

Polyvinyl alcohol Surface Modification

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“The earth is the LORD’s, and everything in it, the world, and all who live in it.”
Psalm 24:1

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Abstract

Poly(vinyl alcohol) (PVA) is a polymer used in numerous applications, principally those in which its high water solubility is a desirable asset. However there are also areas where PVA is limited by its inherent solubility (for example some specific environments in the biomedical field). This work has sought to overcome such limits by manipulating the surface of PVA in order to propose various means by which the surface solvent resistance might be increased while maintaining the bulk properties of the polymer. Both chemical and physical modifications have been tried and in each case progress has been made towards insolubilizing a single surface of the polymer when in film form.

Grafting various species onto the surface of PVA was successfully performed. It is believed that such species bonded to the PVA via attachment to the hydroxyl groups (though this has not been proven conclusively). The data contained herein has led to the conclusion that the primary factor in reducing solubility this way is the removal of the hydroxyl groups, and not the attachment of specifically highly hydrophobic molecules.

Introducing permanent cross-links into the surface region has been attempted via various routes. The data recorded shows promise however the system is far from optimised. The biggest challenge remaining is to optimise the depth of material cross-linked. Some steps have been made towards understanding and controlling this parameter though there is much scope for further investigation. The methods used have built on those used for bulk cross-linking and as such are new for the case of surface specific treatment.

An interesting phenomenon in some semi-crystalline polymers reported in recent years is that of surface specific crystallization. This effect has been successfully induced and observed in PVA to produce what is believed to be a highly crystalline surface layer, and crystalline regions of PVA are generally accepted to be more water resistant than amorphous ones.

In summary, in this work several surface-specific treatments for PVA have been trialled, providing options for post-film forming modification to reduce the surface water sensitivity whilst retaining the bulk properties of the polymer.

Chapter 1

Introduction

This project is concerned with modifying the surface of poly(vinyl alcohol) (PVA) in order to manipulate the polymer's solvent resistance. PVA is a common polymer used in various applications including adhesives, warp sizers and films [1]. It has good tensile and compressive strength, abrasion resistance, chemical resistance and biocompatibility [1, 2]. However whilst in some instances its water solubility has been an asset, in other areas it limits the use of PVA, including the biomedical [3] and packaging fields [4].

This work seeks to modify the solubility of PVA by manipulating the surface region only, thereby maintaining the bulk mechanical and solubility properties. Such a modification lends itself especially well to a triggered release system, whereby typically such a film must release its stored ingredient after an initial delay-time, or where it is important to have one side of a film (untreated side) dissolve away much quicker than the treated surface. Also the treatments attempted in this work are such that they can be applied post-film-forming so that existing film production methods will remain unaffected.

Partially hydrolysed (87-89%) PVA has been predominantly used in this work. This degree of hydrolysis of PVA is the most water soluble form at room temperature and as such can be used in packaging applications requiring release at room temperature

/ in cold water. Furthermore, the majority of the published work to date on solubility manipulation of PVA has been based on higher hydrolysed (98-99%) material, thus this work may add to the understanding of some of the general properties of 87-89% hydrolysed PVA.

Three main avenues have been pursued to induce surface-specific insolubility in PVA. The first has been to modify the hydrophilicity of the polymers via chemical grafting of various molecules onto the PVA surface. Fluorinated compounds underwent significant trials (given their known hydrophobicity [5]). The investigations show that modifying partially hydrolysed PVA via grafting is a viable means of altering the surface solubility. In particular the data presented leads to the conclusion that the primary factor in increasing the insolubility of the surface is not the content of the graft moieties themselves, but is instead the fact that the graft molecules have taken the place of the hydrophilic hydroxyl groups on the polymer's surface.

