-C), 1099 (Alkyl C-O-C), 937, 923, 841, 787, 731, 699, 629; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.82 (3H, t, $J=6.9$ Hz, H-13), 1.23 - 1.69 (8H, m, H-12, -11, -10, -9), 3.45 (2H, t, $J=6.6$ Hz, H-8), 4.52 (2H, s, H-7), 7.30 - 7.44 (4H, m, H-3, -5, -3', 5'), 7.48 - 7.55 (1H, m, H-4'), 7.65 - 7.75 (4H, m, H-2, -6, -2', 6'); δ_{C} (101 MHz; CDCl_3 ; Me_4Si) 14.1 (C-13), 22.7 (C-10), 25.9 (C-12), 29.8 (C-9), 31.7 (C-11), 71.0 (C-8), 72.3 (C-7), 127.0 and 127.1 (C-3', -5'), 128.2 and 128.3 (C-3, -5), 130.0, 130.0, 130.1 and 130.3 (C-2, -6, -2', -6'), 132.4 (C-4'), 136.7 (C-1), 137.7 (C-1'), 143.7 (C-4), 196.53 (C=O); m/z (ESI^+) 297 ($[\text{M}+\text{H}]^+$, 75 %), 319 ($[\text{M}+\text{Na}]^+$, 63 %); HRMS (FI) $\text{C}_{20}\text{H}_{24}\text{O}_2^+$ ($[\text{M}]^+$) requires 296.1776, found 296.1772.

4-((Dodecyloxy)methyl)phenyl(phenyl)methanone (12b)

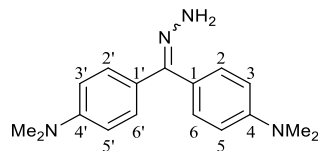
4-Bromomethylbenzophenone **11** (0.56 g, 2.0 mmol) and dodecanol were reacted together with NaH (0.2 g, 8.1 mmol) under conditions in general method **I**. After 24 hrs the reaction was worked up to give a dark yellow oil (0.74 g). Purification *via* silica column chromatography (eluent 100:1 petrol: EtOAc) gave **12b** as a yellow oil (0.39 g, 50 %); ν_{max} (neat)/ cm^{-1} ; 2923 (C-H), 2853 (C-H), 1659 (C=O), 1609 (Ar C=C), 1447, 1308, 1276, 1102 (C-O-C str.), 937, 923, 841, 786, 731, 700, 629; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.80 (3H, t, $J=6.7$ Hz, H-19), 1.19 - 1.32 (16H, m, H-18,-17,-16,-15,-14,-13,-12,-11), 1.52 - 1.62 (4H, m, H-10,-9), 3.44 (2H, t, $J=6.6$ Hz, H-8), 4.51 (2H, s, H-7), 7.36 - 7.44 (4H, m, H-3,-5,-3',5'), 7.48 - 7.57 (1H, m, H-4'), 7.72 - 7.73 (4H, m, H-2,-6,-2',6'); δ_{C} (101 MHz; CDCl_3 ; Me_4Si) 13.1 (C-19), 21.7 (C-18), 25.2 (C-10), 28.3 (C-16), 28.5, 28.6 (C-11,-12,-13,-14-15), 28.8 (C-9), 30.9 (C-17), 70.0 (C-8), 71.25 (C-7), 126.0 and 126.1 (C-3',-5') 127.2 and 127.2 (C-3,-5), 129.0, 129.1 and 129.2 (C-2,-6,-2',-6'), 131.3 (C-4), 135.7 (C-1), 136.7 (C-1'), 142.6 (C-4), 195.4 (C=O); m/z (ESI^+) 381 ($[\text{M}+\text{H}]^+$, 100 %); HRMS (ESI^+) requires 381.2788, 381.2787 found.

1.2.1.2. General Method (II): Synthesis of Hydrazone Compounds²

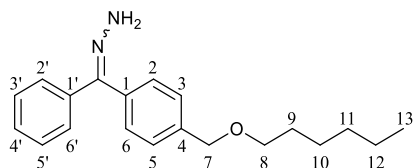
Hydrazine monohydrate was added to a stirring solution of the benzophenone in EtOH (15 mL). The mixture was stirred at reflux, until mass spectrometry showed consumption of the starting materials. The mixture was subsequently cooled to room temperature and following the addition of water (3 mL), ethanol was removed *in vacuo*. The product was redissolved in DCM (10 mL), washed with water (2×10 mL), dried over MgSO_4 , filtered and concentrated *in vacuo* to give the product as an oil. The crude product could not be purified by column chromatography because the hydrazone product is not acid stable. This

product must be stored in the freezer and reacted on as soon as possible, since it is easily prone to decomposition.

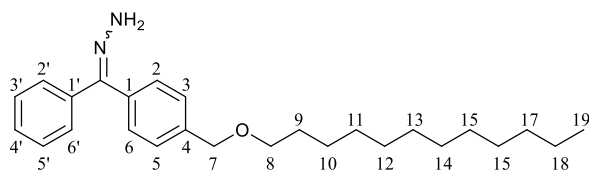
4,4'-Bis-*N,N*-dimethylaminobenzophenone hydrazone **2**⁴



A suspension of Michler's ketone **1** (2.0 g, 7.46 mmol) was treated with hydrazine monohydrate (5.42 mL, 111.86 mmol) under the conditions in general method **II**. After 48 hrs, further hydrazine monohydrate (1.8 mL, 37.29 mmol) was added and the mixture refluxed for a further 24 hrs. The residue was left to cool to allow the product to precipitate out of solution. The solid was collected by filtration, washed with 2-propanol (5 mL) and dried *in vacuo* to yield **2** (1.86 g, 89 %) as a yellow solid; mp 149 °C⁴; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 3226 (N-H br. str.), 2797 (C-H), 1607 (C=N), 1517, 1344, 1124, 1062, 945, 815; δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.87 (2H, s, 2 × NCH₃), 2.94 (2H, s, 2 × NCH₃), 5.18 (2H, s br., NNH₂), 6.56 (2H, d, J =9.0 Hz, H-3',-5'), 6.74 (2H, d, J =8.8 Hz, H-3,-5), 7.10 (2H, d, J =8.8 Hz, H-2,-6), 7.31 (2H, d, J =9.0 Hz, H-2',-6'); δ_{C} (101 MHz; CDCl₃; Me₄Si) 40.4 (2 × NCH₃), 40.5 (2 × NCH₃), 111.8 (C-3,-5), 112.4 (C-3',-5'), 120.6 (C-1,-1'), 127.9 (C-2',6'), 129.9 (C-2,-6'), 150.4 (C-4,-4'), 151.2 (Ar₂C=NNH₂); m/z (ESI⁺) 283 ([M+H]⁺, 100 %).

4-(Hexoxyl) methyl benzophenonehydrazone 13a

Benzophenone **12a** (0.57 g, 1.94 mmol) and hydrazine monohydrate (0.5 mL, 9.71 mmol) were reacted together under the conditions in general method **II**. The mixture was stirred at reflux for 36 hrs giving the product as a yellow oil (0.54 g, 89 %); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3405 (N-H br. str.), 2927, 2856 (C-H), 1454, 1361, 1097 (C-O), 1019 (C-O-C str.), 698; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.81 (3H, m, H-13), 1.15 - 1.37 (4H, m, H-12,-11), 1.43 - 1.69 (4H, m, H-10,-9), 3.32 - 3.50 (2H, m, H-8), 4.40, 4.41 (2H, 2 $\times$ s, H-7), 5.77 (2H, s br., NH_2), 7.17 - 7.32 (5H, m, H-3,-5,-3',-4',-5'), 7.34 - 7.42 (2H, m, H-2',-6'), 7.35 - 7.48 (2H, m, H-2,-6); δ_{C} (101 MHz; CDCl_3 ; Me_4Si) 14.1 (C-13), 22.6 (C-10), 25.9 (C-12), 29.7 (C-9), 31.7 (C-11), 70.6 (C-8), 72.6 (C-7), 126.5 and 126.6 (C-3',-5'), 127.4 and 127.6 (C-3,-5), 127.8 and 128.1 (C-2,-6), 128.5 and 128.5 (C-2',-6'), 128.8 (4'), 128.9 and 129.4 (C-1,1'), 138.1 (C-4), 143.8 ($\text{C}=\text{NNH}_2$); m/z (ESI^+) 311 ($[\text{M}+\text{H}]^+$, 100 %); HRMS (ESI^+) requires 311.2118, 311.2116 found.

-Syn/-anti-(4-((dodecyloxy)methyl)phenyl)(phenyl)methylene)hydrazone 13b

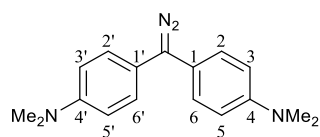
Benzophenone **12b** (0.39 g, 1.02 mmol) and hydrazine monohydrate (0.27 mL, 5.12 mmol) were reacted together under the conditions in general method **II**. The mixture was stirred at reflux for 24 hrs giving the product **13b** as a yellow oil (0.36 g, 88 %); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3403 (N-H br. str.), 2923, 2853 (C-H), 1660 (N-H bend), 1454, 1276, 1100 (C-O-C str.), 698 ; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.81 (3H, m, H-19), 1.13-1.26 (16H, m, H-18,-17,-16,-

15,-14,-13,-12,-11), 1.52- 1.57 (4H, m, H-10,-9), 3.35 - 3.39 (2H, m, H-8), 4.40 (2H, s, H-7), 5.77 (1H, s br., NNH_2), 7.16 - 7.32 (5H, m, H-3,-5,-3',-4',-5'), 7.35 - 7.47 (2H, m, H-2,-6), 7.49 - 7.58 (2H, m, H-2',-6'); δ_{C} (101 MHz; CDCl_3 ; Me_4Si) 14.2 (C-19), 22.7 (C-18), 26.2 (C-10), 29.4, 29.5, 29.6, 29.6 and 29.7 (C-16,-15,-14,-13,-12,-11), 29.8 (C-9), 31.9 (C-17), 70.6 (C-8), 72.6 (C-7), 126.5 and 126.6 (C-3',-5'), 127.6 and 127.8 (C,-2,-6), 128.5 and 128.8 (C-2',6'), 129.3 and 129.4 (C-3,-5), 129.8 (C-4'), 130.0 (C-1), 132.4 (C-1'), 138.1 (C-4), 142.6 (CNNH_2); m/z (ESI^+) 395 ($[\text{M}+\text{H}]^+$, 100%); HRMS (ESI^+) requires 395.3057, found 395.3041.

1.2.1.3. General Method (III): Synthesis of Diazo Compounds²

The hydrazone (1 eq) was dissolved in MeOH (20 mL) and stirred with MnO_2 (2.5 eq), KOH (1.1 eq) and Na_2SO_4 (1.4 eq), until mass spectrometry showed consumption of the hydrazone starting material, which normally requires 4-6 hrs or can be left overnight if necessary. After MeOH removal *in vacuo*, the residue was dissolved in DCM and filtered through a celite plug. The filtrate was washed with water (15 mL), dried over MgSO_4 and concentrated *in vacuo* to yield the diazo product. The crude product could not be purified by column chromatography because it is light sensitive and not acid stable, and required storage at sub-ambient temperature to avoid decomposition.

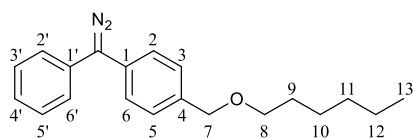
Bis-4,4'-N,N-Dimethylaniline diazomethane **3**⁴



Hydrazone **2** (1.77 g, 6.27 mmol) in EtOH (10 mL) was added to a vigorously stirring mixture of yellow HgO (1.58 g, 7.27 mmol), Na_2SO_4 (1.16 g, 8.15 mmol) and KOH in EtOH (3 mL). The mixture was stirred for 18 hrs in the dark, then filtered through a pad of celite. The filtrate was collected and concentrated *in vacuo* to yield **3** (1.74 g, 99 %) as a

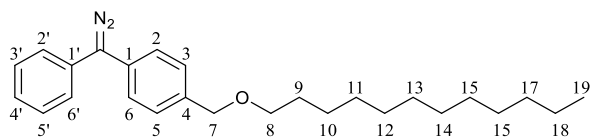
dark green oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2886, 2018 (C=N₂), 1600 (C=N), 1516, 1354, 1061, 945, 814, 769; δ_{H} (400 MHz; CDCl₃; Me₄Si) 2.84 (12H, s, 4 × NCH₃), 6.62 (4H, d, $J=8.9$ Hz, H-3,-3',-5,-5'), 7.12 (4H, d, $J=8.7$, H-2,-2',-6,-6'); δ_{C} (101 MHz; CDCl₃; Me₄Si) 40.8 (4 × NCH₃), 112.5 (C-2,-2',-6,-6'), 127.9 (C-3,-3',-5,-5'), 131.3 (C-1,-1') 155.8 (C-4,-4') ; m/z No MS result showing the diazo peak could be obtained since it is highly unstable to ionization and decomposed. The loss of the hydrazone peak (283 [M+H]⁺) can be reported.

1-(Diazo(phenyl)methyl)-4-((hexyloxy)methyl)benzene 14a



Hydrazone **13a** (0.54 g, 1.74 mmol) was reacted under the condition of general method **III** to yield a dark pink oil (0.52 g, 98 %); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2927, 2856 (C-H), 2037 (C=N₂), 1596, 1511, 1494, 1451, 1361, 1276 (C-O), 1097 (C-O-C str.), 1018, 933, 812, 751, 696; δ_{H} (400 MHz; CDCl₃; Me₄Si) 0.79 - 0.82 (3H, m, H-13), 1.21 - 1.59 (8H, m, H-12,-11,-10,-9), 3.36 - 3.39 (2H, m, H-8), 4.40 (2H, s, H-7), 7.18 - 7.43 (9H, m, H-3,-5,-2,-6,-6',-2',5',4',3'); δ_{C} (101 MHz; CDCl₃; Me₄Si) 14.1 (C-13), 22.6 (C-12), 25.9 (C-10), 29.7 (C-9), 31.7 (C-11), 70.6 (C-9), 72.6 (C-8), 125.2 (C-1), 126.5 (C-1'), 127.1, 127.6, 127.8, 128.3, 128.5, 128.6 and 129.1 (C-2,-6,-2',-3',-4',-5'), 130.0 (C-3,-5), 143.1 (C-4) ; m/z No MS result showing the diazo peak could be obtained since it is highly unstable to ionization and decomposed. The loss of the hydrazone peak (311 [M+H]⁺) can be reported.

1-((Diazo(phenyl)methyl)-4-((dodecyloxy)methyl)benzene 14b



Hydrazone **13b** (0.34 g, 0.89 mmol) was reacted under the conditions in general method **III** to yield a dark pink oil (0.31 g, 93 %) ; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2923, 2853 (C-H), 2039 (C=N₂),

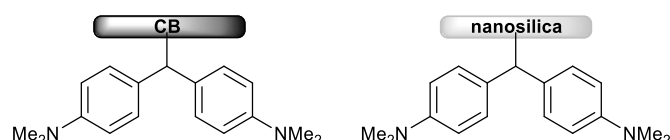
1660, 1454, 1361, 1277 (C-O), 1110 (C-O-C str.), 1019, 698 ; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.80 (3H, t, $J=6.9$ Hz, H-19), 1.18 - 1.33 (16H, m, H-18,-17,-16,-15,-14,-13,-12,-11), 1.46 - 1.61 (4H, m, H-10,-9), 3.35 - 3.56 (2H, m, H-8), 4.40 (2H, s, H-7), 7.17 - 7.33 (6H, m, H-2,-3,-5,-6,-2',-6'), 7.35 - 7.57 (3H, m, H-3',-4',-5'); δ_{C} (101 MHz; CDCl_3 ; Me_4Si) 14.1 (C-19), 22.7 (C-18), 26.2 (C-10), 29.4 (C-16) 29.5, 29.6, 29.7, 29.7 (C-15,-14,-13,-12,-11), 29.8 (C-9), 31.9 (C-17), 70.6 (C-8), 72.6 (C-7), 125.1 (C-1), 125.2 (C-1'), 126.5, 126.6, 127.6, 127.8, 128.3, 128.5, 129.1 (C-2,-6,-2,-3',-4',-5',-6'), 130.0 and 130.3 (C-3,-5), 138.1 (C-4); m/z No MS result showing the diazo peak could be obtained since it is highly unstable to ionization and decomposed. The loss of the hydrazone peak ($395 [\text{M}+\text{H}]^+$) can be reported.

1.2.2. Carbene Functionalisation of Nanofillers

1.2.2.1. General Method (IV): Carbene Modification of Nanoparticles

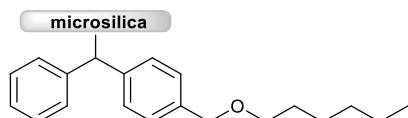
The diazo compound was dissolved in Et_2O (15 mL) and the required nanoparticle substrate added. Following, the dispersion was sonicated for 30 min to improve particle dispersion and assist full surface coverage of the diazo onto the nanoparticles. The solvent was removed *in vacuo*, to afford the nanoparticle with a surface coating of the diazo compound. The flask was heated in an oil bath at 120°C for 30-40 min. For microsilica and nanosilica, the colour change of the pink diazo surface coating to off white was observed during the heating step. When cool, the modified nanoparticles were washed thoroughly with acetone (500 mL) and dried for 1 hr *in vacuo*.

Modification of nanosilica (Si_4) and CB (CB_5)



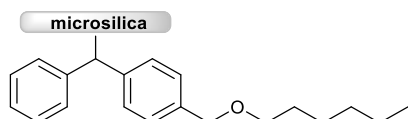
Diazomethane **3** was reacted with nanosilica (at 16 % w/w) and CB (at 66 % w/w) under the conditions in general method **IV** in repeated procedures to give variants modified **Si_4** and **CB_5**, as detailed in Chapter 3.

Modification of microsilica (Si_MP_15a_5)



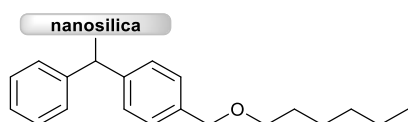
Diazo **14a** (0.25 g, 0.81 mmol) was reacted with microsilica (5.04 g, 5 % w/w) under the conditions of general method **IV**, to afford functionalised **Si_MP_15a_5**.

Modification of microsilica (Si_MP_15a_20)

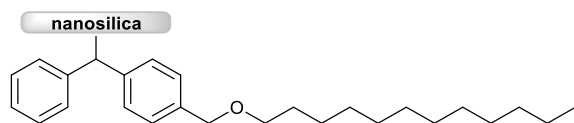


Diazo **14a** (0.14 g, 0.46 mmol) was reacted with microsilica (0.69 g, 20 % w/w) under the conditions of general method **IV**, to give modified **Si_MP_15a_20**.

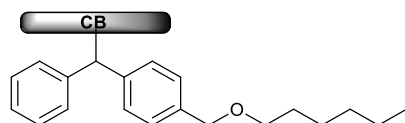
Modification of nanosilica (Si_NP_15a)



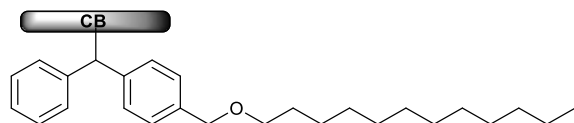
Diazo **14a** (0.52 g, 1.39 mmol) was reacted with nanosilica (0.33 g, 16 % w/w) under the conditions of general method **IV**, to give modified **Si_NP_15a**.

Modification of nanosilica (Si_NP_15b)

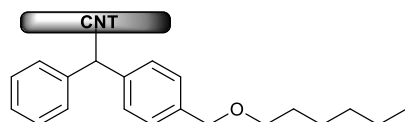
Diazo **14b** (0.12 g, 0.31 mmol) was reacted with nanosilica (0.76 g, 16 % w/w) under the conditions in general method **IV**, to give modified **Si_NP_15b**.

Modification of CB (CB_15a)

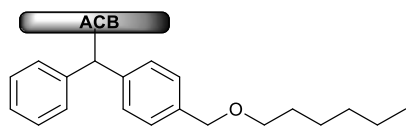
Diazo **14a** (0.59 g, 1.92 mmol) was reacted with CB (0.9 g, 66 % wt.) under the conditions of general method **IV** to afford modified **CB_15a**.

Modification of CB (CB_15b)

Diazo **14b** (0.31 g, 0.80 mmol) was reacted with CB (0.44 g, 66 % wt.) under the conditions in general method **IV** to afford modified **CB_15b**.

Modification of CNT (CNT_15b)

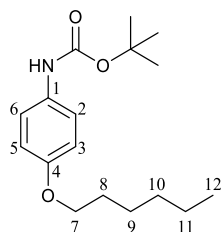
Diazo **14a** (0.01 g, 0.03 mmol) was reacted with CNT (0.2 g, 5 % w/w) under the conditions of general method **IV** (except the sonication step was shortened to 10 minutes) to give functionalised **CNT_15b**.

Modification of silica ACB (ACB_15b)

Diazo **14a** (0.03 g, 0.10 mmol) was reacted with ACB (0.3 g, 10 % w/w) under the conditions of general method **IV**, to afford modified **ACB_15b**.

1.2.3. Synthesis of Diazonium Salts for the Second-Step Coupling Reaction to Modified CB_5.5*1.2.3.1. General Method (V): Carbamate Formation*

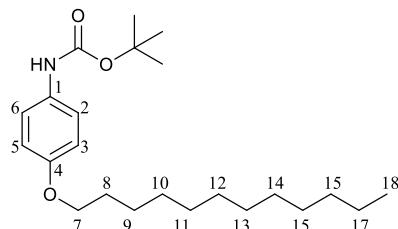
Carbamate **6** (1 eq), the required alkyl halide (1 eq) and K_2CO_3 (2 eq) were added to acetonitrile (15 mL) and the mixture stirred at reflux. After cooling, the solvent was removed *in vacuo*, redissolved in DCM, washed with water (2×10 mL), dried over $MgSO_4$ and the filtrate concentrated *in vacuo*.

***tert*-Butyl -(4-(hexyloxy)phenyl)carbamate (7a)**

Carbamate **6** (0.32 g, 1.15 mmol), 1-bromo hexane and K_2CO_3 were reacted for 21 hrs under the condition in general method **V** affording a light brown solid (0.3 g, 73 %). Purification *via* flash column chromatography (eluent 35:1 petrol:EtOAc) furnished the product **7a** as a white solid (0.25 g, 57 %); mp 108 °C; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3365 (N-H br. str.), 2938, 2869 (C-H), 1695 (C=O), 1515, 1228, 1159 (C-O-C str.), 1055, 1025, 825, 621; δ_H (400 MHz; $CDCl_3$; Me_4Si) 0.81 - 0.85 (3H, m, H-12), 1.24 - 1.27 (4H, m, H-10,-11), 1.35 - 1.39 (2H, m, H-9), 1.44 (9H, s, $C(CH_3)_3$), 1.65 - 1.72 (2H, m, H-8), 3.84 (2H, t, $J=6.6$ Hz, H-7), 6.25 (2H, s br., NH), 6.75 - 6.77 (2H, m, H-3,-5), 7.16 - 7.19 (2H, m, H-2,-6); δ_C (126 MHz; $CDCl_3$; Me_4Si) 14.1 (C-12), 22.6 (C-11), 25.7 (C-9), 28.4 ($C(CH_3)_3$), 29.3 (C-

8), 31.6 (C-10), 68.4 (C-7), 80.2 ($\underline{\text{C}}(\text{CH}_3)_3$), 114.9 (C-3,-5), 120.6 (C-2,-6), 131.2 (C-1), 153.2 ($\underline{\text{C}}=\text{O}$), 155.3 (C-4); m/z (ESI^+) 316 ($[\text{M}+\text{Na}]^+$, 100%). HRMS (ESI^+) requires 316.1883, found 316.1883.

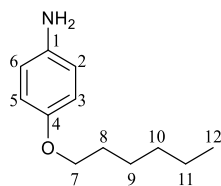
***tert*-Butyl (4-(dodecyloxy)phenyl)carbamate (**7b**)**



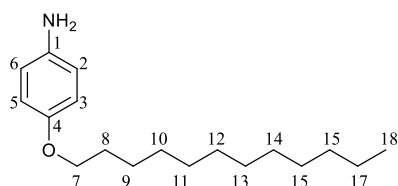
Carbamate **6** (0.21 g, 1.00 mmol), 1-bromododecane and K_2CO_3 were reacted for 24 hrs under the condition in general method **V** affording crude **7b** as a white and brown solid (0.39 g, 104 %). Purification *via* flash column chromatography (75:1 petrol:EtOAc) yielded the product as a white solid (0.26 g, 68 %); mp 96 °C; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ ~3400 (br. N-H), 2918, 2850 (C-H), 1698 (C=O), 1519, 1228, 1116 (C-O-C str.), 1057, 1020, 837; δ_{H} (500 MHz; CDCl_3 ; Me_4Si) 0.80 - 0.82 (3H, H-18), 1.19 - 1.31 (16H, m, H-17,-16,-15,-14,-13,-12,-11,-10), 1.33 - 1.39 (2H, m, H-9), 1.44 (9H, s, $\text{C}(\underline{\text{CH}}_3)_3$), 1.65 - 1.69 (2H, m, H-8), 3.84 (2H, t, $J=6.6$ Hz, H-7), 6.29 (1H, br. s, $\underline{\text{NH}}$), 6.75 - 6.76 (2H, m, H-3,-5), 7.16 - 7.18 (2H, m, H-2,-6); δ_{C} (126 MHz; CDCl_3 ; Me_4Si) 14.2 (C-18), 22.7 (C-17), 26.1 (C-9), 28.4 ($\text{C}(\underline{\text{CH}}_3)_3$), 29.6 and 29.7 (C-15,-14,-13,-12,-11,-10,-8), 32.0 (C-16), 68.4 (C-7), 80.3 ($\underline{\text{C}}(\text{CH}_3)_3$), 114.9 (C-3,-5), 120.6 (C-2,-6), 131.2 (C-1), 153.3 ($\underline{\text{C}}=\text{O}$), 155.3 (C-4); m/z (ESI^+) 400 ($[\text{M}+\text{Na}]^+$, 100%). HRMS (ESI^+) requires 400.2822, found 400.2833.

1.2.3.2. General Method (VI): BOC Group Removal⁵

The required *tert*-Butyl carbamate **7** in a mixture of 6:1 DCM:TFA (7 mL) was stirred at room temperature for 4 hrs. The reaction was quenched with 5 % aq. NaOH solution and the organic phase extracted. The aqueous layer was washed with DCM (2×10 mL) and the combined organic phases dried over MgSO_4 , filtered and concentrated *in vacuo*.

4-(Hexyloxy)aniline (8a)

7a (0.25 g, 3.51 mmol) was reacted under the conditions in method **VI** to yield crude **8a** (0.15 g, 23 %). Purification *via* flash column chromatography (30:1 petrol:EtOAc) furnished the product **8a** as a brown solid (0.14 g, 85 %); mp 33 °C; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 3399 (N-H), 2933, 2852(C-H), 1507, 1388 (Ar C-N), 1229, 1177 (C-O-C str.), 824; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.81 - 0.84 (3H, m, H-12), 1.23 - 1.40 (6H, m, H-11,-10,-9), 1.63 - 1.70 (2H, m, H-8), 3.80 (2H, t, $J=6.7$ Hz, H-7), 5.23 (2H, br. s, NH_2), 6.55 - 6.59 (2H, m, H-3,-5), 6.65 - 6.69 (2H, m, H-2,-6); δ_{C} (101 MHz; CDCl_3 ; Me_4Si) 14.1 (C-12), 22.6 (C-11), 25.8 (C-9), 29.4 (C-8), 31.6 (C-10), 68.7 (C-7), 115.7 and 116.4 (C-5,-3,-2,-6), 139.8 (C-1), 152.4 (C-4); m/z (ESI^+) 194 ($[\text{M}+\text{H}]^+$, 100 %); HRMS (ESI^+) requires 194.1534 , found 194.1539.

4-(Dodecyloxy)aniline (8b)

7b (0.26 g, 0.68 mmol) was reacted under the conditions in method **VI** to yield **8b** (0.19 g, 99 %) as a light brown solid; mp 41 °C; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ ~3400 (N-H br. str.), 2918, 2850 (C-H), 1719 (Ar C=C), 1513, 1394 (Ar C-N), 1233, 1207 (C-O-C str.), 828, 721; δ_{H} (400 MHz; CDCl_3 ; Me_4Si) 0.79 - 0.83 (3H, m, H-17), 1.19 - 1.39 (16H, m, H-16,-15,-14,-13,-12,-11,-10), 1.62 - 1.71 (2H, m, H-8), 3.81 (2H, t, $J=6.60$ Hz, H-7), 4.13 (2H, br. s, NH_2), 6.61 - 6.71 (4H, m, H-2,-3,-5,-6); δ_{C} (101 MHz; CDCl_3 ; Me_4Si) 14.1 (C-17), 22.7 (C-16), 26.1 (C-9), 29.4 and 29.6 (C-15,-14,-13,-12,-11,-10,-8), 31.9 (C-16), 68.7 (C-7), 115.7 and

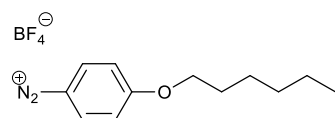
117.5 (C-2,-3,-5,-6), 137.4 (C-1), 153.3 (C-4); m/z (ESI⁺) 278 ([M+H]⁺, 100 %); HRMS (ESI⁺) requires 278.2478, found 278.2490.

1.2.4. Diazonium Coupling Reaction of the Carbene Modified Carbon Black

1.2.4.1. General Method (VII): Diazonium Salt Formation^{2, 6}

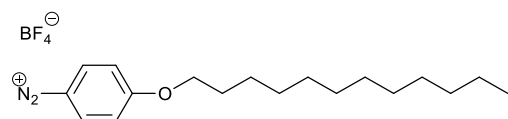
A stirring solution of the required amine **8** (1 eq) in EtOH (15 mL) was cooled to -5 °C and treated with isoamylnitrite (1 eq) and tetrafluoroboric acid (2 eq). The mixture was stirred for 1 hr, until the colour satisfied a constant level of intensity and the H-acid test was conducted: (1 mL) was removed from the reaction mixture and adjusted to pH 4 using sodium acetate. H-acid (4-amino-5-hydroxy-2,7-naphthalene disulfonic acid, 1 mg) was added and the suspension thoroughly mixed. After 15-30 minutes, a positive result is indicated by suspension turning from light brown to dark pink/purple. This confirmed the presence of the diazonium functionality in the reaction mixture, which was subsequently used immediately to react with **CB 5.5**.

4-(Hexyloxy)benzenediazonium (9a)



Amine **8a** (0.09 g, 0.48 mmol) reacted under the conditions in general method **VII** to give the diazonium salt **9a** as a dark brown solution which was used to treat **CB 5.5** immediately.

4-(Bodecyloxy)benzenediazonium (9a)



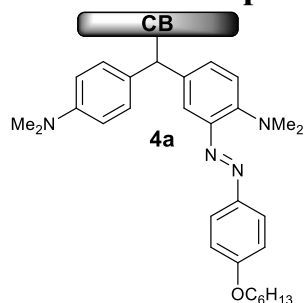
Amine **8b** (0.19 g, 0.67 mmol) reacted under the conditions in general method **VII** to give the diazonium salt as a light brown solution which was used to treat **CB 5.5** immediately.

1.2.5. Diazonium Coupling Reaction of Carbene Modified Carbon Black

General Method (VIII): Coupling of Diazonium Salt to Pre-Modified CB_5.5

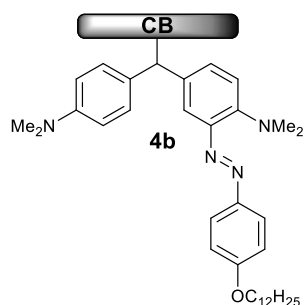
CB_5.5 (1 eq) was submerged in the desired diazonium salt solution **9** (2 eq). The mixture was covered and left to stand at 5 °C for 18 hrs. The modified CB was washed thoroughly with acetone (500 mL) on filter paper in a funnel until washings were colorless, and dried for 1 hr *in vacuo*.

Diazonium coupling of CB_5.5 with 9a (CB_10a)



CB_5.5 (0.10 g, 0.24 mmol of functionalised surface) was reacted with **9a** under the conditions in method VIII to give modified **CB_10a**.

Diazonium coupling of CB_5.5 with 9b (CB_10b)



CB_5.5 (0.10 g, 0.24 mmol of functionalised surface) was reacted with **9b** under the conditions in method VIII to give modified CB **CB_10b**.

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Appendix II - Chapter 3

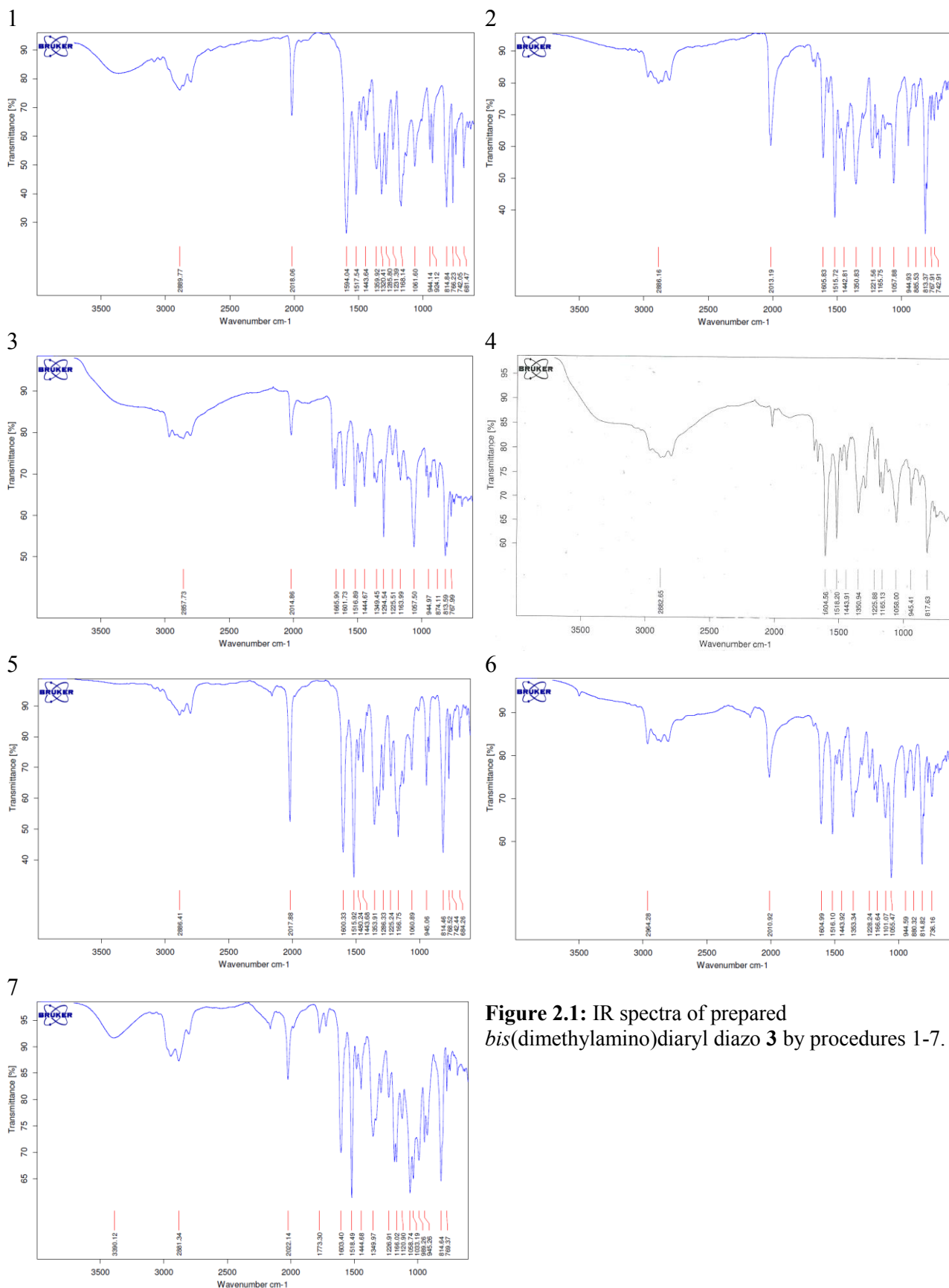


Figure 2.1: IR spectra of prepared *bis*(dimethylamino)diaryl diazo **3** by procedures 1-7.

Silica Nanoparticle Characterisation

BET

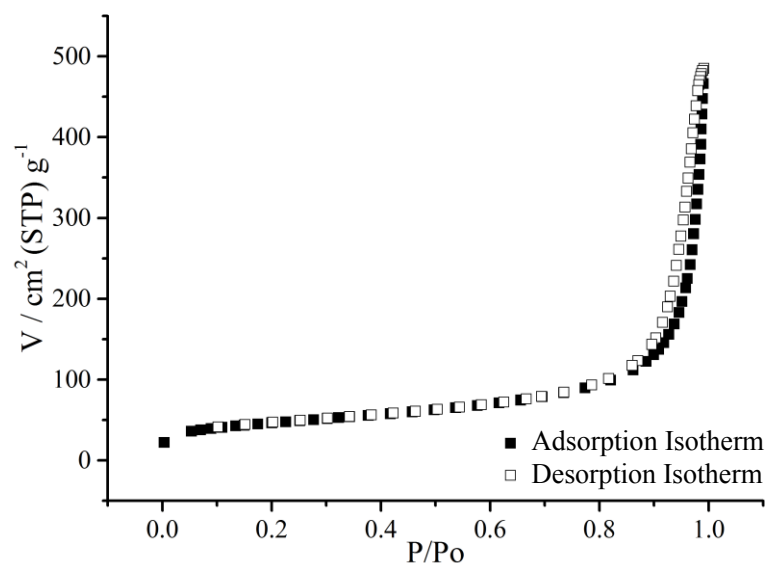


Figure 2.2: A graph showing the BET adsorption and desorption isotherms of nitrogen gas by Si_Pristine.

XPS

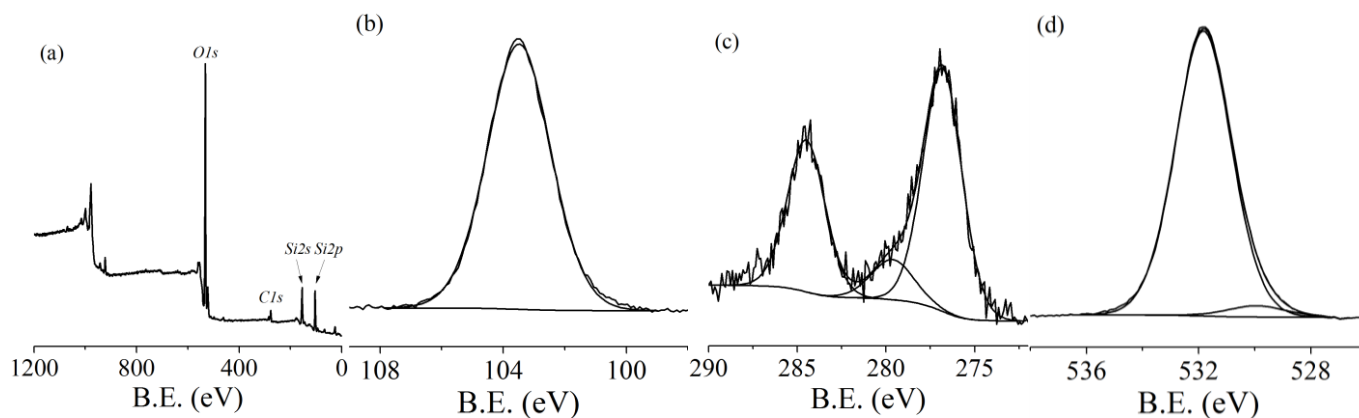


Figure 2.3: XPS spectra of processed nanosilica displaying (a) the wide scan spectrum and the high resolution scans of (b) Si 2p (c) C 1s and (d) O 1s regions.

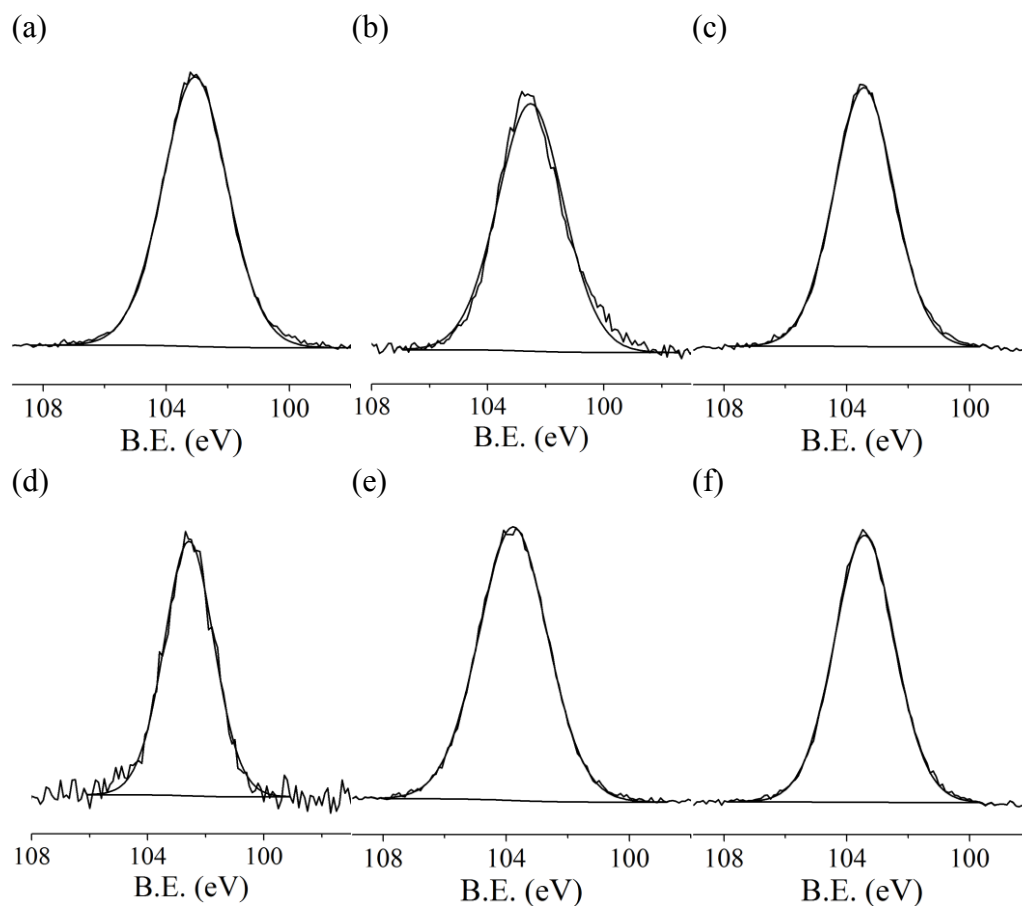


Figure 2.4: XPS high resolution spectra of the Si 2p region of modified silica nanoparticles (a) Si_4.1 (b) Si_4.2 (c) Si_4.3 (d) Si_4.6; (e) Si_4.7a and (f) Si_4.7b.

Table 2.1: XPS Si 1s, C 1s, O 1s and N 1s binding energies and charging values for nanosilica.

Sample	Binding Energies (eV)							Charging (eV)		
	Si 2p		C 1s				O 1s		N 1s	Relative to C 1s (284.5)
	SiO ₂	C-C C-H	C-N C-O	C=O	COOH	Si-C	C=O	Si-O-Si Si-OH	NMe ₂	
Si_Pristine	103.6	284.5					528.8	531.8		18.0
Si_Processed	103.5	284.5					529.9	531.8		15.4
Si_4.1	103.1	284.5	286.1	287.9			529.8	532.1	399.5	14.9
Si_4.2	102.5	284.5	285.9	287.7		281.4	530.1	532.0	399.5	9.6
Si_4.3	103.4	284.5	286.1	287.5			530.3	532.5	399.8	14.2
Si_4.6	102.6	284.5	285.7	287.3	288.7		530.1	531.4	398.9	11.0
Si_4.7a	103.8	284.5	286.1	287.7	289.1		528.9	532.0	399.4	15.6
Si_4.7b	103.4	284.5	286.2	287.4	288.9		529.8	531.8	399.0	14.5

Figure 2.5: XPS FWHM values for unmodified and modified silica nanoparticles.

Sample	FWHM (eV)							
	Si 2p	C 1s					O 1s	N 1s
	SiO ₂	C-C C-H	C-N C-O	C=O	COOH	Si-C	C=O	Si-O-Si Si-OH
Si_Pristine	2.4	2.6					2.4	2.4
Si_Processed	2.4	2.5					2.5	2.4
Si_4.1	2.5	2.7	2.6	2.7			2.4	2.4
Si_4.2	2.7	2.4	2.4	2.6		2.6	2.3	2.2
Si_4.3	2.3	2.6	2.6	2.5			2.0	2.3
Si_4.6	2.0	2.1	2.0	1.9	2.0		2.2	2.2
Si_4.7a	2.6	2.0	1.8	1.7	1.8		2.8	2.7
Si_4.7b	2.3	2.1	1.9	1.8	2.2		2.2	2.2

Thermal Analysis (STA)

Table 2.2: TGA weight loss raw data of pristine and modified silica nanoparticles.

Sample	Initial sample weight (mg)	TGA weight loss					
		30-200 °C		200-500 °C		500-800 °C	
		mg	%	mg	%	mg	%
Pristine Silica	8.286	0.351	4.359	0.195	2.391	0.198	2.391
	8.064	0.396	4.916	0.217	2.688	0.236	2.925
	12.491	0.479	3.837	0.179	1.43	0.143	1.145
Processed Silica	12.443	0.584	4.691	0.298	2.391	0.253	2.032
	12.165	0.549	4.515	0.282	2.314	0.255	2.093
	12.12	0.525	4.33	0.296	2.44	0.247	2.04
Si_4.1	11.049	0.436	3.949	0.408	3.696	0.256	2.319
	12.106	0.462	3.816	0.54	4.461	0.355	2.933
Si_4.2	7.201	0.665	9.233	0.434	6.034	0.046	0.643
	9.962	0.806	8.091	0.597	5.99	1.467 ^a	0.663 ^a
Si_4.3	12.637	0.486	3.845	0.356	2.815	0.267	2.110
	10.627	0.478	4.498	0.218	2.048	0.089	0.836
Si_4.6	13.718	2.504	18.253	1.197	8.724	0.507	3.694
	11.922	1.571	13.175	1.022	8.573	0.330	2.769
Si_4.7a	12.396	0.516	4.160	0.422	3.404	0.324	2.614
	12.315	0.58	4.707	0.332	2.694	0.239	1.938
Si_4.7b	13.590	1.937	14.256	0.970	7.141	0.135	0.992
	12.100	1.550	12.809	0.864	7.138	0.301	2.491

^a The sample was tested by a different STA Program, with the heating scan set 30-700 °C at a rate of 20 °C /min. The weight loss noted here is therefore in the temperature range 500-693 °C

Table 2.3: Surface modification loadings of modified silica nanoparticles, as calculated from the determined mass losses by the thermal analysis experiments.