The second avenue pursued has been to constrain the swelling of the polymer surface by the introduction of surface-specific cross-links, as this is a well known means of reducing the swelling and solubility [6]. The overwhelming majority of the previous published work has been on the bulk cross-linking of PVA. This is relatively straightforward as the cross-linking can take place simultaneously with film casting or shortly afterwards (if the cross-linking species are embedded into the bulk polymer during casting). There is scarce evidence of the surface-specific cross-linking of PVA in the literature to date. Nonetheless surface-specific cross-linking has been trialled, primarily by adopting and modifying bulk cross-linking methods. Two cross-linking species were used (maleic acid and sodium benzoate) which operate in different ways - thus allowing two schemes to be trialled. Both routes showed promise, however further method optimisation is required before each is a viable option for a scaled up production environment.

The third area investigated was that of surface-specific phase change, by inducing crystals specifically into the surface region. PVA is a semi-crystalline polymer and as such contains both crystalline and amorphous phases. It is well established that it is

possible to manipulate the crystalline fraction and to some degree the distribution of crystals within a semi-crystalline polymer. This is useful as crystalline regions have different properties to amorphous ones, including a greater density, stiffness and solvent resistance. Recent work has found that it is possible to enhance the crystalline fraction on the surface of another semi-crystalline polymer (PET) whilst leaving the bulk of the substrate unaltered [7]. Experiments in this thesis show that such a treatment is also possible on PVA, with extensive surface crystallization having been observed in some cases. The detailed impact of this on the surface solubility properties is still to be established however the phenomena shows great potential as a unique means of surface modifying PVA (and potentially other semi-crystalline polymer systems) to reduce their solvent interaction.

Chapter 2

Literature review

For additional in-depth reading regarding the properties of PVA the reader is directed to Finch [8] and Marten [9] who have both discussed the properties and use of PVA in considerable detail.

2.1 Background information on poly(vinyl alcohol)

Poly(vinyl alcohol) is a copolymer comprising of alcohol and acetate repeat groups (as shown in figure 2.1). The fraction of alcohol groups is known as the degree of hydrolysis. This value has a strong influence on the properties of PVA, with an especially strong influence on the solubility behaviour. The solubility of PVA in cold water is a maximum with a degree of hydrolysis of 87-89% [9, 10]. It is believed that the presence of the acetate groups in the partially hydrolysed material disrupts the intermolecular bonding between hydroxyl groups on neighbouring chains, thus allowing bonding with water molecules and hence a greater solubility than fully hydrolysed material [9]. Further increasing the acetate content reduces the solubility as the acetate groups are hydrophobic [10]. Interestingly the distribution of the acetate groups can impact on the surface tension properties [9].

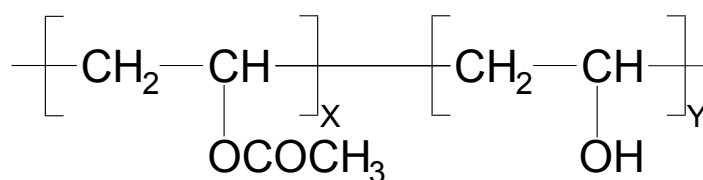


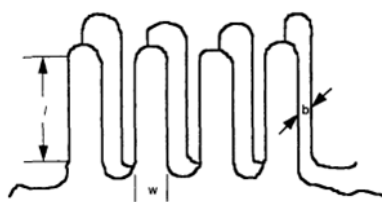
Figure 2.1: PVA repeat unit.

Polyvinyl alcohol was first synthesised by Haehnel & Herrman [11] in 1927. The most common process for producing PVA today is to hydrolyse polyvinyl acetate using an alkaline catalyst such as NaOH, KOH or methoxide [12]. It should be noted that the exact conversion method can have an impact on the final PVA properties (notably the temperature and solvent used in the polyvinyl acetate production) [13].

2.2 Semi-crystalline polymers

2.2.1 Bulk microstructure

PVA is a semi-crystalline polymer and semi-crystalline polymers are defined as those having regions of polymer chains in both amorphous and crystalline phases. The crystalline phase consists of polymer chains arranged in an ordered fashion with a regular repeat lamellae structure, such that it is possible to define a unit-cell ($w \times l \times b$).