Sample	Decomposition					Surface Loading ^b		
	Sample wt, loss due to Mod. (%)	Sample wt, loss due to Mod. (g)	Theoretical wt. loss expected due to Mod. (g) ^a	Moles of Modifier present in sample	Molecules present in sample	Molecules /g	Moles/g	Molecules /cm ²
Si_4.1	1.430	1.58×10^{-4}	1.39×10^{-3}	6.26×10^{-7}	3.77×10^{17}	3.46×10^{19}	5.75×10^{-5}	2.05×10^{13}
	2.676	3.24×10^{-4}	1.52×10^{-3}	1.28×10^{-6}	7.73×10^{17}	6.39×10^{19}	1.06×10^{-5}	3.79×10^{13}
Si_4.2	7.376	5.31×10^{-4}	9.07×10^{-4}	2.10×10^{-6}	1.27×10^{18}	1.90×10^{20}	3.16×10^{-4}	1.13×10^{14}
	6.274	6.25×10^{-4}	1.25×10^{-3}	2.48×10^{-6}	1.49×10^{18}	1.60×10^{20}	2.65×10^{-4}	9.47×10^{13}
Si_4.3	0.236	2.99×10^{-5}	1.59×10^{-3}	1.18×10^{-7}	7.13×10^{16}	5.65×10^{18}	9.39×10^{-6}	3.35×10^{13}
	-1.152	-1.22×10^{-4}	1.34×10^{-3}	-4.85×10^{-7}	-2.92×10^{17}	-2.72×10^{19}	-4.51×10^{-5}	-1.61×10^{13}
Si_4.6	22.137	3.04×10^{-3}	1.73×10^{-3}	1.20×10^{-5}	7.25×10^{18}	6.78×10^{20}	1.13×10^{-3}	4.02×10^{14}
	15.983	1.91×10^{-3}	1.50×10^{-3}	7.55×10^{-6}	4.55×10^{18}	4.54×10^{20}	7.54×10^{-4}	2.69×10^{14}
Si_4.7a	1.644	2.04×10^{-4}	1.56×10^{-3}	8.08×10^{-7}	4.86×10^{17}	3.99×10^{19}	3.22×10^{-5}	2.36×10^{13}
	0.805	9.92×10^{-5}	1.55×10^{-3}	3.93×10^{-7}	2.37×10^{17}	1.94×10^{19}	6.62×10^{-5}	1.15×10^{13}
Si_4.7b	13.855	1.88×10^{-3}	1.71×10^{-3}	7.46×10^{-6}	4.49×10^{18}	3.84×10^{19}	6.37×10^{-4}	2.28×10^{13}
	13.904	1.68×10^{-3}	1.52×10^{-3}	6.67×10^{-6}	4.01×10^{18}	3.85×10^{19}	6.40×10^{-4}	2.28×10^{13}

^a Theoretical mass of modification present as calculated from mass of modified silica used in the STA experiment and theoretical carbene w/w reaction onto the silica (14.5 w/w %) from the diazo loading (16.0 w/w %) used in the modification reactions.

^b Assumes a monolayer surface coverage of the experimentally determined BET silica surface area, 168.7 m²/g.

CHN

Table 2.4: CHN elemental analysis of pristine and modified silica nanoparticles.

Sample	No. of N atoms /molecule of surface modification	% N/g	Moles of nitrogen/g CB	Moles surface modification/g CB	Molecules/g	Molecules /cm ²
Si_4.1	2	0.37	2.64×10^{-4}	1.32×10^{-4}	7.96×10^{19}	1.10×10^{14}
Si_4.2	2	0.00				
Si_4.3	2	0.00				
Si_4.6	2	0.37	2.64×10^{-4}	1.32×10^{-4}	7.96×10^{19}	1.10×10^{14}
Si_4.7a	2	0.25	1.79×10^{-4}	8.93×10^{-5}	5.38×10^{19}	7.41×10^{13}
Si_4.7b	2	0.00				

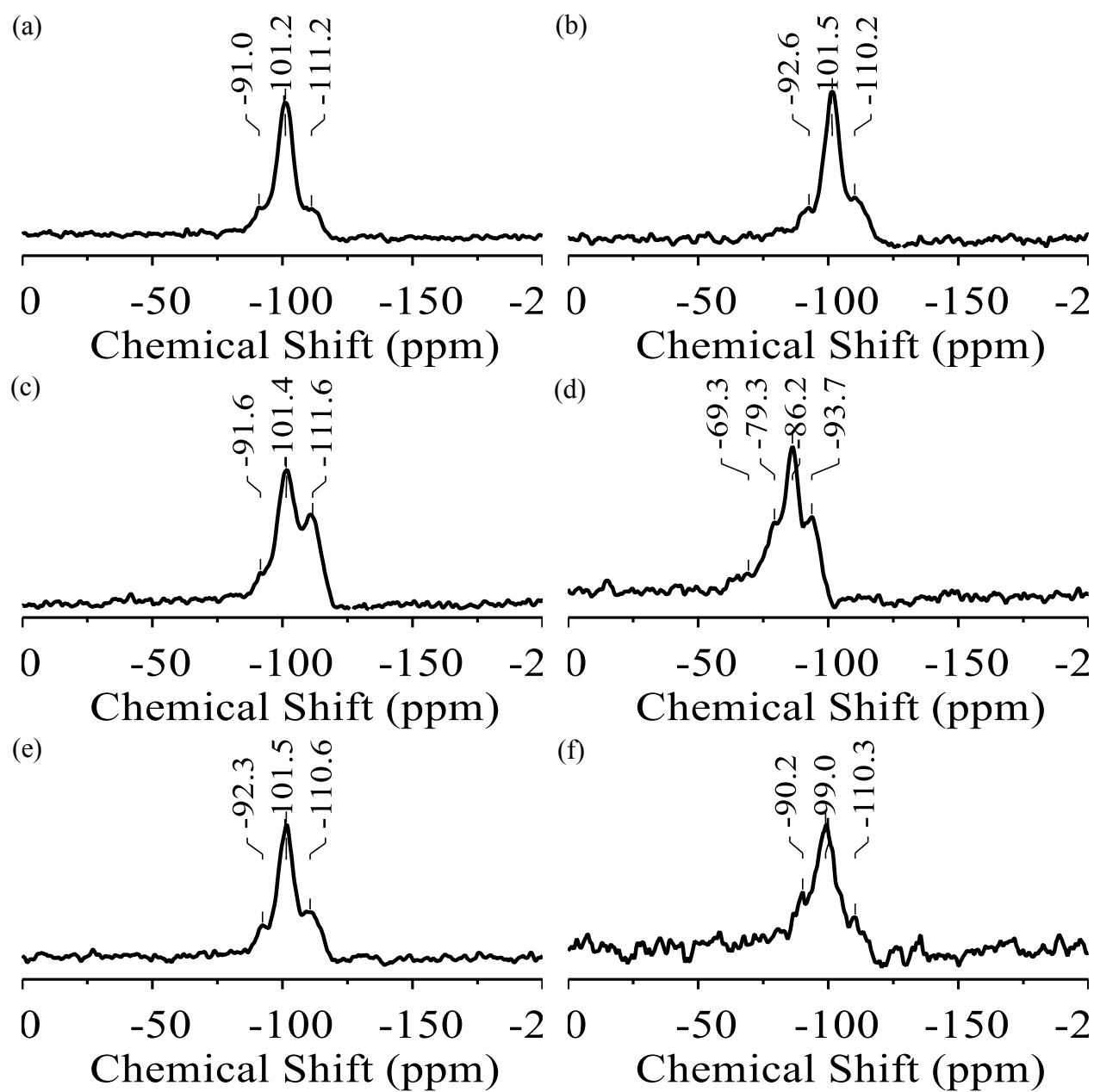
SSNMR

Figure 2.6: ^{29}Si CP MAS SSNMR of (a) Si_Pristine (b) Si_Processed and modified silica (c) Si_4.1 (d) Si_4.6 (e) Si_4.7a and (f) Si_4.7b.

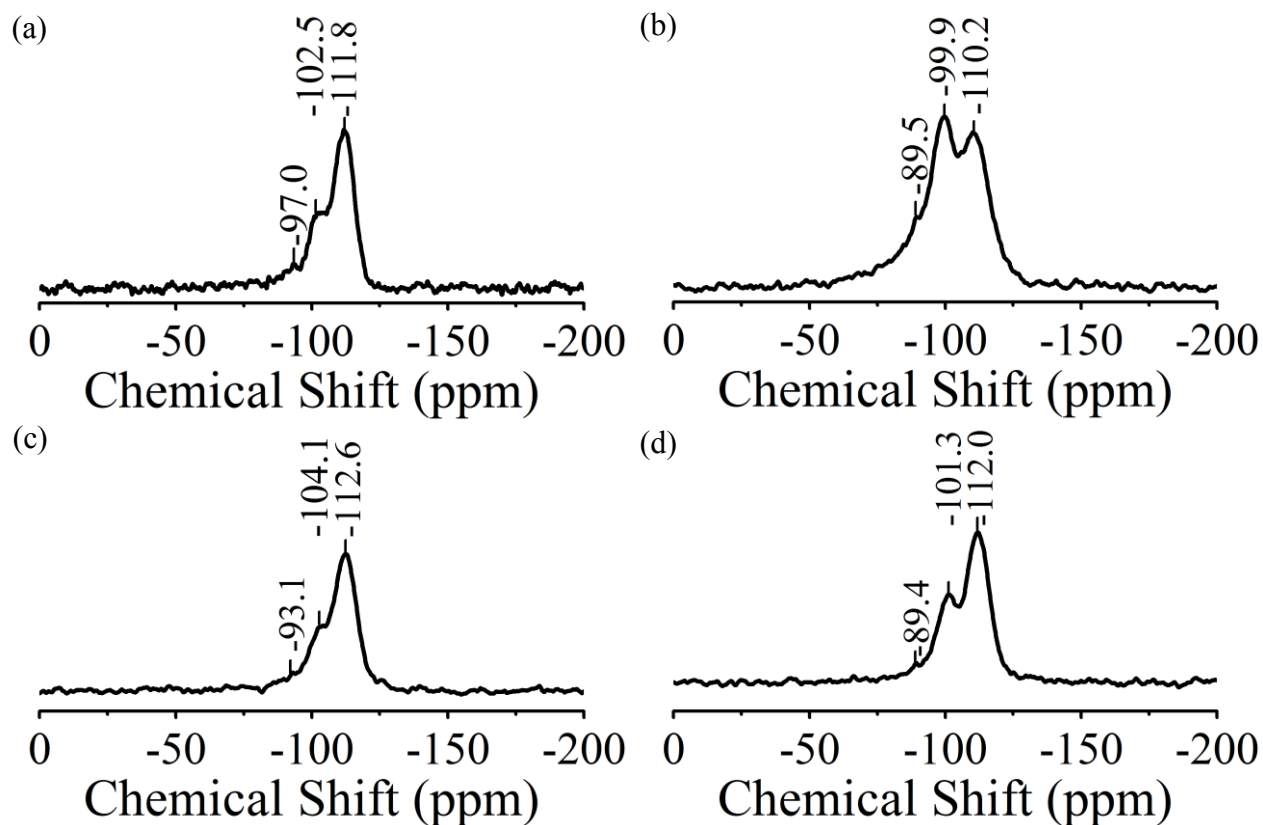


Figure 2.7: ^{29}Si DP MAS SSNMR of (a) Si_Pristine (b) Si_4.2 (c) Si_4.3 (d) Si_4.7b.

CB Nanoparticle Characterisation

BET

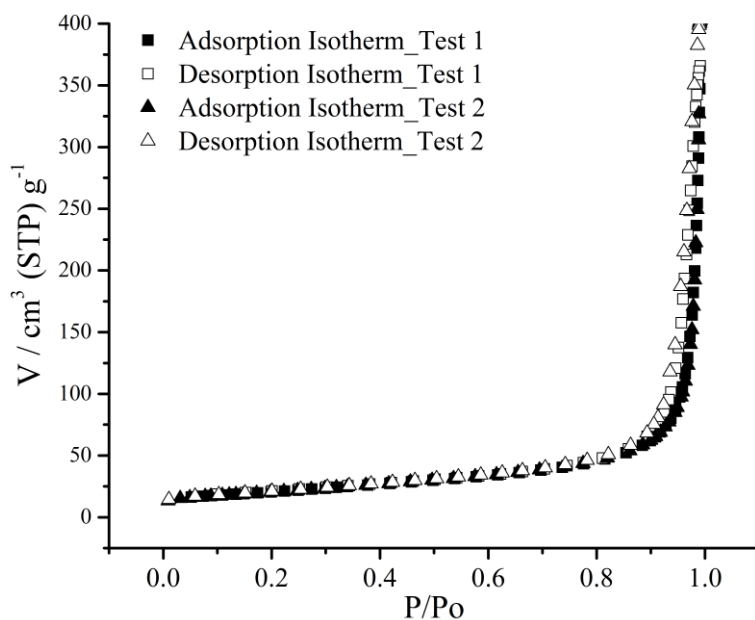


Figure 2.8: BET adsorption and desorption isotherms of nitrogen gas of two samples of pristine CB nanoparticles.

XPS

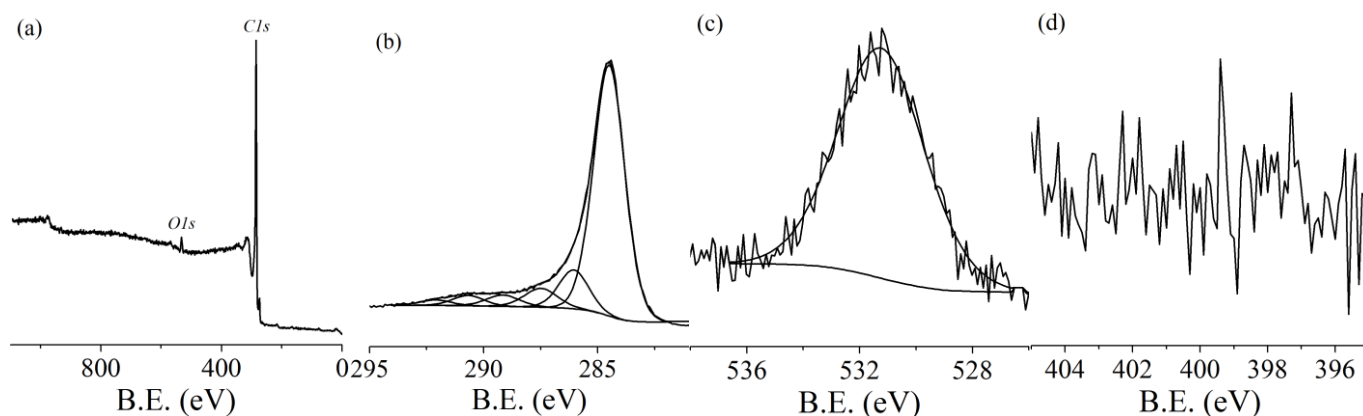


Figure 2.9: XPS spectra of processed CB displaying (a) the wide scan spectrum and the high resolution scan of (b) C 1s (c) O 1s and (d) N 1s regions.

Table 2.5: XPS C 1s, O 1s and N 1s binding energies and charging values for unmodified and modified CB nanoparticles.

Sample	Binding Energies (eV)						Charging (eV)	
	C 1s						O 1s	N 1s
	C-C C-H	C-N C-O	C=O	COOH	π - π^*	π - π^*	C-O C=O	NMe ₂ N=N
CB_Pristine	284.5	286.0	287.2	288.8	290.6	292.4	532.8	
CB_Processed	284.5	286.1	287.5	289.2	290.7	292.1	531.2	
CB_5.1	284.5	286.0	287.4	288.9	290.7	292.2	532.8	400.1
CB_5.2	284.5	286.0	287.3	289.0	290.7	292.0	532.8	399.7
CB_5.3	284.5	286.0	287.3	288.9	290.6	292.1	532.5	399.6
CB_5.4	284.5	285.9	287.3	288.9	290.5	291.6	531.3	398.4
CB_5.5	284.5	286.1	287.7	289.6	291.4	293.4	532.2	399.9
CB_10a	284.5	285.9	287.0	288.7	290.4	291.9	532.5	400.0
CB_10b	284.5	286.0	287.4	288.8	290.1	291.8	532.1	400.6

Table 2.6: XPS FWHM values for the unmodified and modified CB nanoparticles.

Sample	FWHM (eV)							
	C 1s						O 1s	N 1s
	C-C C-H	C-N C-O	C=O	COOH	π - π^*	π - π^*	C-O C=O	NMe ₂
Pristine CB	1.7	1.6	1.8	2.0	1.9	2.0	4.1	
Processed CB	1.6	1.5	1.7	1.7	1.6	1.6	3.6	
CB_5.1	1.6	1.5	1.5	1.6	1.6	1.5	3.0	2.1
CB_5.2	1.6	1.7	1.8	1.8	1.8	1.8	3.2	2.6
CB_5.3	1.6	1.5	1.7	1.7	1.7	1.6	3.2	2.1
CB_5.4	1.7	1.7	1.6	1.7	1.9	1.5	3.0	2.7
CB_5.5	1.6	1.7	1.7	1.7	1.6	1.5	2.9	2.1
CB_10a	1.5	1.5	1.5	1.6	1.6	1.5	3.5	2.7
CB_10b	1.6	1.6	1.6	1.3	1.6	1.6	3.5	3.2

*Thermal Analysis (STA)***Table 2.7:** Thermogravimetric analysis weight loss raw data of pristine and modified CB nanoparticles.

Sample	Initial sample weight (mg)	TGA weight loss					
		30-200 °C		200-500 °C		500-800 °C	
		mg	%	mg	%	mg	%
Pristine CB	12.509	0.064	0.509	0.045	0.357	0.108	0.866
	12.782	0.07	0.547	0.045	0.349	0.099	0.776
	12.917	0.067	0.515	0.039	0.301	0.104	0.808
Processed CB	12.169	0.095	0.777	0.044	0.36	0.085	0.698
	12.696	0.099	0.779	0.047	0.373	0.083	0.653
	12.672	0.087	0.683	0.051	0.406	0.096	0.756
CB_5.1	12.767	0.122	1.105	0.503	6.938	0.230	1.799
	12.538	0.122	0.977	0.504	4.017	0.218	1.738
CB_5.2	12.327	0.719	5.836	0.519	4.208	0.776	6.293
	12.034	0.713	5.926	0.530	4.405	0.759	6.305
CB_5.3	12.868	0.620	4.816	0.462	3.589	0.606	4.709
	12.562	0.597	4.752	0.460	3.658	0.600	4.774
CB_5.4	12.151	0.671	5.518	0.930	4.591	0.788	6.451
	12.659	0.757	5.981	0.942	7.440	1.106	8.739
CB_5.5	12.815	0.125	0.973	0.295	2.306	0.179	1.395
	12.694	0.125	0.982	0.287	2.236	0.19	1.498
CB_10b	7.619	0.055	0.7211	0.828	10.866	0.119	1.562

TGA Surface Loading Calculation (Example CB_5.5 sample 1)

Percentage weight loss of modified CB due to the decomposition of the modifier in 30-800 °C temperature range.

= wt. % loss modified CB - wt. % loss pristine CB (average from 3 samples)

= 4.716 – 1.676 = **3.04 %**

Wt. loss (g) of modified CB due to the decomposition of the modifier (30-800 °C)

= Initial sample wt./100 × % wt. loss of modifier = 0.013/100 × 3.04 % = **3.86×10^{-4} g**

Number of moles of surface modification decomposed (30-800 °C)

= mass (g)/Mr of the modifier = 3.86×10^{-4} g / 252.36 = **1.53×10^{-6} Moles**

Number of molecules of surface modification decomposed (30-800 °C)

= Moles of surface modification × A_v = $(1.53 \times 10^{-6}) \times A_v$ = **9.21×10^{17} Molecules**

Number of molecules of surface modification present per gram on CB.

= Molecules of modification present/mass of CB sample × 1

= Molecules of modification present/(initial CB mass – calculated wt. loss due to decomposition of the modifier) × 1

= $9.21 \times 10^{17} / (1.27 \times 10^{-2} - 3.86 \times 10^{-4}) \times 1$ = $9.21 \times 10^{17} / 1.23 \times 10^{-2}$

= **7.48×10^{19} Molecules/g**

Number of molecules of surface modification per cm² (BET surface area of CB is 725300 cm²/g)

$$= ((\text{molecules/g}^{\text{CB}})/\text{BET surface area}) = (7.48 \times 10^{19}/725300) \\ = 1.03 \times 10^{14} \text{ Molecules/cm}^2$$

Table 2.8: Surface modification loadings of modified CB nanoparticles, as calculated from the determined mass losses by the thermal analysis experiments.

Sample	Decomposition					Surface Loading ^b		
	Sample wt, loss due to Mod. (%)	Sample wt, loss due to Mod. (g)	Theoretical wt. loss expected due to Mod. (g) ^a	Moles of Modifier present in sample	Molecules present in sample	Molecules /g	Moles/g	Molecules /cm ²
CB_5.1	5.166	6.60×10^{-4}	4.78×10^{-3}	2.61×10^{-6}	1.57×10^{18}	1.30×10^{20}	2.16×10^{-4}	1.79×10^{14}
	5.056	6.34×10^{-4}	4.70×10^{-3}	2.51×10^{-6}	1.51×10^{18}	1.27×10^{20}	2.11×10^{-4}	1.75×10^{14}
CB_5.2	14.661	1.81×10^{-3}	4.62×10^{-3}	7.16×10^{-6}	4.31×10^{18}	4.10×10^{20}	6.81×10^{-4}	5.65×10^{14}
	14.960	1.80×10^{-3}	4.51×10^{-3}	7.13×10^{-6}	4.30×10^{18}	4.20×10^{20}	6.97×10^{-4}	5.79×10^{14}
CB_5.3	11.438	1.47×10^{-3}	4.82×10^{-3}	5.83×10^{-6}	3.51×10^{18}	3.08×10^{20}	5.12×10^{-4}	4.25×10^{14}
	11.508	1.45×10^{-3}	4.71×10^{-3}	5.73×10^{-6}	3.45×10^{18}	3.10×10^{20}	5.15×10^{-4}	4.28×10^{14}
CB_5.4	14.884	1.81×10^{-3}	4.53×10^{-3}	7.17×10^{-6}	4.32×10^{18}	4.17×10^{20}	6.93×10^{-4}	5.75×10^{14}
	20.484	2.59×10^{-3}	4.72×10^{-3}	1.03×10^{-5}	6.19×10^{18}	6.15×10^{20}	1.02×10^{-3}	8.48×10^{14}
CB_5.5	2.998	3.84×10^{-4}	4.54×10^{-3}	1.52×10^{-6}	9.17×10^{17}	7.38×10^{19}	1.22×10^{-4}	1.02×10^{14}
	3.040	3.86×10^{-4}	4.73×10^{-3}	1.53×10^{-6}	9.21×10^{17}	7.48×10^{19}	1.24×10^{-4}	1.03×10^{14}
CB_10b ^c	11.473	8.74×10^{-4}	4.50×10^{-4}	1.62×10^{-6}	9.73×10^{17}	1.44×10^{19}	1.44×10^{-4}	1.99×10^{14}
CB_10b ^d			6.90×10^{-4}	1.05×10^{-6}	6.35×10^{17}	9.41×10^{19}	9.41×10^{-4}	1.30×10^{14}

^a Calculated from the mass of modified CB used in the STA experiment and the theoretical carbene w/w reaction onto the CB (59.9 wt. %) from the diazo loading (66.0 wt. %) used in the modification reactions.

^b Assumes monolayer surface coverage of the experimentally determined BET CB surface area, 72.5 m²/g

^c Estimated number of modifier molecules/cm² calculation assumes single azo-coupling reactions of the diazonium salt to pre-modified CB_5.5, as shown in Figure 1.21(b)-Chapter 3.

^d Estimated number of modifier molecules/cm² calculation assumes dual azo-coupling reactions of the diazonium salt to pre-modified CB_5.5, as shown in Figure 1.21(c)-Chapter 3.

CHN

CHN Surface Loading Calculation (Example CB_5.5 sample 1)

The number of moles of nitrogen present per gram of CB

$$= (\%N/\text{Mr}(N))/100 = (0.77/14)/100 = 5.50 \times 10^{-4} \text{ Moles}$$

Number of moles of surface modification per gram of CB

$$= (\text{moles N/g}^{\text{CB}})/\text{atoms of N} = 5.50 \times 10^{-4} / 2 = 2.75 \times 10^{-4} \text{ mol/g}$$

Number of molecules of surface modification per gram of CB

$$= \text{moles of surface modification} \times N_A = (2.75 \times 10^{-4}) \times N_A = 1.66 \times 10^{20} \text{ Molecules}$$

Number of molecules of surface modification per cm² (BET surface area of CB is 725510 cm²/g)

$$= ((\text{molecules/g}^{\text{CB}})/\text{BET surface area}) = (1.66 \times 10^{20}/725300) \\ = 2.28 \times 10^{14} \text{ molecules/cm}^2$$

Table 2.9: Combustion analysis - modified CB surface loading calculations.

Sample	No. of N atoms /molecule of surface modification	% N/g	Moles of nitrogen/g CB	Moles surface modification/g CB	Molecules/g	Molecules /cm ²
CB_5.1	2	0.76	5.43×10^{-4}	2.71×10^{-4}	1.64×10^{20}	2.25×10^{14}
CB_5.2	2	0.00				
CB_5.3	2	0.00				
CB_5.4	2	0.69	4.93×10^{-4}	2.46×10^{-4}	1.48×10^{20}	2.05×10^{14}
CB_5.5 (1)	2	0.77	5.50×10^{-4}	2.75×10^{-4}	1.66×10^{20}	2.28×10^{14}
CB_5.5 (2)	2	0.54	3.86×10^{-4}	1.93×10^{-4}	1.16×10^{20}	1.60×10^{14}
CB_10a ^a	4	0.40	2.86×10^{-4}	7.14×10^{-5}	4.30×10^{19}	5.93×10^{13}
CB_10a ^b	6	0.40	2.86×10^{-4}	4.76×10^{-5}	2.87×10^{19}	3.95×10^{13}
CB_10b ^a	4	0.91	6.50×10^{-4}	1.63×10^{-4}	9.79×10^{19}	1.35×10^{14}
CB_10b ^b	6	0.40	6.50×10^{-4}	1.08×10^{-4}	6.52×10^{19}	8.99×10^{13}

^a Estimated number of modifier molecules/cm² calculation assumes single azo-coupling reactions of the diazonium salt to pre-modified CB_5.5, as shown in Figure 1.21(b)-Chapter 3.

^b Estimated number of modifier molecules/cm² calculation assumes dual azo-coupling reactions of the diazonium salt to pre-modified CB_5.5, as shown in Figure 1.21(c)-Chapter 3.

Table 2.10: The repeated CHN measurements for sample CB_5.5 means the relative error for the surface loading can be calculated:

Sample	% N/g	Moles of nitrogen/g CB	Moles surface modification/g CB	Molecules/g	Molecules /cm ²
CB_5.5 (1)	0.77	5.50×10^{-4}	2.75×10^{-4}	1.66×10^{20}	2.28×10^{14}
CB_5.5 (2)	0.54	3.86×10^{-4}	1.93×10^{-4}	1.16×10^{20}	1.60×10^{14}
Average	0.66	4.68×10^{-4}	2.34×10^{-4}	1.41×10^{20}	1.94×10^{14} ^a
S.D.	0.16	1.16×10^{-4}	5.81×10^{-5}	3.50×10^{19}	4.82×10^{13}

^aThe Relative error between the repeated measurement is calculated at 25 %. Therefore, for the average calculated surface loading measurement of 1.94×10^{14} molecules/cm², this could mean 1.43×10^{14} - 2.43×10^{14} molecules/cm². Importantly this is within the same order of magnitude of loading.

Appendix III - Chapter 4

Silica Nanoparticle Characterisation

BET

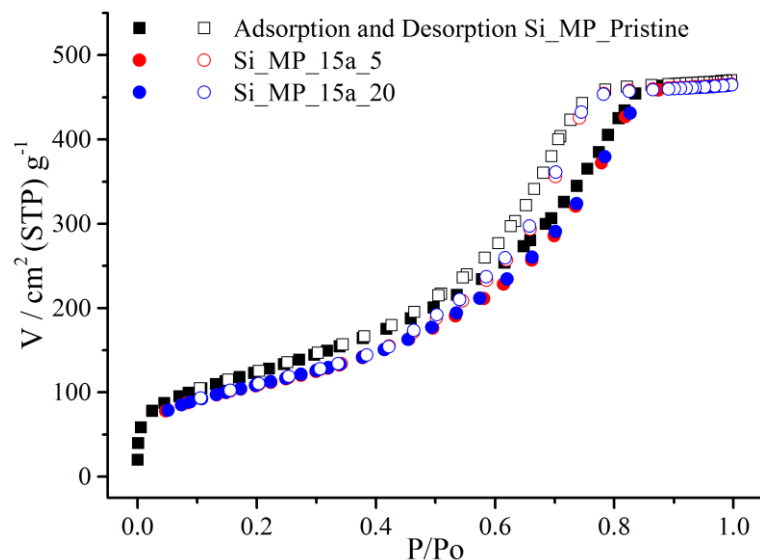


Figure 3.1: A graph showing the BET adsorption and desorption isotherms of nitrogen by pristine microsilica and hexyl modified (Si_MP_15a) microsilica at 5 % and 20 % diazo loading.

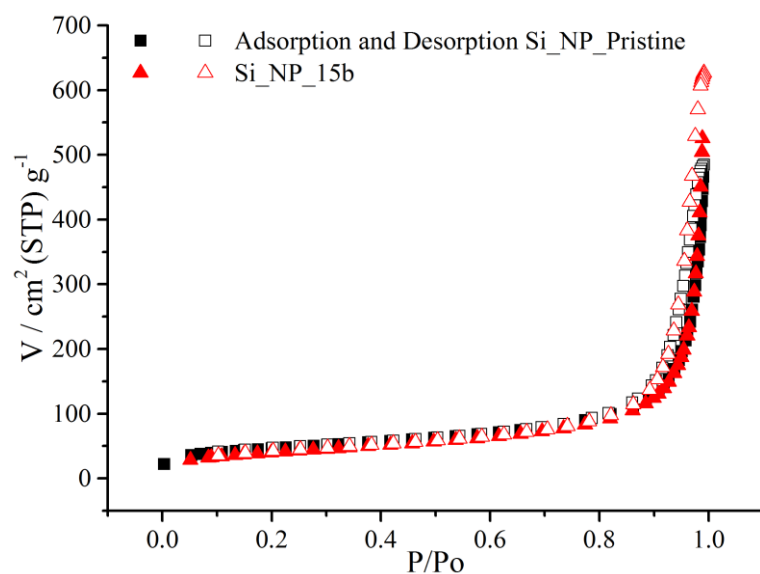


Figure 3.2: A graph showing the BET adsorption and desorption isotherms of nitrogen by pristine and dodecyl modified nanosilica (Si_NP_15b) modified at 16 wt. % surface loading.

*Thermal Analysis (STA)***Table 3.1:** Thermogravimetric analysis weight loss raw data of pristine and modified silica nanoparticles.

Sample	Initial sample weight (mg)	TGA weight loss					
		30-200 °C		200-500 °C		500-800 °C	
		mg	%	mg	%	mg	%
Si_MP_Pristine	12.308	0.554	1.502	0.180	1.465	0.175	1.242
Si_MP_Processed	12.590	0.753	5.983	0.186	1.474	0.187	1.489
Si_MP_15a_5	12.296	0.610	4.959	0.274	2.228	0.221	1.801
Si_MP_15a_20	12.502	0.474	3.793	0.434	3.471	0.267	2.137
Si_NP_15a	12.336	0.453	3.674	0.494	4.006	0.333	2.679
Si_NP_15b	12.316	0.456	3.704	0.402	3.266	0.272	2.212

Table 3.2: Surface modification loadings of modified silica nanoparticles, as calculated from the determined mass losses by the thermal analysis experiments.

Sample	Decomposition					Surface Loading ^b		
	Sample wt, loss due to Mod. (%)	Sample wt, loss due to Mod. (g)	Theoretical wt. loss expected due to Mod. (g) ^a	Moles of Modifier present in sample	Molecules present in sample	Molecules /g	Moles /g	Molecules /cm ²
Si_MP_15a_5	1.596	1.96×10^{-4}	5.35×10^{-4}	5.38×10^{-7}	3.24×10^{17}	2.68×10^{19}	4.45×10^{-5}	6.81×10^{12}
Si_MP_15a_20	2.009	2.51×10^{-4}	1.92×10^{-3}	6.89×10^{-7}	4.15×10^{17}	3.39×10^{19}	5.62×10^{-5}	8.61×10^{12}
Si_NP_15a	1.843	2.27×10^{-4}	1.57×10^{-3}	8.11×10^{-7}	4.88×10^{17}	4.03×10^{19}	6.70×10^{-5}	2.39×10^{13}
Si_NP_15b	0.648	7.98×10^{-5}	1.59×10^{-3}	2.19×10^{-7}	1.32×10^{17}	1.08×10^{19}	1.79×10^{-5}	6.39×10^{12}

^aTheoretical mass of modification present as calculated from mass of modified silica used in the STA experiment and theoretical carbene w/w reaction onto the silica (14.5 w/w %) from the diazo loading (16.0 w/w %) used in the modification reactions.

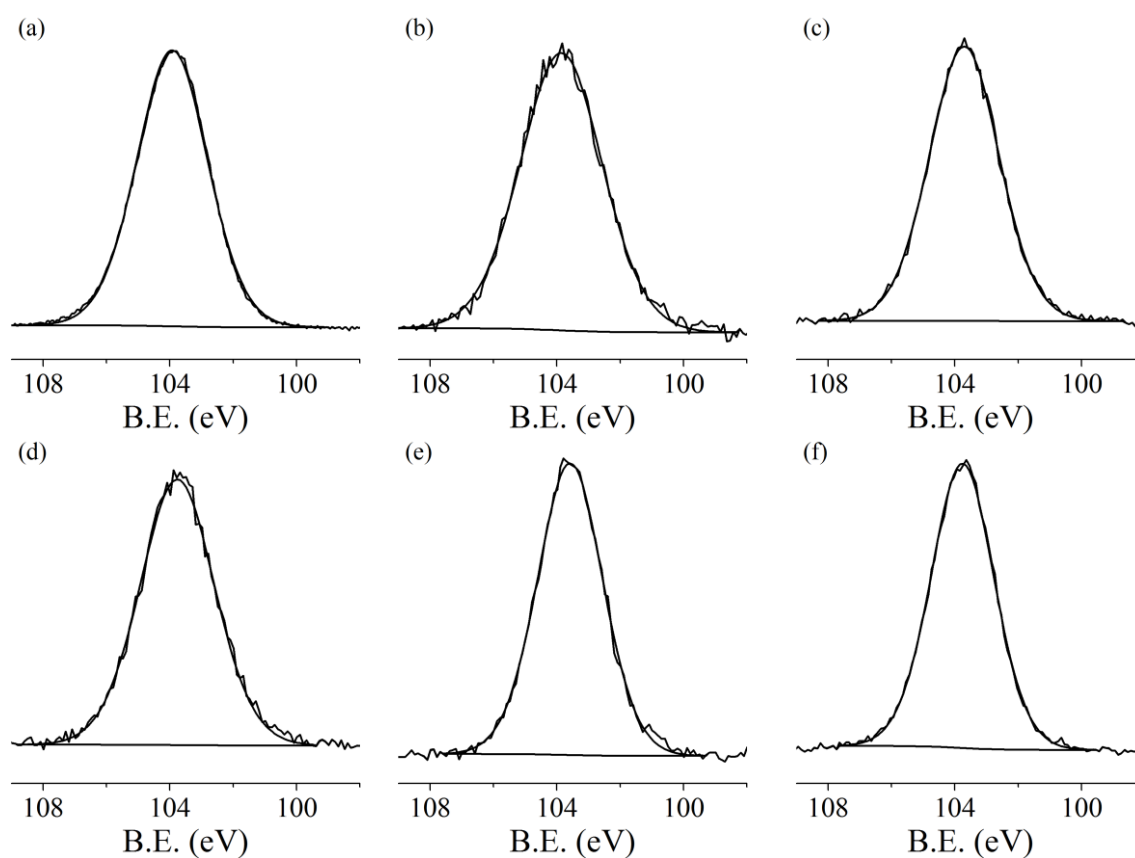
^b Assumes monolayer surface coverage of the experimentally determined BET surface areas of Si_MP_Pristine (393.5 m²/g) and Si_NP_Pristine (168.7 m²/g).

*XPS***Table 3.3:** XPS Si 2p, C 1s and O 1s binding energies and charging values for unmodified and modified silica nanoparticles.

Sample	Binding Energies (eV)						Charging (eV)	
	Si 2p	C 1s			O 1s		Relative to C 1s (284.5)	
	SiO ₂	C-C C-H	C-N C-O	C=O	C=O	Si-O-Si Si-OH		
Si_MP_Pristine	103.9	284.5	286.0	287.6	528.8	532.3		
Si_MP_Processed	103.9	284.5	286.3	287.6	529.3	532.3	17.2	
Si_MP_15a_5	103.7	284.5	286.3	287.6	529.1	532.0	16.8	
Si_MP_15a_20	103.8	284.5	286.1	287.7	277.9	529.3	532.0	15.1
Si_NP_Pristine	103.6	284.5			528.8	531.8	18.0	
Si_NP_Processed	103.5	284.5			276.8	529.9	531.8	15.4
Si_NP_15a	103.8	284.5	286.1	287.7	277.1	529.5	532.0	15.5
Si_NP_15b	103.8	284.5	286.0	287.8	528.9	532.3	17.2	

Table 3.4: XPS FWHM values for unmodified and modified Silica nanoparticles.

Sample	FWHM (eV)					
	Si 2p	C 1s			O 1s	
	SiO ₂	C-C C-H	C-N C-O	C=O	C=O	Si-O-Si Si-OH
Si_MP_Pristine	2.6	2.3	2.1	2.4	2.6	2.7
Si_MP_Processed	3.0	2.7	2.7	2.7	3.1	3.0
Si_MP_15a_5	2.6	2.4	2.3	2.4	2.4	2.6
Si_MP_15a_20	2.8	2.7	2.6	2.6	2.8	2.7
Si_NP_Pristine	2.4	2.6			2.4	2.4
Si_NP_Processed	2.4	2.5			2.5	2.4
Si_NP_15a	2.4	2.4	2.6	2.2	2.3	2.4
Si_NP_15b	2.3	1.9	1.9	1.9	2.5	2.4


Figure 3.3: XPS high resolution spectra of the Si 2p region of (a) Si_MP_Pristine (b) Si_MP_Processed (c) Si_MP_15a_5 (d) Si_MP_15a_20 (e) Si_NP_15a and (f) Si_NP_15b.

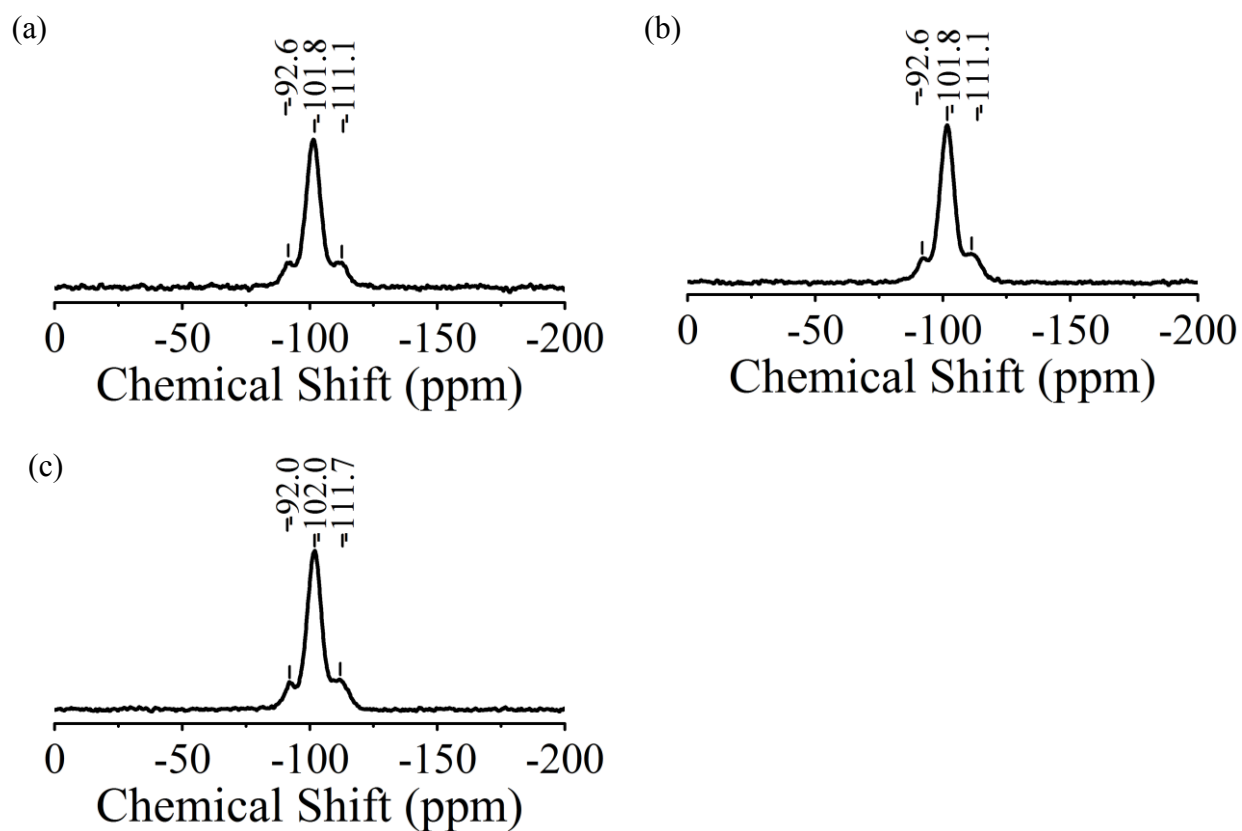
SSNMR

Figure 3.4: ^{29}Si CP MAS SSNMR of (a) Si_MP_Processed (b) Si_MP_15a_5 and (c) Si_MP_15a_20.

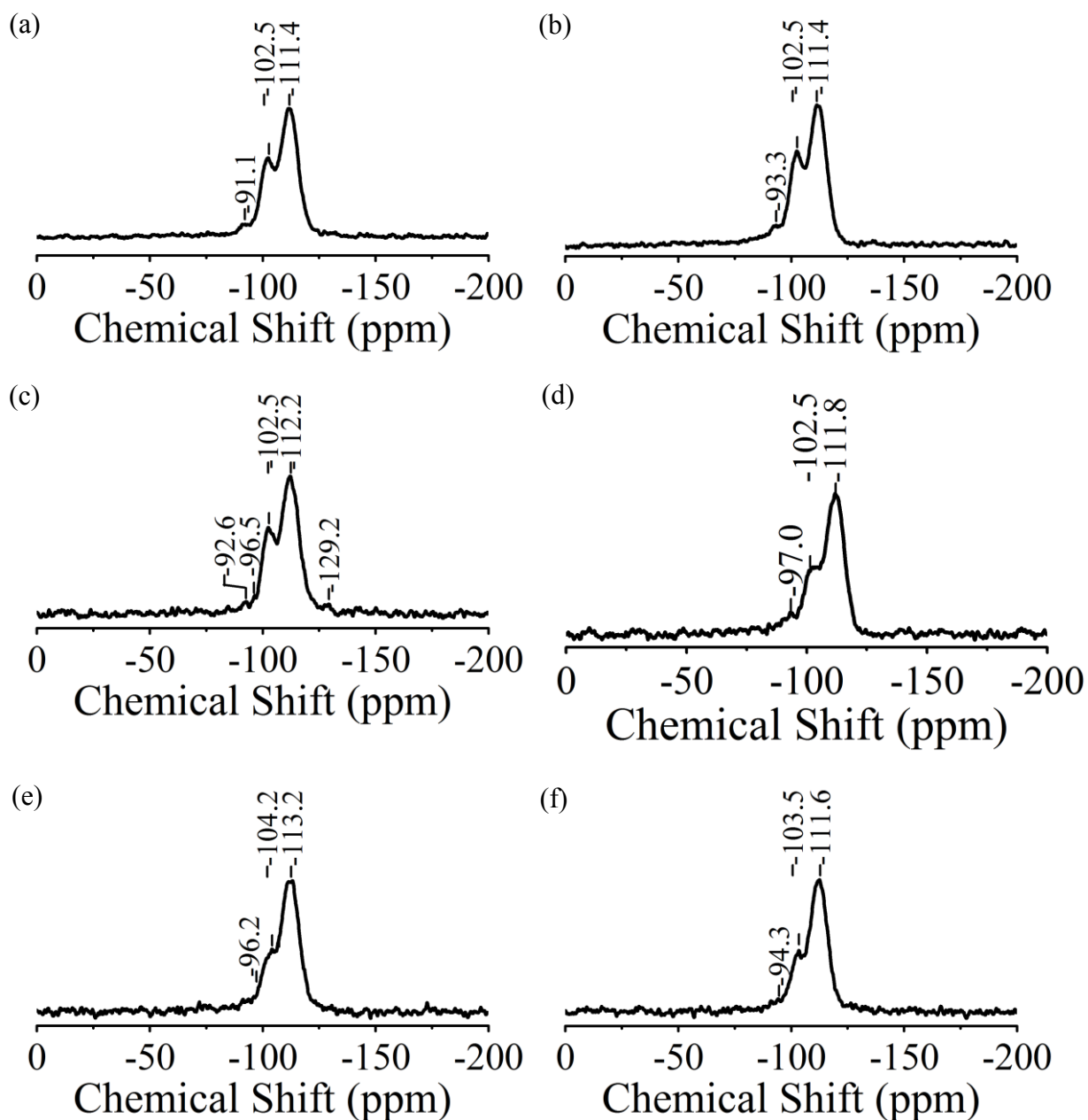


Figure 3.5: ^{29}Si CP MAS SSNMR of (a) Si_MP_Processed (b) Si_MP_15a_5 (c) Si_MP_15a_20 (d) Si_NP_Processed (e) Si_NP_15a (f) Si_NP_15b .

Carbon Based Nanoparticle Characterisation

BET

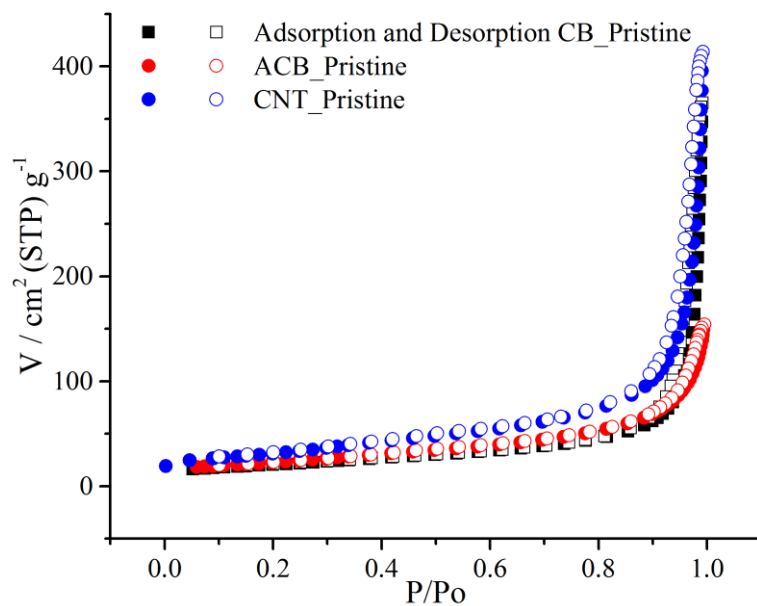


Figure 3.6: BET adsorption and desorption isotherms of pristine CB, ACB and CNTs.