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Figure 2.2: A typical lamella structure in a semi-crystalline polymer (taken from [14]).

R

An excellent overview of polymer crystallization is provided by Qian [15]. Crystallization is a nucleation and growth process which can be approached from several routes: dilute solution, the melt or rubbery state & the oriented state. Since polymer reptation times are long (compared with small molecules) crystallization cannot be described as proceeding to thermodynamic equilibrium, indeed kinetic hindrances

make full crystallization essentially impossible under typical experimental conditions.

The kinetics of crystalline growth are often described by the Avrami equation [16–18], like so:

$$1 - X_r = \exp(-kt^n) \quad (2.1)$$

Where X_r = fraction crystallized, n = Avrami exponent (an integer providing information on growth geometry) and k = rate constant. It is also possible to carry out an Avrami-approach by considering crystallization from the melt. This is a kinetic approach which relies on establishing a relationship between the density of crystalline and melt phases as a function of time.

$$\frac{W_l}{W_0} = e^{-kt^n} \quad (2.2)$$

Where W_0 = mass of melt at $t=0$, W_l = mass of melt left after time t (this falls with t).

The kinetics of crystallization in polyethylene are discussed at length by Hoffman *et al.* [19] and other general information on crystallization has been given by Piorkowska *et al.* [20]. The Hoffman-Lauritzen theory is discussed by Cheng *et al.* [21] and over the past forty years or so has been key in describing how polymers are thought to crystallize. Recent modelling of the crystallization process (from the melt) has been performed by Yamamoto [22].

The exact proportion of crystalline material will vary between systems depending on several factors; these include the previous thermal history of the sample, the molecular weight, the strength of the intermolecular bonding, the backbone stiffness, the symmetry of the backbone, the amount of branching and the level of tacticity, amongst other things. Typical crystallization percentages are between 30 and 70% [15] (and for PVA it has been found to vary between 0 and 54% [9] - though Peppas *et al.* claim a 65% crystallinity for a PVA hydrogel [23]). It is extremely rare to produce a fully crystalline polymer sample [24].

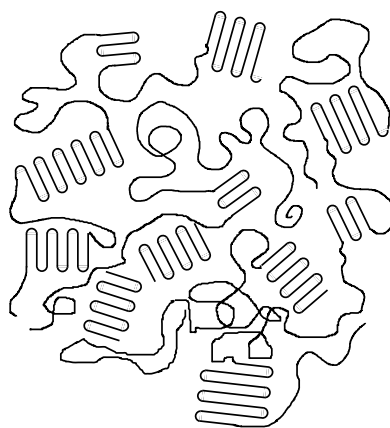


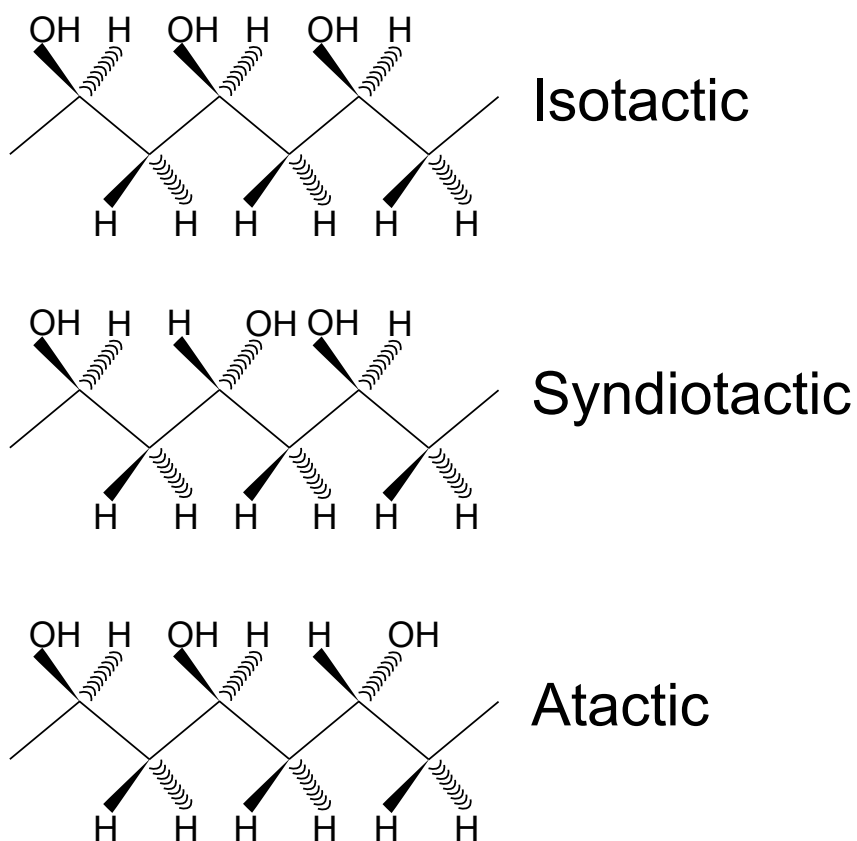
Figure 2.3: Typical microstructure of a semi-crystalline polymer (free volume exaggerated for clarity).

The amorphous and crystalline regions have different properties, crystalline regions are denser, stiffer and more brittle. However of particular interest is the different solubility between the two phases, crystalline regions are generally considered to be much less soluble than amorphous ones [25]. This is both a thermodynamic and kinetic effect. This is because the mixing equilibrium between the crystalline PVA and water will be different between that of amorphous PVA and water, whilst kinetically time is required for a crystalline chain to migrate out of its tightly packed state to then allow solvent molecules in. Spindura also found that samples with a higher crystallinity took up less water than their more amorphous counterparts [12].

2.2.1.1 Bulk crystallization of PVA

Previous work on the bulk crystallinity of PVA has been carried out by Endo *et al.* [26], Hu *et al.* [27], Kenney *et al.* [28] and Assender *et al.* [29, 30]. The tacticity of PVA influences the ease with which crystallinity can occur. Assender *et al.* [30] and Matsuzawaw [31] have looked at the influence of tacticity on crystallinity and Kenney *et al.* have stated the ease of crystallization for PVA as atactic > syndiotactic > isotactic [28]. The stereoregularity of the PVA also proved to be important when it was blended with poly(3-hydroxybutyric acid) in order to manipulate the crystallization behaviour [32] & [33]. (Prior NMR data [34–36] suggests that the structure of ‘standard’ PVA is typically atactic and all of the experiments in this work used atactic PVA).

The tacticity of a polymer describes its arrangement in 3-dimensional space. More specifically it illustrates the position of a polymer's functional group about the carbon-carbon bond axis. Three types of tacticity are possible, and they are each illustrated for the case of PVA in figure 2.4.



— = C-C bond in the plane

↗ = C-X bond coming out of the plane

↘ = C-X bond going into the plane

Figure 2.4: The three tacticities possible in PVA.

2.2.2 Surface microstructure

The morphology and chemistry of any polymer film surface is controlled by a few principal factors. The film production process will dictate the initial morphology. For example processes where flow of material is induced (such as spin coating [37] or melt-extrusion) will result in alignment of the polymer chains (unless the polymer is given sufficient time above T_g to fully relax). Any inherent chemistry differences will also impact on the surface properties, for example the inclusion of lower surface energy molecules will again mean that they are most likely to migrate to the surface [38].

The exact depth of material which actually constitutes the polymer ‘surface’ varies depending on the exact surface treatment and desired finished properties. Satomi *et al.* defined the ‘outermost surface region’ as, “the region extending to twice the radius of gyration of an unperturbed chain from the top surface into the film” [39].

$$\text{surface depth} = 2 \langle S^2 \rangle^{\frac{1}{2}} \quad (2.3)$$

Where S = the radius of gyration [25].