Thermal analysis (STA)

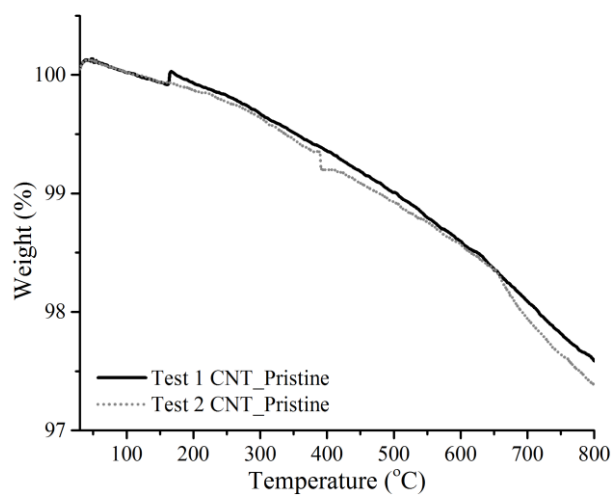


Figure 3.7: TGA curves of two repeat tests of CNT_Pristine.

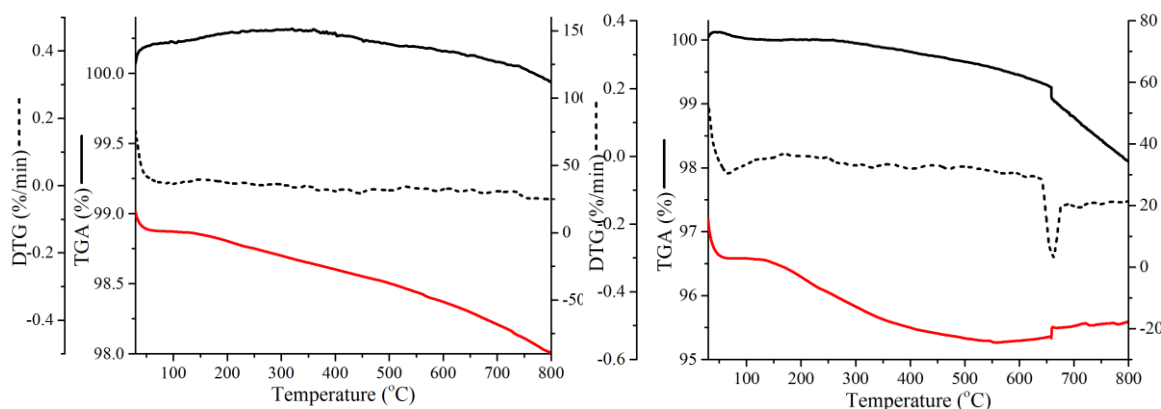


Figure 3.8: Thermal Analysis data displaying TGA, DTG and DSC curves (heat flow endo down) of (a) ACB_Processed and (b) CNT_Processed.

Table 3.5: Thermogravimetric analysis weight loss data of the unmodified and modified carbon-based nanomaterials.

Sample	Initial sample weight (mg)	TGA weight loss					
		30-200 °C		200-500 °C		500-800 °C	
		mg	%	mg	%	mg	%
CB_15a_STA	2.747	0.0250	0.908	0.211	7.977	0.155	5.638
CB_15a	12.485	0.088	0.704	0.237	1.899	0.175	1.402
CB_15b 22	9.370	0.024	0.257	0.144	1.539	0.086	0.918
ACB_Pristine ^a	12.591	+0.022	+0.174	0.005	0.040	0.030	0.235
ACB_Processed ^a	12.864	+0.028	+0.216	0.010	0.079	0.035	0.271
ACB_15a	12.748	0.008	0.064	0.096	0.753	0.052	0.404
CNT_Pristine ^a	12.353	+0.016	+0.132	0.039	0.315	0.163	1.319
CNT_Processed	12.024	0.005	0.038	0.042	0.348	0.188	1.561
CNT_15a	12.668	0.014	0.109	0.127	1.002	0.112	0.884

^a +weight losses for these samples is noted as was an increase in weight in the 30-200 °C temperature range, due to the observed buoyancy effect for these samples.

Table 3.6: Surface modification loadings of modified carbon-based nanomaterials, as calculated from the determined mass losses by the thermal analysis experiments.

Sample	Decomposition				Surface Loading ^a			
	Sample wt, loss due to Mod. (%)	Sample wt, loss due to Mod. (g)	Theoretical wt. loss expected due to Mod. (g) ^a	Moles of Modifier present in sample	Molecules present in sample	Molecules /g	Moles /g	Molecules /cm ²
CB_15a_STA	1.038	3.45×10^{-4}	1.03×10^{-3}	1.23×10^{-6}	7.40×10^{17}	3.08×10^{20}	5.12×10^{-4}	4.25×10^{14}
CB_15a	2.329	2.91×10^{-4}	4.68×10^{-3}	1.04×10^{-6}	6.24×10^{17}	5.12×10^{19}	8.50×10^{-5}	7.06×10^{13}
CB_15b 22	1.038	9.73×10^{-5}	3.56×10^{-3}	2.67×10^{-6}	1.61×10^{17}	1.73×10^{19}	2.88×10^{-5}	2.39×10^{13}
ACB_15a	1.120	1.43×10^{-4}	1.06×10^{-3}	5.09×10^{-7}	3.07×10^{17}	2.43×10^{19}	4.04×10^{-5}	3.05×10^{13}
CNT_15a	0.493	6.25×10^{-5}	5.51×10^{-4}	2.23×10^{-7}	1.34×10^{17}	1.06×10^{19}	1.77×10^{-5}	1.33×10^{13}

^a Assumes a monolayer surface coverage of the determined BET surface areas of CB (72.5 m²/g), ACB (79.8 m²/g) and CNT (112.6 m²/g).

*XPS***Table 3.7:** XPS C 1s and O 1s binding energies and charging values for unmodified and modified CB, ACB and CNT nanoparticles.

Sample	Binding Energies (eV)						Charging (eV)	
	C 1s						O 1s	Relative to C 1s (284.5)
	C-C C-H	C-N C-O	C=O	COOH	π - π^*	π - π^*	C-O C=O	
CB_Pristine	284.5	286.0	287.2	288.8	290.6	292.4	532.8	7.6
CB_Processed	284.5	286.1	287.5	289.2	290.7	292.1	531.2	7.8
CB_15a	284.5	285.9	287.0	288.5	290.0	291.6	532.4	6.7
CB_15b	284.5	286.0	287.6	289.2	290.8	292.2	532.4	6.7
ACB_Pristine	284.5	286.0	287.5	289.1	290.7	292.1	531.6	7.3
ACB_Processed	284.5	286.0	287.5	289.1	290.7	292.2	532.2	6.8
ACB_15a	284.5	286.0	287.5	289.0	290.6	292.0	532.0	6.8
CNT_Pristine	284.5	286.0	287.5	289.2	290.7	292.2	532.0	9.1
CNT_Processed	284.5	286.0	287.5	289.2	290.7	292.2	532.0	9.2
CNT_15a	284.5	286.0	287.5	289.2	290.8	292.4	532.0	7.0

Table 3.8: XPS FWHM values for unmodified and modified CB nanoparticles.

Sample	FWHM (eV)						O 1s
	C 1s						
	C-C C-H	C-N C-O	C=O	COOH	π - π^*	π - π^*	C-O C=O
CB_Pristine	1.7	1.6	1.8	2.0	1.9	2.0	4.1
CB_Processed	1.6	1.5	1.7	1.7	1.6	1.6	3.6
CB_15a	1.5	1.3	1.4	1.6	1.6	1.3	3.5
CB_15b	1.6	1.6	1.6	1.5	1.6	1.5	3.1
ACB_Pristine	1.3	1.3	1.3	1.3	1.3	1.3	2.2
ACB_Processed	1.3	1.3	1.3	1.3	1.3	1.3	2.8
ACB_15a	1.3	1.3	1.3	1.3	1.3	1.3	2.7
CNT_Pristine	1.3	1.3	1.3	1.3	1.3	1.3	2.8
CNT_Processed	1.3	1.3	1.3	1.3	1.3	1.3	2.9
CNT_15a	1.3	1.4	1.4	1.4	1.4	1.4	3.0

Table 3.9: The relative peak areas of devolved C 1s peaks in the high resolution XPS spectra of the unmodified and modified carbon-based samples.

Sample	C-C/C-H (284.5)	C-N/C-O (285.9)	C=O (287.3)	COOH (289.0)	π - π^* (290.6)	π - π^* (292.2)
CB_Pristine	74.4	9.8	5.5	4.2	4.0	2.2
CB_Processed	74.8	11.0	5.9	3.6	3.1	1.6
CB_15a	71.0	12.6	6.8	4.2	3.3	1.9
CB_15b	74.4	14.1	5.0	2.6	2.7	1.1
ACB_Pristine	76.2	11.0	4.1	2.7	3.7	2.3
ACB_Processed	71.5	12.5	5.1	3.9	4.1	2.8
ACB_15a	73.0	11.7	4.8	3.4	4.1	3.0
CNT_Pristine	73.2	11.1	4.9	3.6	4.2	3.1
CNT_Processed	74.8	10.9	4.5	3.1	4.1	2.7
CNT_15a	73.2	11.9	5.0	3.5	4.1	2.4

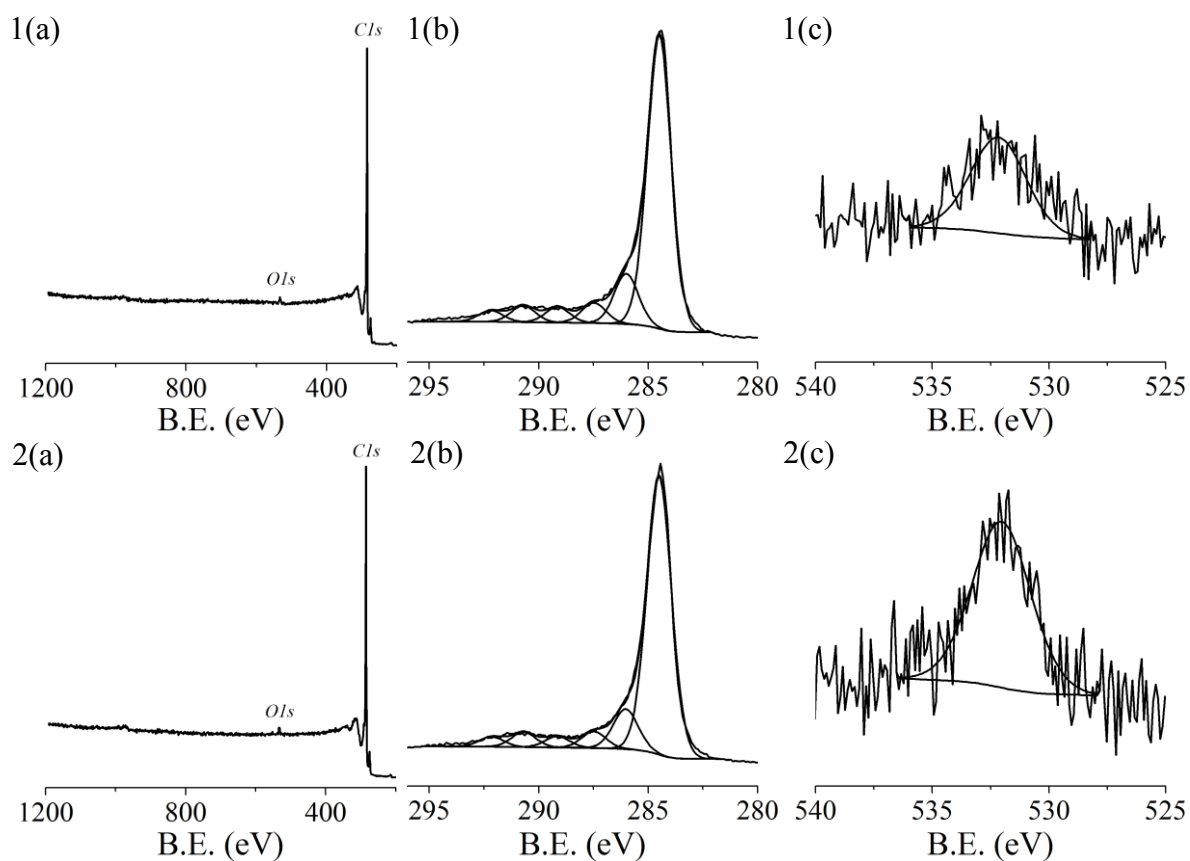


Figure 3.9: XPS (a) wide scan spectra and (b) C 1s and (c) O 1s high resolution spectra of 1. ACB_Processed 2. CNT_Processed.

Appendix IV - Chapter 5

Table 4.1: Extracted DSC, TGA and DTG data from thermal analysis runs of pristine and modified microsilica and nanosilica PP nanocomposites.

		DSC												TGA		DTG		
Sample	Sample weight (mg)	Filler Loading (Wt.%)	Initial Heating and Cooling (30-250-30 °C)										Secondary Heating and Decomposition (30-850-30 °C)					
			Melting I			Crystallisation				Melting II			X _c (%)	Decomposition				
			T _{on} ^a (°C)	T _{pm} ^b (°C)	ΔH _m (J/g)	T _{oc} (°C)	T _{pc} (°C)	ΔH _c (J/g)	T _{on} (°C)	T _{pm} (°C)	ΔH _m (J/g)	T _{od} (°C)		T _{pd} (°C)	ΔH _d (J/g)	T _{od} ^b (°C)	T _{pd} ^c (°C)	
PP_Pristine 1	12.141		154.0	170.2	67.5	122.2	117.9	-82.8	152.1	164.0	79.2	38.2	453.1	472.7	419.2	438.0	468.9	
PP_Pristine 2	13.327		157.9	172.1	66.1	121.1	116.6	-79.6	150.4	162.9	76.6	37.0	453.1	470.1	369.9	444.1	468.3	
PP_Pristine 3	13.649	0	157.9	171.8	62.9	121.1	116.4	-80.6	151.1	163.1	77.4	37.4	462.8	471.7	363.3	445.1	468.6	
PP_Processed 1	12.318		149.6	165.9	67.5	129.3	124.6	-73.7	147.3	162.5	70.7	34.1	416.5	474.4	456.2	444.4	472.0	
PP_Processed 2	12.550		148.5	168.0	69.7	125.8	120.9	-76.6	150.9	163.8	70.8	34.2	434.4	474.6	629.0	448.6	473.5	
PP_Processed 3	12.122		150.7	166.7	63.8	127.8	123.3	-62.9	149.2	163.5	71.9	34.7	435.0	473.1	515.1	445.8	471.6	
Si_MP_Pristine/PP	12.649	1	149.8	167.4	50.9	127.1	120.9	-67.5	149.8	165.1	64.3	31.4	400.0	475.0	551.4	447.2	472.7	
	12.712		147.6	164.4	53.6	126.8	120.7	-66.3	148.0	162.2	66.7	32.5	442.4	473.7	461.4	436.8	470.4	
	12.270	3	150.6	166.5	42.3	127.4	119.7	-55.5	147.8	167.4	52.1	25.9	458.9	477.9	431.5	438.8	475.2	
	12.291		150.6	166.1	55.9	127.8	122.1	-64.6	146.8	164.0	63.8	31.8	434.5	475.4	545.7	439.0	473.3	
	12.895	5	150.9	170.2	59.3	128.3	122.0	-73.0	148.1	165.0	71.2	36.2	452.0	474.2	599.7	439.6	473.5	
	12.678		150.4	165.2	46.3	127.7	121.3	-54.6	148.2	163.7	53.0	26.9	458.2	475.4	548.0	437.1	472.8	
Si_MP_15a_5/PP	12.298	1	150.7	171.0	69.4	128.5	124.0	-83.8	147.3	163.1	79.6	38.8	445.2	473.6	729.7	442.4	471.4	
	12.627		151.1	168.8	70.6	128.6	123.5	-83.7	146.8	16449.0	80.1	39.0	455.2	472.8	637.0	444.1	470.6	
	12.772	3	150.3	167.5	55.7	127.4	120.1	-72.4	149.3	164.6	67.6	33.6	445.5	473.3	446.0	441.5	472.2	
	12.506		150.9	167.5	62.7	127.7	121.9	-72.4	148.2	162.8	69.1	34.4	455.7	473.1	601.6	439.4	470.4	
	12.672	5	152.2	172.0	59.5	128.3	121.6	-76.9	148.7	166.1	72.7	37.0	456.1	474.7	419.6	441.2	473.1	
	12.19		150.5	169.4	63.3	128.3	122.4	-79.2	147.7	164.5	76.6	38.9	455.4	473.3	423.2	437.2	470.2	
Si_MP_15a_20/PP	12.017	1	148.6	166.2	53.2	126.4	119.2	-67.6	148.0	165.9	64.6	31.5	446.4	474.9	420.4	439.0	471.6	
	12.641		149.6	165.5	64.8	127.4	122.63	-74.5	148.0	161.8	71.5	34.9	434.0	473.3	560.0	431.9	470.1	
	12.869	3	151.8	167.2	64.1	127.6	122.4	-79.0	146.6	164.0	75.1	37.4	441.9	472.9	436.4	437.5	470.1	
	12.38		150.6	164.4	66.3	127.5	122.7	-76.5	147.0	162.0	77.1	38.4	449.8	469.8	421.3	435.8	469.1	
	12.104	5	149.4	168.6	59.1	127.9	120.8	-67.7	147.1	166.2	63.3	32.2	454.1	471.7	549.1	443.5	472.7	
	12.653		151.1	166.2	64.3	128.4	123.5	-75.7	147.6	163.3	70.0	35.6	453.8	472.8	525.5	439.4	472.4	

			DSC										TGA		DTG			
			Initial Heating and Cooling (30-250-30 °C)										Secondary Heating and Decomposition (30-850-30 °C)					
Sample	weight (mg)	Filler loading (Wt.%)	Melting I			Crystallisation			Melting II			X _c (%)	Decomposition					
			T _{on} (°C) ^a	T _{pm} (°C) ^b	ΔH _m (J/g)	T _{oc} (°C)	T _{pc} (°C)	ΔH _c (J/g)	T _{on} (°C)	T _{pm} (°C)	ΔH _m (J/g)		T _{od} (°C)	T _{pd} (°C)	ΔH _d (J/g)	T _{od} ^b (°C)	T _{pd} ^c (°C)	
Si_NP_Pristine	1	3	12.198	151.1	168.7	65.8	126.4	120.7	-70.1	149.5	164.4	75.2	36.7	448.7	474.5	497.0	444.4	470.8
			12.566	153.1	172.6	63.0	127.1	120.8	-71.6	149.4	165.4	76.0	37.0	451.3	475.1	459.7	443.4	470.2
			12.317	150.8	167.2	59.8	127.9	120.4	-66.8	148.3	166.4	70.0	34.8	432.8	471.6	588.8	445.9	468.7
			12.483	151.4	166.7	66.7	127.7	121.6	-69.8	147.2	163.6	75.3	37.5	441.2	470.8	5119.3	442.7	467.9
			12.561	150.4	167.4	59.9	127.3	119.0	-62.5	146.8	166.7	67.0	34.0	433.6	471.4	565.4	443.3	468.1
Si_NP_Pristine	5	10	12.746	150.2	171.8	68.4	127.3	118.5	-76.2	147.4	167.3	76.6	38.9	440.5	470.7	576.6	441.2	468.4
			12.497	147.0	162.3	65.2	125.7	118.4	-71.7	144.9	160.9	66.1	35.5	431.6	469.4	386.2	440.9	468.1
			12.605	150.4	164.0	64.7	127.7	121.6	-64.6	147.7	162.5	66.5	35.7	434.8	473.9	494.6	446.5	472.4
			12.351	150.6	165.4	58.5	127.6	122.3	-61.2	147.8	162.4	64.9	31.6	442.6	473.8	500.0	443.8	472.2
			12.710	160.6	168.6	45.0	126.7	121.2	-68.0	145.9	160.8	69.3	33.8	425.3	472.9	537.6	443.6	470.8
Si_NP_15a	3	10	12.884	150.7	166.5	58.9	127.6	120.5	-71.3	147.8	166.6	72.4	36.0	444.1	470.3	479.6	442.6	468.9
			12.211	150.6	169.9	62.3	127.4	120.8	-73.3	146.4	166.6	75.4	37.5	445.5	472.3	559.4	444.5	469.7
			12.490	148.6	168.0	59.6	128.6	122.2	-72.7	147.1	165.6	77.4	39.3	451.0	470.8	279.4	442.0	467.7
			12.360	151.3	167.9	59.4	128.8	122.5	-71.2	146.8	164.9	71.6	36.4	429.9	470.0	392.7	4441.4	466.7
			12.253	148.8	163.8	71.1	127.0	120.9	-70.9	147.1	162.0	75.7	40.6	426.9	470.1	577.9	440.5	469.6
Si_NP_15a	10	5	12.559	149.2	164.1	70.7	127.1	121.0	-69.0	147.2	162.7	72.5	38.9	431.2	471.8	488.3	438.1	470.3
			12.935	151.4	166.9	53.7	127.7	122.0	-60.7	149.2	163.1	65.0	31.7	445.7	474.1	461.3	450.8	471.7
			12.522	150.7	172.1	62.7	128.2	122.5	-71.7	147.6	164.6	71.5	34.9	453.8	475.4	500.7	449.6	472.1
			12.062	152.0	167.8	67.5	127.9	122.0	-72.0	150.0	164.4	73.1	36.4	438.5	473.7	445.3	447.5	470.2
			12.371	151.4	168.8	53.1	127.1	119.0	-68.4	147.7	166.7	70.8	35.2	444.5	473.8	435.1	445.9	470.0
Si_NP_15b	5	10	12.254	150.3	168.4	61.8	127.1	119.5	-71.3	148.8	165.5	71.9	36.6	444.5	470.9	424.3	442.8	468.4
			12.484	152.7	167.6	65.7	127.0	119.0	-67.7	148.0	167.3	70.9	36.0	441.2	471.9	572.4	444.2	468.9
			12.640	147.5	163.6	68.2	124.9	118.2	-70.6	145.0	162.0	71.9	38.6	439.9	467.4	306.6	435.5	463.6
			12.621	148.9	163.9	67.5	126.4	120.2	-67.7	147.4	162.5	69.6	37.3	438.4	468.7	462.7	438.0	465.3

^a T_x is the x onset temperature ^b T_x is the x peak temperature ^c X_c is the degree of crystallinity

Table 4.2: Calculated average, S.D. and error for the thermal analysis data for pristine and modified microsilica and nanosilica PP nanocomposites.