However on the macro-length scale unless a polymer has undergone any specific treatment typical processing routes tend to leave a relatively feature-less surface. Indeed a typical image of a PVA film (obtained via AFM) is shown in figure 2.5.

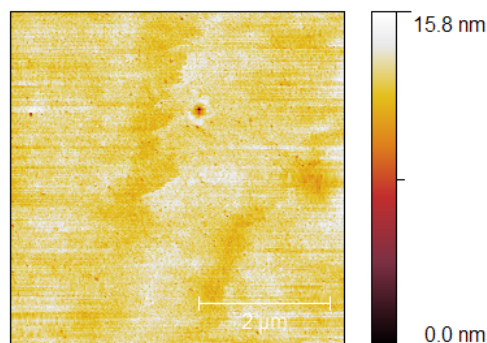


Figure 2.5: Topographical AFM image of untreated PVA.

Rougher surfaces are also possible and these are more likely to result if we have a polymer blend which segregates, if we have inclusions (such as filler particles) in the film or if we have a system which has been dried very quickly [40].

2.2.3 T_g and surface T_g

Every polymer with material in the amorphous phase will go through a transition upon heating through a certain narrow temperature range. By going through it the amorphous material changes from being hard and brittle below it to being viscous or rubbery above it. This transformation is called the glass transition [41] (though it is not a true phase transition [41, 42]).

Another way of thinking of the T_g is the temperature at which the polymer chains are given enough thermal energy to allow conformational motion of the chains to take place. The energy barrier which must be overcome is entanglement and interaction with neighbouring chains. Hence it follows that those chains on or near to the surface are less constrained than those in the bulk, and so it can reasonably be expected that they will have a lower T_g than the bulk T_g . This is a theory which has had good acceptance but is still undergoing research.

2.2.3.1 The thin film effect

Since it is difficult to measure the glass transition of a sample's surface directly many authors began by measuring the T_g of progressively thinner films in an attempt to represent the T_g of the surface region in a bulk film. Keddie *et al.* reported a depression in T_g for samples of PS as the thickness of the films fell to 10's of nm's [42]. T_g 's were measured via monitoring the change in volume by ellipsometry.

Sharp *et al.* [43] also looked at the T_g of PS films by embedding 10 and 20nm gold spheres into the surface of spin-cast PS films. Above the T_g (~ 370 K) the spheres were able to migrate through the whole film. However at temperatures approaching

the bulk T_g ($363\text{ K} < T < 370\text{ K}$) the spheres only embedded 3-4nm into the film. The authors suggested that a, “liquid-like surface layer exists in glassy PS films” [43] with a thickness of $\sim 3\text{-}4\text{nm}$. Weber *et al.* performed similar experiments and revealed the, “presence of a surface layer with an increased mobility of the polymer chains” [44]. Kawaguchi *et al.* [45] found that for a PS film with $M_n \leq 40\text{k}$ the surface T_g was below room temperature, whilst the bulk T_g was significantly above 20°C .

Other techniques for studying the T_g of thin films include Brillouin light scattering, positron annihilation spectroscopy and lateral force microscopy [46].

2.2.3.2 Molecular weight

A further factor of significance when considering the surface T_g is the molecular weight. An empirical equation is quoted by many authors for the influence of M_w on bulk T_g (where K is a constant):

$$T_g = T_{g\infty} - \frac{K}{M_n} [46-49] \quad (2.4)$$

Where $T_{g\infty}$ is the T_g for an infinite molecular mass and K is a constant. Lin [47] also plotted T_g as a function of M_w for nearly monodisperse PS (see figure 2.6). Further data on PS was obtained by Satomi *et al.* [39].

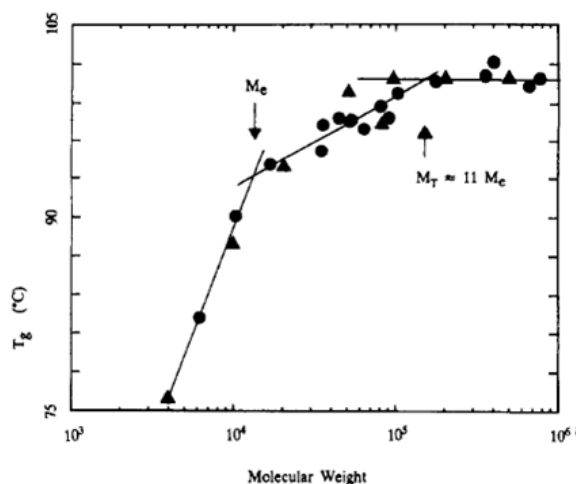


Figure 2.6: Reproduction of figure 2 from [47], showing T_g as a function of M_w .

Reprinted with permission from: Kalika, D. S. et al. (1990). Structural, dielectric, and rheological characterization of a thermotropic polyester displaying smetic A, nematic, and isotropic phases, *Macromolecules* 23:25, 5292-5294. Copyright 1990 American Chemical Society.

Bliznyuk *et al.* used scanning force microscopy (SFM) to probe the surface T_g of monodisperse PS samples. The presence or absence of hysteresis for approach-retract curves was used to determine whether the polymer surface was rubbery (above T_g) or glassy (below T_g) [48]. Their results agreed that there was a depression in T_g as the films got thinner (below $\sim 200\text{nm}$).

Mayes added another dimension to the surface T_g discussion, by arguing that chain-end enrichment at a polymer surface will lead to a depression in the T_g [49]. However importantly she also conceded that, "There is still only limited evidence for the segregation of chain ends to the surface of amorphous polymer systems" [49]. Some evidence for such migration is given by Fengchao *et al.*, who introduced lower energy end groups into PS which migrated to the surface [50]. This led to a significant decrease in sample T_g as anticipated [50].

Various groups have attempted to model the behaviour of surface T_g s. Notably Morita *et al.* [51] conclude that there is increased motion of polymer chains at the surface of a modelled polymer film which gives good agreement with previous SFM data.

2.2.3.3 Surface crystallization

Hyun *et al.* sought to measure the bulk and surface T_g of PET [52]. This is of more interest to this work as unlike PS (which is amorphous) PET is semi-crystalline; and hence may be closer in behaviour to PVA. Hyun *et al.* took depth-specific measurements (using variable wavelength ellipsometry [52]) and they reported that a lower density of material at the surface resulted in a lower T_g at the surface. Some success has also been obtained by Hayes *et al.* [53] who used XPS to record conformational changes in the surface of PET.

Macdonald *et al.* reported that, "at temperatures just above T_g , crystalline ordering in thin films of PET occurs at a faster rate near to the free surface than in the bulk of the film" [54]. They used grazing X-ray diffraction as a means of, "determining the

structure of the surface region.” [54] (as with grazing XRD it is possible to vary the penetration depth of the beam to as little as 50Å, Khalfin *et al.* [55] provide further discussion on the uses of X-rays in this manner).

Jukes *et al.* produced similar results to [54] and went on to discuss the process of forming crystallites, primarily by suggesting prior local alignment as a precursor to crystallization [56]. Also of significance from this paper are the quantitative fits showing the crystalline fraction at the surface (0.76) and in the bulk (0.35) at 90°C in PET.

Other authors have recorded evidence of enhanced crystallinity at the surface of various polymers [54, 56–58] and they have sought to examine the crystalline morphology in thin films in the hope of representing the morphology of ‘surface’ crystallinity.

Jradi *et al.* used an AFM to introduce surface crystals in isotactic PS. They observed that this was possible even for the case of being well below the glass transition temperature [59].

Padermshoke *et al.* used ATR to study the surface crystallization behaviour of polyhydroxyalkanoates. They suggest that, “the polymer crystals tend to grow at the surface in a manner different from that in the bulk” [60].