DSC																	TGA	DTG
Sample	Filler Loading (Wt. %)	Initial Heating and Cooling (30-250-30 °C)										Secondary Heating and Decomposition (30-850-30 °C)						
		Melting I			Crystallisation				Melting II			X _c (%)	Decomposition					
		T _{om} (°C) ^a	T _{pm} (°C) ^b	ΔH (J/g)	T _{oc} (°C)	T _{pc} (°C)	ΔH (J/g)	T _{om} (°C)	T _{pm} (°C)	ΔH (J/g)	T _{od} (°C)		T _{pd} (°C)	ΔH (J/g)	T _{od} ^b (°C)	T _{pd} ^c (°C)		
PP_Pristine 1	Average	157.9	171.9	64.5	121.1	116.5	-80.1	150.8	163.0	77.0	37.2	458.0	470.9	366.6	444.6	468.5		
PP_Pristine 2	SD	0.0	0.2	2.3	0.0	0.1	0.7	0.5	0.1	0.6	0.3	6.9	1.1	4.7	0.7	0.2		
PP_Pristine 3	Error ^d	0.0	0.1	1.6	0.0	0.1	0.5	0.3	0.1	0.4	0.2	4.9	0.8	3.3	0.5	0.1		
PP_Processed 1	Average	149.6	166.9	67.0	127.6	122.9	-71.0	149.1	163.2	71.1	34.3	428.6	474.0	533.4	446.3	472.3		
PP_Processed 2	SD	1.1	1.1	3.0	1.7	1.9	7.2	1.8	0.7	0.7	0.3	10.5	0.8	87.8	2.1	1.0		
PP_Processed 3	Error	0.6	0.6	1.7	1.0	1.1	4.2	1.0	0.4	0.4	0.2	6.1	0.5	50.7	1.2	0.6		
Si_MP_Pristine/PP	Average	148.7	165.9	52.3	126.9	120.8	-66.9	148.9	163.7	65.5	31.9	421.2	474.4	506.4	442.0	471.6		
	SD	1.5	2.1	1.9	0.3	0.1	0.8	1.2	2.1	1.7	0.8	29.9	1.0	63.7	7.4	1.6		
	Error	1.1	1.5	1.4	0.2	0.1	0.6	0.9	1.5	1.2	0.6	21.2	0.7	45.0	5.2	1.1		
	Average	150.6	166.3	49.1	127.6	120.9	-60.1	147.3	165.7	57.9	28.8	446.7	476.6	488.6	438.9	474.3		
	SD	0.1	0.3	9.6	0.3	1.7	6.4	0.7	2.4	8.3	4.1	17.2	1.8	80.8	0.1	1.3		
	Error	0.0	0.2	6.8	0.2	1.2	4.5	0.5	1.7	5.9	2.9	12.2	1.3	57.1	0.1	0.9		
Si_MP_Pristine/PP	Average	150.6	167.7	52.8	128.0	121.6	-63.8	148.1	164.4	62.1	31.6	455.1	474.8	573.9	438.3	473.2		
	SD	0.3	3.5	9.2	0.4	0.5	13.0	0.1	0.9	12.9	6.5	4.4	0.8	36.6	1.8	0.4		
	Error	0.2	2.5	6.5	0.3	0.4	9.2	0.1	0.6	9.1	4.6	3.1	0.6	25.9	1.3	0.3		
	Average	150.9	169.9	70.0	128.5	123.7	-83.8	147.0	163.8	79.9	38.9	450.2	473.2	683.3	443.3	471.0		
	SD	0.3	1.5	0.9	0.1	0.4	0.1	0.3	1.0	0.3	0.1	7.0	0.6	65.6	1.2	0.6		
	Error	0.2	1.1	0.6	0.0	0.3	0.1	0.2	0.7	0.2	0.1	5.0	0.4	46.4	0.9	0.4		
Si_MP_15a_5/PP	Average	150.6	167.5	59.2	127.6	121.0	-72.4	148.8	163.7	68.4	34.0	450.6	473.2	523.8	440.4	471.3		
	SD	0.4	0.0	5.0	0.2	1.3	0.0	0.8	1.2	1.1	0.5	7.2	0.2	110.0	1.4	1.3		
	Error	0.3	0.0	3.5	0.2	0.9	0.0	0.6	0.9	0.8	0.4	5.1	0.1	77.8	1.0	0.9		
	Average	151.3	170.7	61.4	128.3	122.0	-78.0	148.2	165.3	74.7	38.0	455.7	474.0	421.4	439.2	471.6		
	SD	1.2	1.8	2.7	0.0	0.6	1.6	0.7	1.1	2.7	1.4	0.5	1.0	2.6	2.9	2.0		
	Error	0.9	1.3	1.9	0.0	0.4	1.1	0.5	0.8	1.9	1	0.3	0.7	1.8	2.0	1.4		

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Sample		Filler Loading (Wt. %)	DSC															TGA			DTG
			Initial Heating and Cooling (30-250-30 °C)															Secondary Heating and Decomposition (30-850-30 °C)			
			Melting I					Crystallisation					Melting II					X _c (%)	Decomposition		
			T _{on} (°C) ^a	T _{pm} (°C) ^b	ΔH (J/g)	T _{oc} (°C)	T _{pc} (°C)	ΔH (J/g)	T _{om} (°C)	T _{pm} (°C)	ΔH (J/g)	T _{od} (°C)	T _{pd} (°C)	ΔH (J/g)	T _{od} ^b (°C)	T _{pd} ^c (°C)					
Si_MP_15a_20/PP	1	Average	149.1	165.8	59.0	126.9	120.9	-71.0	148.0	163.9	68.1	33.2	440.2	474.1	490.2	435.4	470.8				
		SD	0.7	0.5	8.1	0.7	2.4	4.9	0.0	2.9	4.8	2.4	8.8	1.2	98.7	5.1	1.1				
		Error ^d	0.5	0.3	5.8	0.5	1.7	3.5	0.0	2.0	3.4	1.7	6.2	0.8	69.8	3.6	0.8				
	3	Average	151.2	165.8	65.2	127.5	122.5	-77.7	146.8	163.0	76.1	37.9	445.9	471.3	428.9	436.7	469.6				
		SD	0.8	2.0	1.6	0.1	0.3	1.8	0.3	1.4	1.4	0.7	5.6	2.2	10.7	1.2	0.7				
		Error	0.6	1.4	1.1	0.1	0.2	1.3	0.2	1.0	1.0	0.5	4.0	1.6	7.6	0.8	0.5				
Si_NP_Pristine/PP	5	Average	150.3	167.4	61.7	128.1	122.1	-71.7	147.4	164.8	66.6	33.9	454.0	472.2	537.3	441.4	472.6				
		SD	1.2	1.8	3.6	0.3	1.9	5.7	0.4	2.0	4.7	2.4	0.2	0.8	16.7	2.9	0.3				
		Error	0.8	1.2	2.6	0.2	1.4	4.0	0.3	1.4	3.3	1.7	0.2	0.5	11.8	2.1	0.2				
	1	Average	152.1	170.7	64.4	126.8	120.8	-70.8	149.4	164.9	75.6	36.9	450.0	474.8	478.3	443.9	470.5				
		SD	1.4	2.8	2.0	0.5	0.1	1.0	0.1	0.7	0.6	0.3	1.8	0.5	26.4	0.7	0.4				
		Error	1.0	2.0	1.4	0.4	0.1	0.7	0.1	0.5	0.4	0.2	1.3	0.3	18.6	0.5	0.3				
Si_NP_15a	3	Average	151.1	167.0	63.3	127.8	121.0	-68.3	147.8	165.0	72.7	36.2	437.0	471.2	554.1	444.3	468.3				
		SD	0.5	0.3	4.9	0.1	0.9	2.1	0.8	2.0	3.8	1.9	5.9	0.5	49.1	2.3	0.6				
		Error	0.3	0.2	3.4	0.1	0.6	1.5	0.5	1.4	2.7	1.3	4.2	0.4	34.7	1.6	0.4				
	5	Average	150.3	169.6	64.2	127.3	118.7	-69.3	147.1	167.0	71.8	36.5	437.0	471.1	571.0	442.3	468.3				
		SD	0.1	3.1	6.0	0.0	0.3	9.7	0.4	0.4	6.8	3.4	4.9	0.5	7.9	1.5	0.2				
		Error	0.1	2.2	4.2	0.0	0.2	6.9	0.3	0.3	4.8	2.4	3.4	0.3	5.6	1.1	0.1				
Si_NP_15a	10	Average	148.7	163.2	65.0	126.7	120.0	-68.2	146.3	161.7	66.3	35.6	433.2	471.6	440.4	443.7	470.2				
		SD	2.4	1.2	0.4	1.4	2.3	5.0	1.9	1.2	0.3	0.1	2.2	3.1	76.7	3.9	3.1				
		Error	1.7	0.9	0.3	1.0	1.6	3.6	1.4	0.8	0.2	0.1	1.6	2.2	54.2	2.8	2.2				
	1	Average	155.6	167.0	51.8	127.1	121.8	-64.6	146.9	161.6	67.1	32.6	433.9	473.3	518.8	443.7	471.5				
		SD	7.1	2.3	9.5	0.6	0.8	4.8	1.3	1.1	3.1	1.7	12.3	0.6	26.6	0.1	1.0				
		Error	5.0	1.6	6.8	0.4	0.6	3.4	0.9	0.8	2.2	1.2	8.7	0.5	18.8	0.1	0.7				

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Sample		DSC															TGA		DTG							
		Initial Heating and Cooling (30-250-30 °C)															Secondary Heating and Decomposition (30-850-30 °C)									
		Filler Loading (Wt. %)		Melting I					Crystallisation					Melting II					X _c (%)	Decomposition						
				T _{on} (°C) ^a	T _{pm} (°C) ^b	ΔH (J/g)	T _{oc} (°C)	T _{pc} (°C)	ΔH (J/g)	T _{om} (°C)	T _{pm} (°C)	ΔH (J/g)	T _{od} (°C)	T _{pd} (°C)	ΔH (J/g)	T _{od} ^b (°C)	T _{pd} ^c (°C)									
Si_NP_15a	Average		150.7	168.2	60.6	127.5	120.7	-72.3	147.1	166.6	73.9	36.8	444.8	471.3	519.5	443.6	469.3									
	SD	3	0.1	2.4	2.4	0.1	0.2	1.4	1.0	0.0	2.1	1.1	1.0	1.4	56.4	1.3	0.6									
	Error ^d		0.1	1.7	1.7	0.1	0.1	1.0	0.7	0.0	1.5	0.7	0.7	1.0	39.9	0.9	0.4									
	Average		150.0	168.0	59.5	128.7	122.4	-71.9	146.9	165.2	74.5	37.8	440.5	470.4	336.0	441.7	467.2									
	SD	5	1.9	0.0	0.1	0.1	0.2	1.1	0.2	0.5	4.1	2.1	14.9	0.6	80.1	0.4	0.7									
	Error		1.3	0.0	0.1	0.1	0.2	0.8	0.2	0.3	2.9	1.5	10.6	0.4	56.7	0.3	0.5									
	Average		149.0	163.9	70.9	127.0	120.9	-70.0	147.1	162.4	74.1	39.7	429.1	470.9	533.1	439.3	469.9									
	SD	10	0.3	0.2	0.2	0.0	0.0	1.4	0.1	0.5	2.3	1.2	3.0	1.2	63.4	1.7	0.5									
	Error		0.2	0.1	0.2	0.0	0.0	1.0	0.0	0.4	1.6	0.9	2.2	0.9	44.8	1.2	0.3									
	Si_NP_15b	Average		151.0	169.5	58.2	128.0	122.3	-66.2	148.4	163.8	68.2	33.3	449.8	474.7	481.0	450.2	471.9								
SD		1	0.5	3.6	6.4	0.3	0.3	7.8	1.2	1.0	4.5	2.2	5.7	0.9	27.9	0.8	0.3									
Error			0.3	2.6	4.5	0.2	0.2	5.5	0.8	0.7	3.2	1.6	4.0	0.7	19.7	0.6	0.2									
Average			151.7	168.3	60.3	127.5	120.5	-70.2	148.9	165.5	71.9	35.8	441.5	473.7	440.2	446.7	470.1									
SD		3	0.4	0.7	10.2	0.6	2.2	2.5	1.6	1.6	1.6	0.8	4.2	0.1	7.2	1.1	0.2									
Error			0.3	0.5	7.2	0.4	1.5	1.8	1.2	1.2	1.2	0.6	3.0	0.0	5.1	0.8	0.1									
Average			151.5	168.0	63.7	127.1	119.3	-69.5	148.4	166.4	71.4	36.3	442.8	471.4	498.3	443.5	468.6									
SD		5	1.7	0.6	2.8	0.0	0.3	2.6	0.6	1.3	0.7	0.4	2.3	0.7	104.7	1.0	0.4									
Error			1.2	0.4	2.0	0.0	0.2	1.8	0.4	0.9	0.5	0.3	1.6	0.5	74.0	0.7	0.3									
Average			148.2	163.8	67.8	125.7	119.2	-69.1	146.2	162.2	70.7	38.0	439.2	468.0	384.6	436.8	464.5									
SD	10	1.0	0.2	0.5	1.0	1.5	2.1	1.7	0.3	1.6	0.9	1.0	0.9	110.4	1.7	1.2										
Error		0.7	0.2	0.3	0.7	1.0	1.5	1.2	0.2	1.1	0.6	0.7	0.7	78.0	1.2	0.9										

^a T_x is the x onset temperature ^b T_x is the x peak temperature ^c X_c is the degree of crystallinity ^d Error = $\sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}}$.

Table 4.3: Raw data of the resistivity measurements, and calculations, for determining the volume electrical conductivity of modified CB/PP.

CB/PP Nanocomposite	Filler Loading (Wt. %)	Measured Plaque Side	Measured Resistance (Ω/sq)	Plaque Thickness (cm)	Volume Resistivity (Ωcm)	Volume Conductivity (Scm^{-1})	Log Conductivity (Scm^{-1})	Average Log Conductivity (Scm^{-1})	Error ^a
Pure PP ^b	10	1	3.60×10^{15}	0.11	4.10×10^{14}	2.44×10^{-15}	-14.61	-14.60	0.03
		2	3.10×10^{15}	0.12	3.57×10^{14}	2.81×10^{-15}	-14.55		
	15	1	2.11×10^4	0.12	2.49×10^3	4.01×10^{-4}	-3.40	-3.84	0.44
		2	1.54×10^5	0.12	1.88×10^4	5.31×10^{-4}	-4.27		
	20	1	5.34×10^3	0.13	6.67×10^2	1.50×10^{-3}	-2.82	-2.47	0.35
		2	1.02×10^3	0.13	1.32×10^2	7.59×10^{-3}	-2.12		
Pristine CB/PP	25	1	1.45×10^3	0.11	1.58×10^2	6.32×10^{-3}	-2.20	-2.15	0.05
		2	1.11×10^3	0.11	1.27×10^2	7.89×10^{-3}	-2.10		
	30	1	5.60×10^2	0.13	7.05×10^1	1.42×10^{-2}	-1.85	-1.84	0.01
		2	5.23×10^2	0.13	6.80×10^1	1.47×10^{-2}	-1.83		
	10	1	5.24×10^{12}	0.13	6.81×10^{11}	1.47×10^{-12}	-11.83	-13.15	1.32
		2	2.30×10^{15}	0.13	2.99×10^{14}	3.34×10^{-15}	-14.48		
Processed CB ^c /PP	15	1	9.05×10^4	0.12	1.04×10^4	9.61×10^{-5}	-4.02	-3.40	0.02
		2	8.06×10^4	0.12	9.59×10^3	1.04×10^{-4}	-3.98		
	20	1	3.18×10^4	0.11	3.53×10^3	2.83×10^{-4}	-3.55	-3.38	0.17
		2	1.30×10^4	0.13	1.36×10^3	6.12×10^{-4}	-3.21		
	25	1	3.34×10^3	0.12	4.07×10^2	2.46×10^{-3}	-2.61	-2.62	0.01
		2	3.58×10^3	0.12	4.30×10^2	2.33×10^{-3}	-2.63		
CB _{9a} /PP	30	1	3.40×10^2	0.12	4.04×10^1	2.48×10^{-2}	-1.61	-1.58	0.03
		2	2.73×10^2	0.13	3.53×10^1	2.84×10^{-2}	-1.55		
	10	1	2.38×10^{15}	0.13	3.07×10^{14}	3.26×10^{-15}	-14.49	-13.82	0.67
		2	1.09×10^{15}	0.13	1.41×10^{13}	7.11×10^{-14}	-13.15		
	15	1	1.65×10^{14}	0.12	1.93×10^{13}	5.19×10^{-14}	-13.28	-12.24	1.05
		2	1.31×10^{12}	0.12	1.54×10^{11}	6.49×10^{-12}	-11.19		
CB _{9a} /PP	20	1	5.52×10^4	0.12	6.62×10^3	1.51×10^{-4}	-3.82	-4.20	0.37
		2	3.09×10^5	0.12	3.71×10^4	2.69×10^{-5}	-4.57		
	25	1	1.25×10^3	0.14	1.71×10^2	5.84×10^{-3}	-2.23	-2.20	0.04
		2	1.05×10^3	0.14	1.45×10^2	6.90×10^{-3}	-2.16		
	30	1	1.52×10^3	0.13	1.94×10^2	5.15×10^{-3}	-2.29	-2.25	0.04
		2	1.21×10^3	0.13	1.63×10^3	6.15×10^{-3}	-2.21		

CB/PP Nanocomposite	Filler Loading (Wt. %)	Measured Plaque Side	Measured Resistance (Ω/sq)	Plaque Thickness (cm)	Volume Resistivity (Ωcm)	Volume Conductivity (Scm^{-1})	Log Conductivity (Scm^{-1})	Average Log Conductivity (Scm^{-1})	Error ^a
CB_9b/PP	5	1	3.79×10^{14}	0.13	4.09×10^{13}	2.45×10^{-14}	-13.61	-13.91	0.30
		2	1.29×10^{15}	0.13	1.62×10^{14}	6.16×10^{-15}	-14.21		
	10	1	6.41×10^4	0.12	7.56×10^3	1.32×10^{-4}	-3.88	-3.93	0.05
		2	8.33×10^4	0.11	9.50×10^3	1.05×10^{-4}	-3.98		
	15	1	3.51×10^3	0.13	4.26×10^2	2.19×10^{-3}	-2.66	-2.79	0.13
		2	6.46×10^3	0.13	8.27×10^2	1.21×10^{-3}	-2.92		
	20	1	1.03×10^3	0.12	1.22×10^2	8.22×10^{-3}	-2.09	-1.52	0.57
		2	7.40×10^1	0.12	8.95×10^0	1.12×10^{-1}	-0.95		
	25	1	6.07×10^2	0.12	7.46×10^1	1.34×10^{-2}	-1.87	-1.86	0.01
		2	6.14×10^2	0.11	7.00×10^1	1.43×10^{-2}	-1.84		
	30	1	3.07×10^2	0.13	3.87×10^1	2.58×10^{-2}	-1.59	-1.6	0.01
		2	3.42×10^2	0.12	4.11×10^1	2.44×10^{-2}	-1.61		

^a Error calculated using the following equation: $\text{Error} = \frac{\sqrt{\frac{\sum(\alpha - \bar{\alpha})^2}{(n-1)}}}{\sqrt{n}}$ of the conductivity measurements across perpendicular sides of the nanocomposite plaque samples ($\sim 1 \times 1 \times \sim 0.1$ cm).

^b Pure PP Volume Resistivity = Manufacturers Data

^c Processed CB = Pristine CB treated in the modification process in the absence of the diazo modification compound.

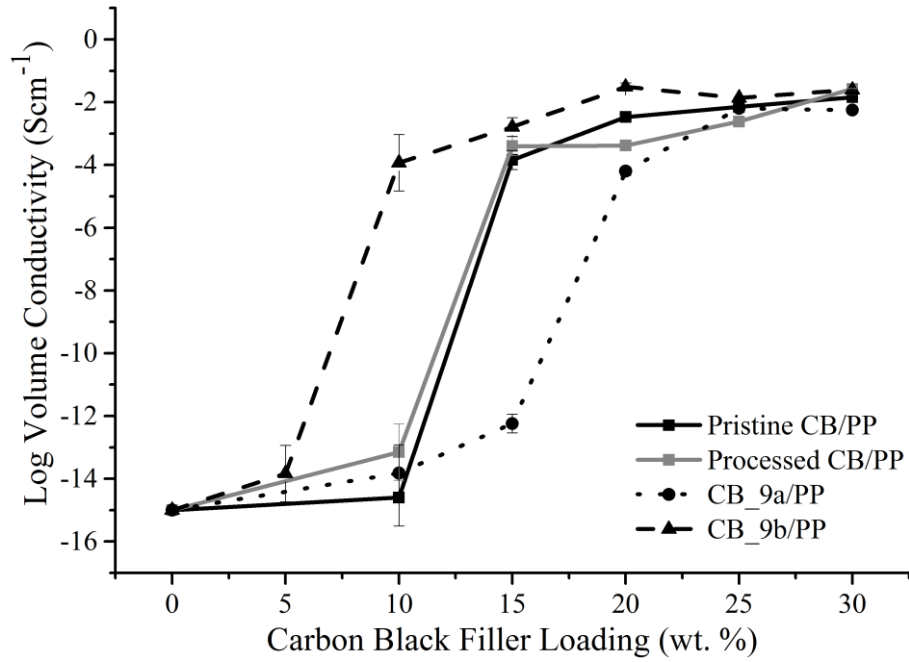


Figure 4.1: Logarithm of the volume electrical conductivity of CB/PP nanocomposites with pristine, processed and modified CB as a function of nanofiller loading. The error bars indicate the error of the measurement method calculated from the results of the pristine and processed CB sample measurements (include in Table 4.4).

Table 4.4: Calculated standard deviation (S.D.) and measurement error from the pristine and processed CB sample electrical conductivity measurements.

Filler Loading (Wt. %)	S.D.	Measurement Error
10	1.30	0.90
15	0.42	0.30
20	0.18	0.13
25	0.04	0.03
30	0.02	0.02

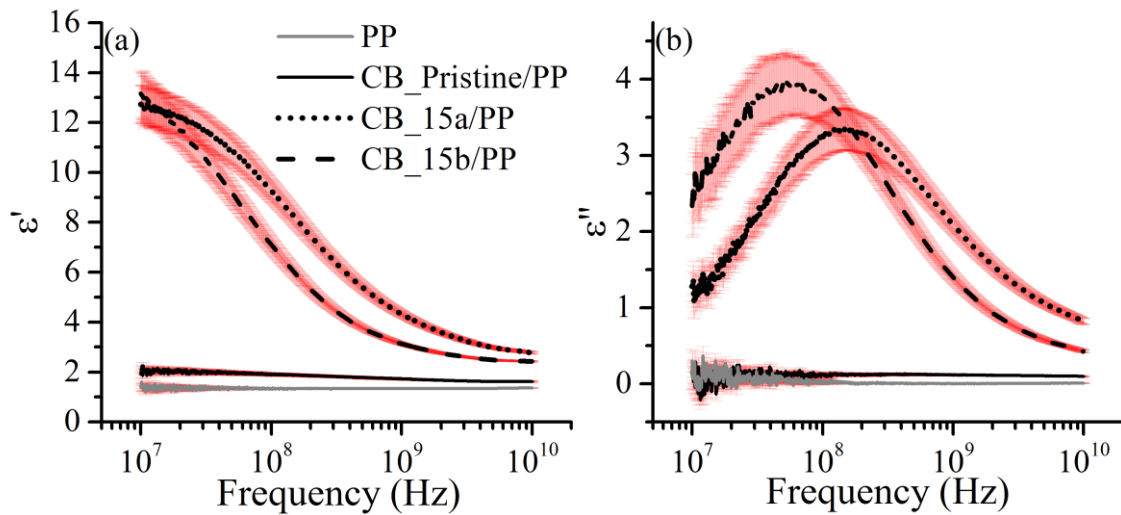


Figure 4.2: The average dielectric analysis result displaying the measurement error in red,

calculated using $\frac{\sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}}}{\sqrt{n}}$.

STA

Table 4.5: Extracted DSC, TGA and DTG data from thermal analysis runs of pristine and modified CB/PP nanocomposites.

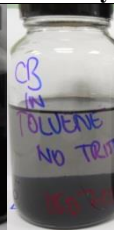
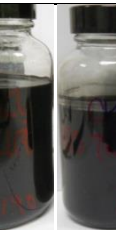
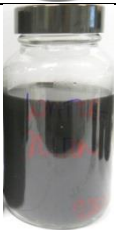
DSC DATA Decomposition															TGA	DTG	
Sample	Filler Loading (Wt. %)	Initial Heating and Cooling (30-250-30 °C)										Secondary Heating and Decomposition (30-850-30 °C)					
		Melting I			Crystallisation			Melting II			X _c (%)	Decomposition					
		T _{on} (°C) ^a	T _{pm} (°C) ^b	ΔH (J/g)	T _{oc} (°C)	T _{pc} (°C)	ΔH (J/g)	T _{om} (°C)	T _{pm} (°C)	ΔH (J/g)		T _{od} (°C)	T _{pd} (°C)	ΔH (J/g)	T _{od} ^b (°C)	T _{pd} ^c (°C)	
CB_Pristine/PP	10	149.7	165.9	59.1	128.9	124.1	-67.1	145.6	161.9	68.0	36.5	446.7	475.9	268.6	449.2	475.1	
	15	150.6	166.8	49.6	125.1	119.6	-64.9	149.3	164.2	62.7	35.6	449.9	477.3	256.6	450.5	475.7	
	20	151.8	168.4	44.5	132.5	125.5	-59.1	146.7	165.5	59.4	35.9	438.6	477.7	300.3	456.4	477.2	
	25	150.4	166.0	44.8	131.5	123.8	-59.2	146.8	165.1	60.0	38.6	462.8	476.1	178.1	458.9	476.1	
	30	150.6	166.1	50.1	133.8	126.6	-58.1	147.6	166.0	59.2	40.8	457.0	484.5	320.9	464.9	483.2	
CB_15a/PP	10	153.9	165.6	51.2	121.3	115.8	-69.8	151.9	162.5	57.7	31.0	451.7	476.5	255.8	453.0	474.5	
	15	150.1	166.2	45.0	125.2	117.4	-63.4	149.0	166.2	57.8	32.8	450.1	476.4	263.7	450.5	474.4	
	20	150.0	165.6	46.7	126.3	120.7	-57.4	150.0	163.7	57.3	34.6	453.4	476.1	194.8	456.5	476.9	
	25	151.5	166.5	43.1	127.7	121.2	-56.7	148.2	165.8	56.8	36.6	454.4	478.1	277.5	458.9	477.4	
	30	149.0	166.9	52.8	129.1	121.7	-58.5	149.3	167.4	54.8	37.8	459.3	488.9	273.2	467.4	487.6	
CB_15b/PP	10	149.1	165.7	50.6	133.3	126.7	-57.7	146.6	165.7	67.3	36.1	456.4	482.8	311.4	458.6	481.6	
	15	151.1	165.9	55.1	127.8	122.8	-61.0	146.8	163.7	62.3	34.3	443.6	476.2	283.2	454.3	473.9	
	20	149.7	167.3	55.4	134.0	127.3	-64.2	148.5	166.9	62.2	37.5	460.3	485.2	320.9	464.3	484.3	
	25	150.1	165.7	54.1	132.1	124.7	-59.3	148.8	165.6	60.4	38.9	455.9	485.4	318.9	465.0	483.9	
	30	150.0	165.7	54.1	133.9	126.5	-60.4	148.7	166.2	59.6	41.1	459.3	486.5	285.9	466.8	485.2	

^a T_x is the x onset temperature ^b T_x is the x peak temperature ^c X_c is the degree of crystallinity ^d Error = $\frac{\sqrt{\frac{\sum(x_i - \bar{x})^2}{(n-1)}}}{\sqrt{n}}$

Appendix V - Chapter 6

Triton CB Study A

Table 5.1: The CB/Triton X-100 dispersions in water, toluene, xylene and chloroform solvents immediately after the dispersions was prepared and after 7 days.

	Solvent							
	Water		Toluene		Xylene		Chloroform	
	T=0	T=7 Days	T=0	T=7 Days	T=0	T=7 Days	T=0	T=7 Days
No Triton X100								
Triton X-100 (0.24 mM)								

Modified CB Characterisation

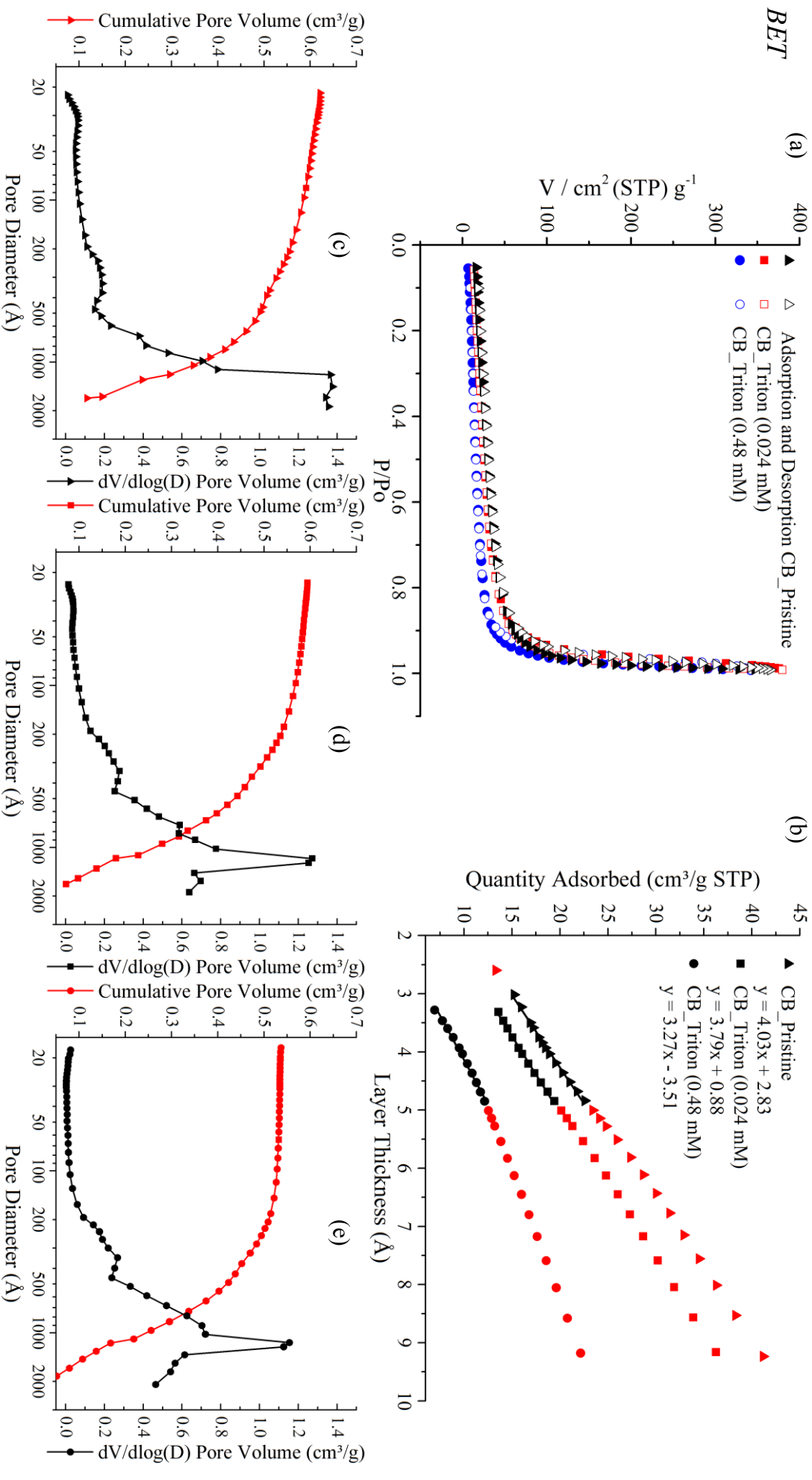


Figure 5.1: (a) The BET adsorption and desorption isotherms of nitrogen (b) the t-Plot data and the BJH adsorption pore volume data of (c) of CB_Pristine (d) CB_Triton (0.024 mM) and (e) CB_Triton (0.48 mM).

*Thermal Analysis***Table 5.2:** Thermogravimetric analysis weight loss raw data of pristine and triton X-100 modified CB nanoparticles in Study A and B.

Sample	Initial Sample Weight (mg)	TGA weight loss			
		30-150 °C		150-500 °C	
		mg	%	mg	%
CB_Pristine 1 ^a	12.509	0.042	0.336	0.066	0.530
CB_Pristine 2	12.782	0.047	0.365	0.068	0.531
CB_Pristine 3	12.917	0.044	0.340	0.061	0.476
CB_Processed (Water)	11.862	0.037	0.314	0.089	0.752
CB_Processed (Toluene)	11.459	0.035	0.305	0.092	0.800
CB_Triton (Water, 0.24 mM)	12.402	0.019	0.153	0.699	5.689
CB_Triton (Toluene, 0.24 mM)	13.035	0.073	0.564	1.763	13.528
CB_Triton (0.024 mM)	12.656	0.023	0.180	0.173	1.370
CB_Triton (0.072 mM)	11.137	0.049	0.442	0.352	3.157
CB_Triton (0.12 mM)	12.987	0.037	0.285	0.586	4.512
CB_Triton (0.24 mM)	12.402	0.033	0.266	0.699	5.639
CB_Triton (0.48 mM)	11.761	0.012	0.105	1.018	8.652

^a The same CB samples as presented in Chapter 3 and 4 but with the calculated weight losses of different temperature ranges in this analysis.

Table 5.3: Surface modification loadings of the Triton X-100 modified CB nanoparticles, as calculated from the determined mass losses by the thermal analysis experiments.

Sample	Decomposition				Surface Loading ^b		
	Sample Wt, loss due to Mod. (%) ^a	Sample wt, loss due to Mod. (g)	Moles of Modifier present in sample	Molecules present in sample	Molecules /g	Moles /g	Molecules /cm ²
CB_Triton (Water, 0.24 mM)	5.127	6.36×10^{-4}	1.02×10^{-6}	6.13×10^{17}	5.24×10^{19}	8.71×10^{-5}	7.23×10^{13}
CB_Triton (Toluene, 0.24 mM)	13.016	1.07×10^{-3}	2.72×10^{-6}	1.64×10^{18}	1.46×10^{20}	2.43×10^{-4}	2.01×10^{14}
CB_Triton (0.024 mM)	0.858	1.09×10^{-4}	1.74×10^{-7}	1.05×10^{17}	8.40×10^{18}	1.39×10^{-5}	1.16×10^{13}
CB_Triton (0.072 mM)	2.645	2.95×10^{-4}	4.71×10^{-7}	2.84×10^{17}	2.64×10^{19}	4.39×10^{-5}	3.64×10^{13}
CB_Triton (0.12 mM)	4.000	5.19×10^{-4}	8.31×10^{-7}	5.01×10^{17}	4.05×10^{19}	6.72×10^{-5}	5.58×10^{13}
CB_Triton (0.24 mM)	5.127	6.36×10^{-4}	1.02×10^{-6}	6.13×10^{17}	5.25×10^{19}	8.72×10^{-5}	7.24×10^{13}
CB_Triton (0.48 mM)	8.140	1.01×10^{-3}	1.53×10^{-6}	9.23×10^{17}	8.60×10^{19}	1.43×10^{-4}	1.19×10^{14}

^a The TGA surface loading calculations were the same as used in Chapter 3 and 4 except the temperature of decomposition was measured at 150-500 °C.

^b Assumes monolayer surface coverage of the experimentally determined BET surface areas of CB_Pristine (72.5 m²/g).

UV-Vis

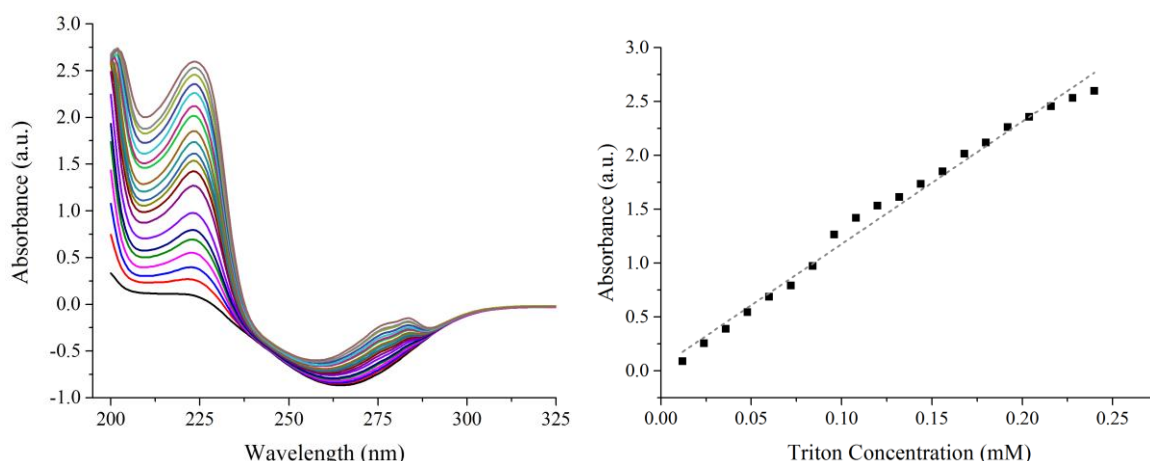


Figure 5.2: A calibration graph displaying the absorbance of the $\lambda_{\max}$ peak at 224 nm, as a function of Triton X-100 solution (aq.) concentration. The line of best fit gave an intercept of 0.04 and the slope 11.36.

Calculation of the CB Triton X-100 Surface Loading by UV-Vis Analysis

Concentration of the Triton X-100 supernatant solution.

$$= \lambda_{\max} \text{ peak at } 224 \text{ nm for CB_Triton (0.48 mM) supernatant solution} = 1.29$$

$$= \text{From the calibration plot } y = 11.36x - 0.04$$

$$= (1.29 - 0.04) / 11.36 = \mathbf{0.11 \text{ mM}}$$

Actual concentration which modified CB_Triton (0.48 mM)

$$= 0.48 \text{ mM} - 0.11 \text{ mM} = 0.37 \text{ mM}$$

Number of moles of Triton surface modified CB (0.15 g) in 200 mL Triton X-100 solution (0.37 mM)

$$= \text{Concentration} \times \text{Volume} = 0.37 \text{ mM} \times 0.2 \text{ L} = 7.42 \times 10^{-2} \text{ mmol}, \mathbf{7.42 \times 10^{-5} \text{ moles}}$$

Number of molecules of surface modification present on 0.15 g of CB_Triton (0.48 mM)

$$= \text{Moles of surface modification} \times N_A = (7.42 \times 10^{-5}) \times N_A = \mathbf{4.47 \times 10^{19} \text{ molecules}}$$

Number of molecules of surface modification present per gram on CB.

$$= \text{Molecules of modification present} / \text{mass of CB sample (0.15 g)} \times 1$$

$$= 4.47 \times 10^{19} / 0.15 \times 1 = \mathbf{2.98 \times 10^{20} \text{ Molecules/g}}$$

Number of molecules of surface modification per cm^2 (BET surface area of CB is 725300 cm^2/g)

$$= ((\text{molecules/g}^{\text{CB}}) / \text{BET surface area}) = (2.98 \times 10^{20} / 725300)$$

$$= \mathbf{4.10 \times 10^{14} \text{ Molecules/cm}^2}$$

Table 5.4: Surface modification loadings of the Triton X-100 modified CB nanoparticles, as calculated from the determined adsorption peaks by UV-Vis analysis.

Sample	UV Data				Surface Loading ^b			
	Sample λ_{max} peak at 224 nm	Supernatant Triton conc. solution (mM)	Triton Conc. used to Mod. CB (mM)	Moles of Modifier present in CB	Molecules present in sample	Molecules /g	Moles /g	Molecules /cm ²
CB_Triton (0.24 mM)	0.10	0.01	0.23	4.70×10^{-5}	2.83×10^{19}	1.89×10^{20}	3.13×10^{-4}	2.60×10^{14}
CB_Triton (0.48 mM)	1.29	0.11	0.37	7.42×10^{-5}	4.47×10^{19}	2.98×10^{20}	4.94×10^{-4}	4.10×10^{14}

Table 5.5: Range of surface modification loadings of the Triton X-100 modified CB nanoparticles, as calculated from the absence of adsorption peaks by UV-Vis analysis. The calibration experiments indicated that no absorbance peak at 224 nm could be observed for solutions of a lower concentration than 0.012 Mm.

Sample	UV Data			Surface Loading ^b		
	Triton Conc. used to Mod. CB (mM)	Moles of Modifier present in CB	Molecules present in sample	Molecules /g	Moles /g	Molecules /cm ²
CB_Triton (0.024 mM)	0.012-0.024	$2.40-4.80 \times 10^{-6}$	$1.45-2.26 \times 10^{18}$	9.64×10^{18} - 1.93×10^{19}	$1.60-3.20 \times 10^{-5}$	$1.33-2.66 \times 10^{13}$
CB_Triton (0.072 mM)	0.06-0.072	$2.20-1.44 \times 10^{-5}$	$7.23-8.67 \times 10^{18}$	$4.82-5.78 \times 10^{19}$	$8.00-9.60 \times 10^{-5}$	$6.64-7.97 \times 10^{13}$
CB_Triton (0.12 mM)	0.108-0.12	$2.16-2.40 \times 10^{-5}$	$1.30-1.45 \times 10^{19}$	$8.67-9.64 \times 10^{19}$	$1.44-1.60 \times 10^{-4}$	$1.20-1.33 \times 10^{14}$

XPS

Table 5.6: XPS C 1s and O 1s binding energies and charging values for Triton X-100 modified CB.

Sample	Binding Energies (eV)							Charging (eV)
	C 1s						O 1s	Relative to C 1s (284.5)
	C-C C-H	C-O	C=O	COOH	$\pi-\pi^*$	$\pi-\pi^*$	C-O C=O	
CB_Pristine	284.5	286.0	287.2	288.8	290.6	292.4	532.8	7.6
CB_Triton (0.024 mM)	284.5	286.2	287.7	289.3	290.9	292.4	532.6	6.7
CB_Triton (0.072 mM)	284.5	286.2	287.7	289.3	290.9	292.6	532.5	6.9
CB_Triton (0.12 mM)	284.5	286.3	287.6	289.1	290.8	292.5	532.4	6.4
CB_Triton (0.24 mM)	284.5	286.3	287.6	289.1	290.5	291.8	532.3	9.1
CB_Triton (0.48 mM)	284.5	286.2	287.4	289.3	291.1	293.1	532.7	7.3

Table 5.7: XPS FWHM values for Triton X-100 modified CB.

Sample	FWHM (eV)						
	C 1s						O 1s
	C-C C-H	C-O	C=O	COOH	$\pi-\pi^*$	$\pi-\pi^*$	C-O C=O
CB_Pristine	1.7	1.6	1.8	2.0	1.9	2.0	4.1
CB_Triton (0.024 mM)	1.6	1.6	1.5	1.6	1.6	1.5	2.5
CB_Triton (0.072 mM)	1.6	1.5	1.5	1.5	1.5	1.6	2.2
CB_Triton (0.12 mM)	1.6	1.5	1.4	1.5	1.5	1.4	2.0
CB_Triton (0.24 mM)	1.6	1.6	1.4	1.5	1.5	1.6	1.8
CB_Triton (0.48 mM)	1.6	1.5	1.7	1.8	1.7	1.5	1.9

Electrical Conductivity - Study B

Table 5.8: Raw data of the resistivity measurements, and calculations, for determining the volume electrical conductivity of the Triton X-100 modified CB/PP nanocomposite samples prepared by melt mixing.

CB/PP Nanocomposite	Measured Plaque Side	Measured Resistance (52/sq)	Plaque Thickness (cm)	Volume Resistivity (Ωcm)	Volume Conductivity (Scm ⁻¹)	Log Conductivity (Scm ⁻¹)	Average Log Conductivity (Scm ⁻¹)	Error ^a
Pure PP ^b								
CB_Pristine	1	4.07 × 10 ⁷	0.12	4.84 × 10 ⁶	2.06 × 10 ⁻⁷	-6.69	-15	-15
	2	9.82 × 10 ²	0.12	1.17 × 10 ²	8.56 × 10 ⁻³	-2.07	-4.38	2.31
CB_Triton (0.024 mM)	1	3.86 × 10 ⁶	0.12	4.63 × 10 ⁵	2.16 × 10 ⁻⁶	-5.67	-4.82	0.85
	2	7.84 × 10 ⁴	0.12	9.41 × 10 ³	1.06 × 10 ⁻⁴	-3.97		
CB_Triton (0.072 mM)	1	1.40 × 10 ¹⁴	0.12	1.68 × 10 ¹³	5.95 × 10 ⁻¹⁴	-13.23	-11.96	1.27
	2	4.10 × 10 ¹¹	0.12	4.92 × 10 ¹⁰	2.03 × 10 ⁻¹¹	-10.69		
CB_Triton (0.12 mM)	1	7.20 × 10 ¹³	0.12	8.64 × 10 ¹²	1.16 × 10 ⁻¹³	-12.94	-12.94	0.01
	2	7.40 × 10 ¹³	0.12	8.88 × 10 ¹²	1.13 × 10 ⁻¹³	-12.95		
CB_Triton (0.24 mM)	1	5.00 × 10 ¹¹	0.12	6.00 × 10 ¹⁰	1.67 × 10 ⁻¹¹	-10.78	-12.08	1.30
	2	2.00 × 10 ¹⁴	0.12	2.40 × 10 ¹³	4.17 × 10 ⁻¹⁴	-13.38		
CB_Triton (0.48 mM)	1	1.63 × 10 ⁸	0.12	1.96 × 10 ⁷	5.11 × 10 ⁻⁸	-8.34	-7.81	0.52
	2	1.81 × 10 ⁹	0.12	2.17 × 10 ⁸	4.60 × 10 ⁻⁹	-7.29		

^a Error calculated using the following equation: Error = $\frac{\sqrt{\frac{\sum(\alpha - \bar{\alpha}^2)}{(n-1)}}}{\sqrt{n}}$ of the conductivity measurements across perpendicular sides of the nanocomposite plaque samples ($\sim 1 \times 1 \times \sim 0.1$ cm³).

^b Pure PP Volume Resistivity = Manufacturers Data

Electrical Conductivity - Study B

Table 5.9: The raw data of the resistivity measurements, and calculations, for determining the volume electrical conductivity of the Triton X-100 modified CB/PP nanocomposite samples prepared at different loadings by melt and solvent mixing, is displayed on the next page.