A very interesting technique was used by Hobbs *et al.* to study crystallization in PEO. They used a ‘video-rate AFM’ to examine PEO films during crystal growth [61]. They were able to estimate the growth rate of crystals at the lamellar-scale. This is a relatively new technique with good potential for tracking morphology changes of polymer surfaces.

Prediction of surface crystallinity in PVA

The T_g for bulk PVA has been reported as 85°C [9] for high M_w fully hydrolysed material and as 58°C for 87-89% hydrolysed material [9]. No work has been pre-

viously carried out to determine whether or not the surface T_g of PVA is different from the bulk. If (as with the case of semi-crystalline PET) it is determined to be less than the bulk then the possibility of producing samples with enhanced surface crystallinity exists, as when annealing from cold crystals only begin to be produced in a given region once the T_g has been surpassed [24]. This would be highly significant, as given the improved solvent resistance of higher crystallinity regions (see section 2.4.1.4) such a treatment would be an excellent method of improving the surface dissolution behaviour.

2.2.4 Methods to examine crystallinity

There are several methods currently in use to examine the crystallinity of a bulk specimen of PVA. XRD is a particularly common technique and gives a relatively quick method of determining a sample's crystallinity. The relative areas of the amorphous 'halo' and the crystalline peak(s) are compared to give the crystalline fraction.

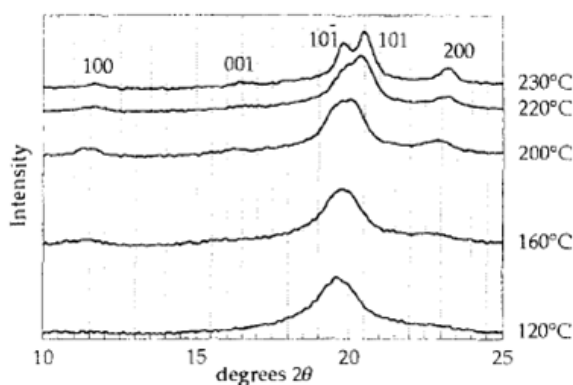


Figure 2.7: Example XRD profiles of PVA films annealed at various temperatures taken from [29].

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Several groups have all successfully used FTIR to study the crystallinity of a PVA-containing blended polymer [28, 32, 62, 63]. This technique relies on the response of specific infrared absorption bands for amorphous and crystalline C-O bands. These are generally accepted to be at 1096 ± 5 and 1144 ± 5 cm^{-1} [8].

DSC is another common technique used to analyse crystallinity and figure 2.8 is

typical of the sort of data obtained.

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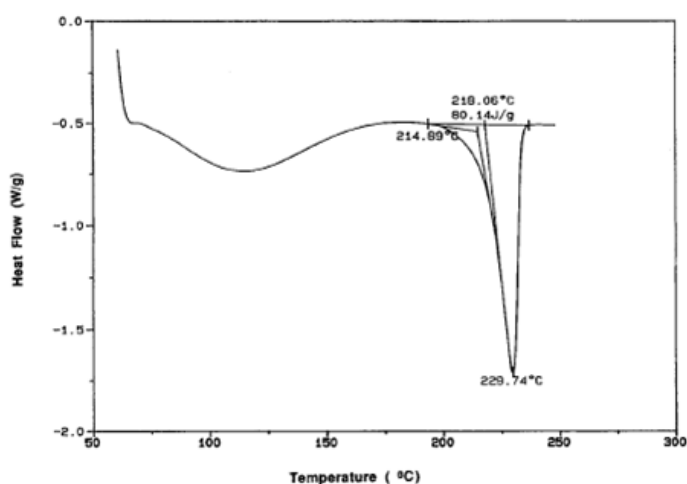


Figure 2.8: DSC thermogram for PVA crystallized for 60 min at 110°C taken from Mallapragada *et al.* [64].

Iwamoto *et al.* show how Laser Raman Spectroscopy can be used to determine the crystallinity of swollen PVA [65].