CB/PP Nanocomposite	Filler Loading (Wt. %)	Measured Plaque Side	Measured Resistance (Ω /sq)	Plaque Thickness (cm)	Volume Resistivity (Ω cm)	Volume Conductivity (Scm^{-1})	Log Conductivity (Scm^{-1})	Average Log Conductivity (Scm^{-1})	Error ^a
MM_CB_Pristine/PP	5	1	0.00 ^a	0.12	1.00×10^{15}	1.00×10^{-15}	-15	-15	
		2	0.00	0.12	1.00×10^{15}	1.00×10^{-15}	-15	-15	
	10	1	4.07×10^7	0.12	4.84×10^6	2.06×10^{-7}	-6.69	-4.38	2.31
		2	9.82×10^2	0.12	1.17×10^2	8.56×10^{-3}	-2.07		
	15	1	2.43×10^4	0.12	2.94×10^3	3.40×10^{-4}	-3.47	-3.53	0.03
		2	3.26×10^4	0.12	3.98×10^3	2.51×10^{-4}	-3.60		
	20	1	1.41×10^4	0.11	1.58×10^3	6.34×10^{-4}	-3.20	-3.12	0.11
		2	9.55×10^3	0.11	1.09×10^3	9.18×10^{-4}	-3.04		
	25	1	5.58×10^3	0.12	6.59×10^2	1.52×10^{-3}	-2.82	-2.84	0.03
		2	6.41×10^3	0.12	7.37×10^2	1.36×10^{-3}	-2.87		
MM_CB_Triton (0.024 mM)/PP	5	1	3.84×10^{14}	0.12	4.57×10^{13}	2.19×10^{-14}	-13.66	-13.98	0.32
		2	1.70×10^{15}	0.12	2.02×10^{14}	4.94×10^{-15}	-14.31		
	10	1	4.63×10^6	0.12	5.33×10^5	1.88×10^{-6}	-5.73	-3.86	1.86
		2	8.34×10^2	0.12	9.93×10^1	1.01×10^{-2}	-2.00		
	15	1	2.03×10^4	0.12	2.38×10^3	4.21×10^{-4}	-3.38	-3.36	0.01
		2	1.88×10^4	0.12	2.23×10^3	4.48×10^{-4}	-3.35		
	20	1	1.08×10^2	0.12	1.25×10^1	8.02×10^{-2}	-1.10	-2.04	0.94
		2	8.48×10^3	0.11	9.50×10^2	1.05×10^{-3}	-2.98		
	25	1	8.48×10^2	0.13	1.08×10^2	9.29×10^{-3}	-2.03	-2.01	0.02
		2	7.66×10^2	0.13	1.01×10^1	1.01×10^{-2}	-1.99		
SM_CB_Triton (0.024 mM)/PP	10	1	1.28×10^{14}	0.12	1.59×10^{13}	6.30×10^{-14}	-13.20	-13.44	0.24
		2	4.12×10^{14}	0.12	4.86×10^{13}	2.06×10^{-14}	-3.69		
	15	1	3.48×10^7	0.12	4.11×10^6	2.44×10^{-7}	-6.61	-6.46	0.15
		2	1.57×10^7	0.13	2.05×10^6	4.87×10^{-7}	-6.31		
	20	1	1.20×10^4	0.12	1.45×10^3	6.90×10^{-4}	-3.16	-3.16	0.00
		2	1.20×10^4	0.12	1.44×10^3	6.93×10^{-4}	-3.16		
	25	1	9.71×10^2	0.12	1.13×10^2	8.88×10^{-3}	-2.05	-2.02	0.03
		2	8.29×10^2	0.12	9.70×10^1	1.03×10^{-2}	-1.99		
	30	1	4.50×10^2	0.12	5.36×10^1	1.87×10^{-2}	-1.73	-1.81	0.08
		2	6.70×10^2	0.12	7.78×10^1	1.29×10^{-2}	-1.89		

^a The resistance of the sample could not be measured even with a voltage applied and therefore is assumed to be non-conductive, the same as pure PP -15 Scm^{-1} .

Study C – Thermal Analysis (STA)

Table 5.10: Extracted DSC, TGA and DTG data from thermal analysis runs of pristine and triton modified CB/PP nanocomposites.

Sample		Filler Loading (mg)	Weight (Wt. %))	DSC										TGA		DTG							
				Initial Heating and Cooling (30-250-30 °C)										Secondary Heating and Decomposition (30-850-30 °C)									
				Melting I			Crystallisation				Melting II			X _c (%)	Decomposition								
T _{on} (°C) ^a	T _{pm} (°C) ^b	ΔH _m (J/g)	T _{oc} (°C)	T _{pc} (°C)	ΔH _c (J/g)	T _{on} (°C)	T _{pm} (°C)	ΔH _m (J/g)	T _{od} (°C)	T _{pd} (°C)	ΔH _d (J/g)	T _{od} ^b (°C)	T _{pd} ^c (°C)										
SM_CB_Triton (0.024 mM)/PP	12.649	10	151.3	166.2	42.4	128.3	121.7	-54.9	148.4	164.5	59.8	32.1	447.0	476.4	242.5	449.3	472.7						
	12.623	15	151.9	166.6	44.1	127.1	121.3	-53.4	150.6	164.5	57.8	32.8	455.8	477.3	231.8	447.2	472.5						
	12.295	20	151.5	165.9	48.1	127.5	122.4	-51.9	149.5	163.6	55.2	36.2	459.4	474.5	174.1	450.3	472.2						
	12.465	25	151.3	165.8	43.4	128.3	121.2	-50.4	147.4	166.6	52.5	33.8	457.0	475.3	173.1	454.2	473.1						
	12.121	30	150.8	165.5	43.9	129.0	122.7	-41.7	147.9	164.6	47.0	32.4	443.0	478.6	224.2	452.7	476.7						
MM_PP_Processed	12.260	0	157.4	163.0	58.3	127.9	121.4	-77.7	135.2	160.7	60.2	29.1	442.6	466.7	456.2	433.0	465.0						
	12.649	5	149.2	165.4	62.6	129.7	124.2	-65.1	143.3	161.8	64.6	32.8	440.0	469.2	279.1	437.6	466.4						
	12.899	10	150.9	168.3	64.7	134.6	129.3	-68.4	147.5	166.3	71.8	38.5	447.1	476.5	278.3	456.4	474.2						
MM_CB_Pristine /PP	12.545	15	151.3	168.2	57.1	128.9	122.0	-60.7	147.5	166.7	58.9	33.4	457.4	479.6	271.6	457.2	477.0						
	12.757	20	149.4	166.1	54.1	130.2	119.0	-60.6	145.9	162.7	61.2	36.9	450.2	472.1	219.1	439.7	469.0						
	12.567	25	145.3	164.0	50.7	128.7	117.8	-57.2	142.5	161.7	56.3	36.3	450.9	472.7	236.2	437.4	470.1						
	12.494	5	141.2	160.9	63.3	126.8	119.2	-63.1	139.8	157.2	54.7	27.8	436.2	467.0	324.0	427.2	464.5						
MM_CB_Triton (0.024 mM)/PP	12.969	10	150.2	169.0	62.7	134.9	129.6	-70.6	147.7	166.3	71.5	38.3	454.0	476.4	270.5	450.6	473.3						
	12.553	15	152.1	168.2	51.1	129.4	122.8	-60.5	146.6	167.1	59.0	33.5	454.3	476.3	312.8	451.9	474.0						
	12.709	20	152.1	167.0	52.8	129.3	123.8	-60.4	147.9	165.1	58.1	35.1	455.6	479.8	356.1	458.5	477.2						
	12.585	25	148.9	165.6	51.0	130.3	119.7	-59.8	145.8	163.0	58.4	37.6	446.5	471.9	295.1	438.7	469.2						

^a T_x is the x onset temperature ^b T_x is the x peak temperature ^c X_c is the degree of crystallinity ^d Error = $\frac{\sqrt{\sum(x_i - \bar{x})^2}}{\sqrt{n}}$.

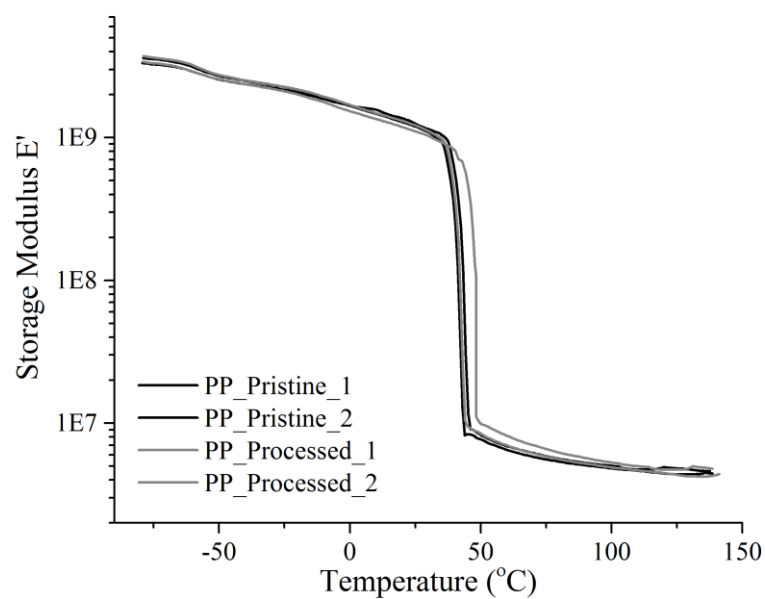
DMA Analysis

Figure 5.3: Storage Modulus E' for the PP control samples, PP_Pristine (PP pellets as received) and PP_Processed (PP subjected to the solvent mixing protocol without CB filler addition).

Appendix VI - Chapter 7

Modified ACB Characterisation

BET

Table 6.1: BET summary data for the repeated granulated pristine ACB and Triton modified ACB granulated sample measurements.

Sample	BET Surface Area (m ² /g)	t-Plot External Surface Area (m ² /g)	t-Plot Micropore area (Å) ?	BJH Adsorption Average Pore Diameter (Å)	BJH Desorption Average Pore Diameter (Å)
ACB_Processed (Granulated)_1	77.5	72.8	4.7	144.1	141.3
ACB_Processed (Granulated)_2	78.0	72.9	5.2	144.3	141.8
ACB_Processed (Granulated)_3	77.4	72.6	4.8	145.5	142.9
ACB_Triton (Granulated)_1	43.6	51.6	-	173.0	190.9
ACB_Triton (Granulated)_2	44.3	51.7	-	190.8	201.8
ACB_Triton (Granulated)_3	44.2	51.8	-	186.2	197.3

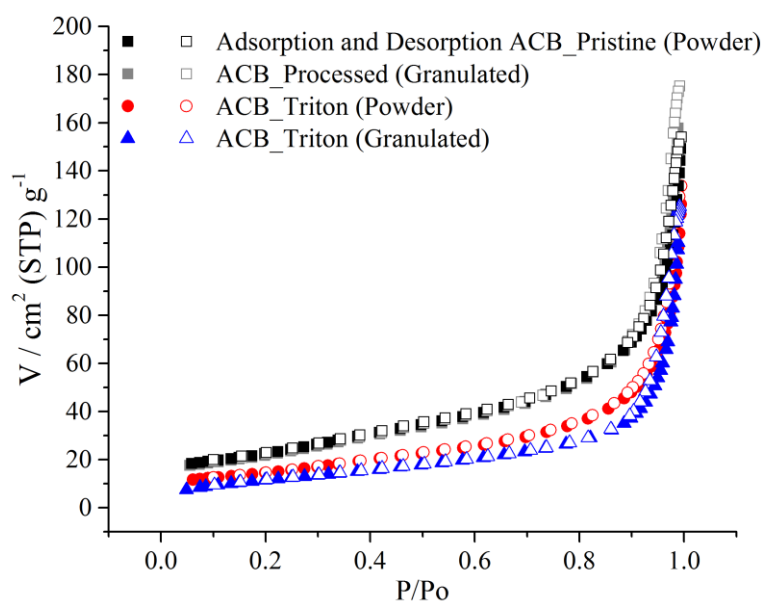


Figure 6.1: BET adsorption and desorption isotherms of pristine ACB, granulated pristine ACB and Triton modified ACB powder and granulated samples.

XPS

Table 6.2: XPS C 1s and O 1s binding energies and charging values for Triton X-100 modified ACB.

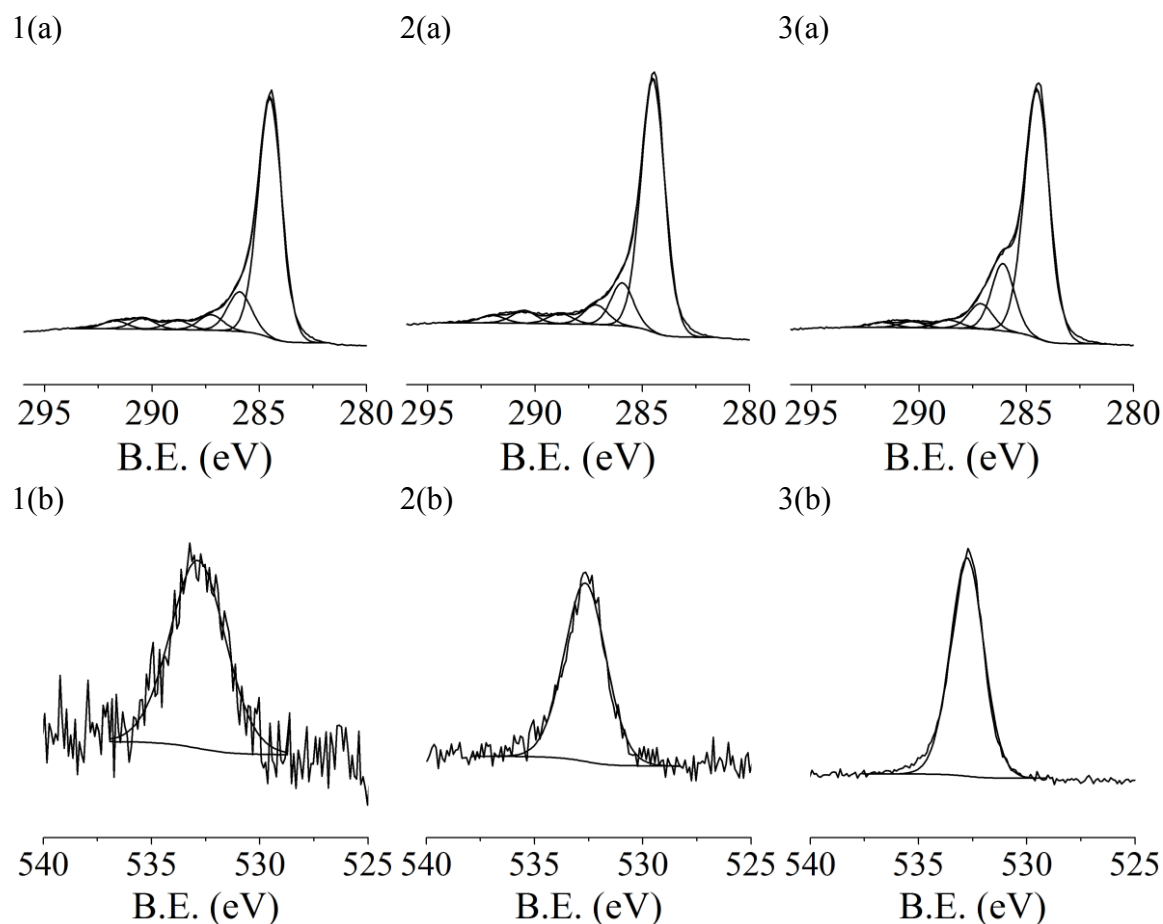
Sample	Binding Energies (eV)							Charging (eV)
	C 1s						O 1s	Relative to C 1s (284.5)
	C-C C-H	C-O	C=O	COOH	π - π^*	π - π^*	C-O C=O	
ACB_Processed (Granulated)	284.5	285.9	287.2	288.8	290.4	291.7	532.8	5.6
ACB_Triton (Powder)	284.5	285.9	287.2	288.8	290.5	292.0	532.7	5.8
ACB_Triton (Granulated)	284.5	286.1	287.1	288.6	290.3	291.7	532.8	4.3

Table 6.3: XPS FWHM values for Triton X-100 modified ACB.

Sample	FWHM (eV)						O 1s
	C 1s						C-O
	C-C C-H	C-O	C=O	COOH	π - π^*	π - π^*	C=O
ACB_Processed (Granulated)	1.3	1.3	1.3	1.3	1.3	1.3	3.0
ACB_Triton (Powder)	1.3	1.2	1.3	1.3	1.3	1.3	2.3
ACB_Triton (Granulated)	1.4	1.2	1.3	1.4	1.3	1.3	1.8

Table 6.4: The relative peak areas of devolved C 1s peaks in the high resolution XPS spectra of the unmodified and modified carbon-based samples for Triton X-100 modified ACB.

Sample	C-C/C-H (284.5)	C-O (286.2)	C=O (287.6)	COOH (289.2)	π - π^* (290.8)	π - π^* (292.5)
ACB_Processed (Granulated)	74.0	12.3	4.9	2.9	3.4	2.5
ACB_Triton (Powder)	73.6	11.7	5.8	3.0	3.7	2.3
ACB_Triton (Granulated)	70.8	17.2	6.7	2.3	1.6	1.4


Figure 6.2: XPS (a) C 1s and (a) O 1s high resolution spectra of 1. ACB_Processed (Granulated) 2. ACB_Triton (Powder) 3. ACB_Triton (Granulated).

Thermal Analysis (STA)

Table 6.5: Thermogravimetric analysis weight loss raw data and calculated modification loadings of the Triton X-100 modified ACB nanoparticles.

Sample	TGA Weight Loss Data					Decomposition		Surface Loading ^e				
	Initial Sample Weight (mg)	30-150 °C		150-500 °C		Sample Wt, Loss due to Mod. (%)	Sample Wt, Loss due to Mod. (g)	Moles of Modifier present in sample	Molecules present in sample	Molecules /g	Moles /g	Molecules /cm ²
		mg	%	mg	%							
ACB_Pristine (Powder) ^a	12.591	+0.020 ^b	0.16	0.007	0.057							
ACB_Processed (Granulated)	12.799	+0.027	0.21	0.021	0.166							
ACB_Triton (Powder)	12.807	0.017	0.133	1.310	1.018	0.961	1.23 × 10 ⁻⁴	1.97 × 10 ⁻⁷	1.19 × 10 ¹⁷	1.03 × 10 ¹⁹	1.72 × 10 ⁻⁵	1.30 × 10 ¹³
ACB_Triton (Granulated)	12.229	0.029	0.234	1.001	8.184	8.127	9.94 × 10 ⁻⁴	1.59 × 10 ⁻⁶	9.58 × 10 ¹⁷	8.55 × 10 ¹⁹	1.42 × 10 ⁻⁴	1.07 × 10 ¹⁴

^a The same ACB sample is the same as presented in Chapter 4 but with the calculated weight losses of different temperature ranges in this analysis.
^b + weight losses recorded for these samples is noted as an increase in mass in the 30-150 °C temperature range, due to the observed buoyancy effect for these samples.
^c Assumes monolayer surface coverage of the experimentally determined BET surface areas of ACB_Pristine (79.8 m²/g).

Electrical Conductivity

Table 6.6: The raw data of the resistivity measurements, and calculations, for determining the volume electrical conductivity of the Triton X-100 modified CB/PP nanocomposite samples prepared at different loadings by melt and solvent mixing, is displayed on the next page.

CB/PP Nanocomposite	Filler Loading (Wt. %)	Measured Plaque Side	Measured Resistance (Ω/sq)	Plaque Thickness (cm)	Volume Resistivity (Ωcm)	Volume Conductivity (Scm ⁻¹)	Log Conductivity (Scm ⁻¹)	Average Log Conductivity (Scm ⁻¹)	Error ^a
ACB_Processed (Granulated)/PP MM	2	1	4.95 × 10 ¹³	0.11	5.64 × 10 ¹²	1.77 × 10 ⁻¹³	-12.75	-12.72	0.05
		2	4.26 × 10 ¹³	0.11	4.85 × 10 ¹²	2.06 × 10 ⁻¹³	-12.69		
	2.5	1	2.19 × 10 ¹⁰	0.11	2.45 × 10 ⁹	4.08 × 10 ⁻¹⁰	-9.39	-9.18	0.30
		2	8.19 × 10 ⁹	0.11	9.34 × 10 ⁸	1.07 × 10 ⁻⁹	-8.97		
	3	1	6.76 × 10 ⁸	0.11	7.64 × 10 ⁷	1.31 × 10 ⁻⁸	-7.88	-7.97	0.12
		2	1.02 × 10 ⁹	0.11	1.14 × 10 ⁸	8.78 × 10 ⁻⁹	-8.06		
	3.5	1	3.55 × 10 ⁸	0.12	4.11 × 10 ⁷	2.43 × 10 ⁻⁸	-7.61	-7.79	0.26
		2	8.14 × 10 ⁸	0.12	9.44 × 10 ⁷	1.06 × 10 ⁻⁸	-7.98		

CB/PP Nanocomposite	Filler Loading (Wt. %)	Measured Plaque Side	Measured Resistance (S/sq)	Plaque Thickness (cm)	Volume Resistivity (S2cm)	Volume Conductivity (Scm-1)	Log Conductivity (Scm-1)	Average Log Conductivity (Scm-1)	Error ^a		
ACB_Processed (Granulated)/PP MM	5	1	1.02 × 10 ⁶	0.11	1.15 × 10 ⁻⁵	8.66 × 10 ⁻⁶	-5.06	-4.95	0.15		
		2	6.13 × 10 ⁵	0.11	6.99 × 10 ⁴	1.43 × 10 ⁻⁵	-4.84				
	7	1	1.48 × 10 ⁵	0.15	2.22 × 10 ⁴	4.51 × 10 ⁻⁵	-4.35	-4.35	0.01		
		2	1.52 × 10 ⁵	0.15	2.27 × 10 ⁴	4.40 × 10 ⁻⁵	-4.36				
ACB_Triton (Powder)/PP MM	2	1	6.15 × 10 ¹³	0.11	6.76 × 10 ¹²	1.48 × 10 ⁻¹³	-12.83	-12.76	0.09		
		2	4.48 × 10 ¹³	0.11	4.98 × 10 ¹²	2.01 × 10 ⁻¹³	-12.70				
		1	4.49 × 10 ⁸	0.12	5.21 × 10 ⁷	1.92 × 10 ⁻⁸	-7.72			-7.69	0.04
		2	3.87 × 10 ⁸	0.12	4.53 × 10 ⁷	2.21 × 10 ⁻⁸	-7.66				
	2.5	1	2.55 × 10 ⁸	0.12	2.98 × 10 ⁷	3.35 × 10 ⁻⁸	-7.47	-8.00	0.75		
		2	3.00 × 10 ⁹	0.11	3.42 × 10 ⁸	2.92 × 10 ⁻⁹	-8.53				
	3	1	3.54 × 10 ⁶	0.12	4.41 × 10 ⁵	2.42 × 10 ⁻⁶	-5.62	-5.63	0.02		
		2	3.82 × 10 ⁶	0.12	4.39 × 10 ⁵	2.28 × 10 ⁻⁶	-5.64				
	5	1	1.63 × 10 ⁵	0.12	1.89 × 10 ⁴	5.29 × 10 ⁻⁵	-4.28	-4.23	0.06		
		2	1.33 × 10 ⁵	0.12	1.54 × 10 ⁴	6.50 × 10 ⁻⁵	-4.19				
	7	1	1.96 × 10 ⁵	0.11	2.19 × 10 ³	4.57 × 10 ⁻⁴	-3.34	-3.38	0.05		
		2	2.33 × 10 ⁵	0.11	2.61 × 10 ³	3.83 × 10 ⁻⁴	-3.42				
ACB_Triton (Granulated)/PP MM	2	1	5.16 × 10 ¹³	0.12	5.93 × 10 ¹²	1.69 × 10 ⁻¹³	-12.77	-13.02	0.35		
		2	1.60 × 10 ¹⁴	0.12	1.84 × 10 ¹³	5.43 × 10 ⁻¹⁴	-13.26				
	2.5	1	2.75 × 10 ⁹	0.11	3.16 × 10 ⁸	3.16 × 10 ⁻⁹	-8.50	-8.44	0.08		
		2	2.12 × 10 ⁹	0.12	2.43 × 10 ⁸	4.11 × 10 ⁻⁹	-8.39				
	3	1	2.55 × 10 ⁹	0.12	2.91 × 10 ⁸	3.44 × 10 ⁻⁹	-8.46	-8.27	0.28		
		2	1.03 × 10 ⁹	0.12	1.19 × 10 ⁸	8.43 × 10 ⁻⁹	-8.07				
	3.5	1	1.08 × 10 ⁸	0.12	1.26 × 10 ⁷	7.93 × 10 ⁻⁸	-7.10	-7.16	0.08		
		2	1.41 × 10 ⁸	0.12	1.65 × 10 ⁷	6.07 × 10 ⁻⁸	-7.22				
	5	1	1.23 × 10 ⁶	0.12	1.47 × 10 ⁵	6.81 × 10 ⁻⁶	-5.17	-5.15	0.03		
		2	1.13 × 10 ⁶	0.12	1.34 × 10 ⁵	7.44 × 10 ⁻⁶	-5.13				
	7	1	1.10 × 10 ⁵	0.12	1.27 × 10 ⁴	7.90 × 10 ⁻⁵	-4.10	-4.21	0.16		
		2	1.80 × 10 ⁵	0.12	2.10 × 10 ⁴	4.75 × 10 ⁻⁵	-4.32				