There is very little of the use of TEM to study polymer crystallinity, mainly because the electron beam quickly causes damage to the specimens. However Sakai *et al.* produced figure 2.9 showing 'terrace' like growth in the crystallization of very thin PET films from the melt [66].

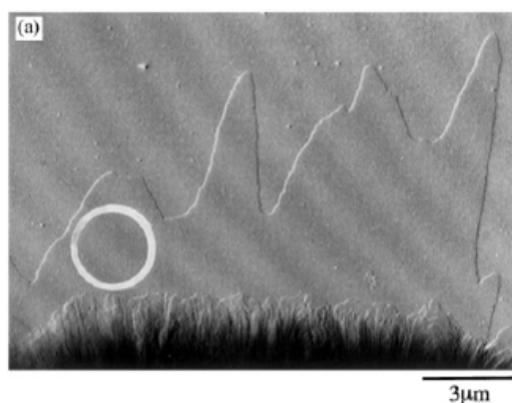


Figure 2.9: TEM photograph showing the terrace structure observed at the growth front of a 2D PET spherulite, taken from Sakai *et al.* [66].

Reprinted from Journal of Crystal Growth, 203(1), Sakai, Y. et al., Tip-splitting crystal growth observed in crystallization from thin films of poly(ethylene terephthalate), 244-254. © 1999, with permission from Elsevier.

2.3 Polymer surface modification

Surface modification is a very wide discipline and Koberstein [38] helpfully sums up its broad aims as either, “to increase the potential for surface interactions (e.g. adhesion promotion)” or, “to decrease the degree to which the surface interacts with a given material (e.g. release or antifouling applications).” [38].

There are several common means by which polymer surfaces have previously been modified and those methods of interest are discussed over the following pages.

2.3.1 Grafting

The grafting of foreign polymer chains onto a substrate film is a common procedure for polymer surface modification and has been discussed at length by Kato *et al.* [67]. Several authors have investigated the grafting of various moieties specifically onto the surface of PVA. Pemberton *et al.* report on the grafting on of a poly(organophosphazene) leading to an increased hydrophobic character of the PVA surface [68]. Zhou *et al.* grafted succinic anhydride onto PVA [69]. Yahya *et al.* looked at modifying the hydrophobicity of PVA (by grafting urethane and alkyl groups onto the main PVA backbone chains) [70]. Akiyama *et al.* introduced photoisomerizable azo units onto the surface of PVA by grafting [71].

Other work includes that by Matsuda *et al.* [72], Mukherjee *et al.* [73], Nishino *et al.* [74] and Subramanyam *et al.* [75]. In many instances the goal was to induce a level of hydrophobicity (to an otherwise relatively hydrophilic surface) in some cases across the entire surface and for others in specific regions [72]. The hydroxyl groups were targeted and often a catalyst of some form was needed (for example UV light).

2.3.1.1 Grafting - molecular level

As mentioned previously grafting takes place when a covalent bond is formed between the grafting species and the polymer to which it is being attached. Considering again the structure of PVA (fig 2.10) it can be seen that on the polymer backbone there are C-H, C-OH and C-OCOCH₃ groups attached. As such the graft molecule must attach in the place of or onto one of these. There are several means by which a necessary reaction can take place, but given that the hydroxyl group is the most reactive this is the easiest to attack.

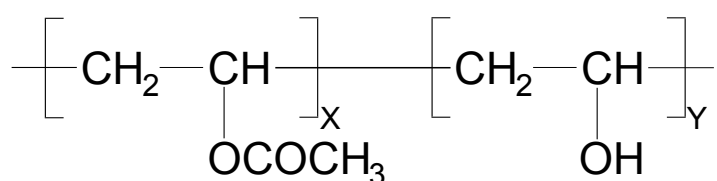


Figure 2.10: PVA repeat unit.

A considerable body of work has previously been done using a -trichlorosilane end group to attack a hydroxyl bond. The reaction is essentially a substitution one, and it proceeds thus: (figure 2.11).

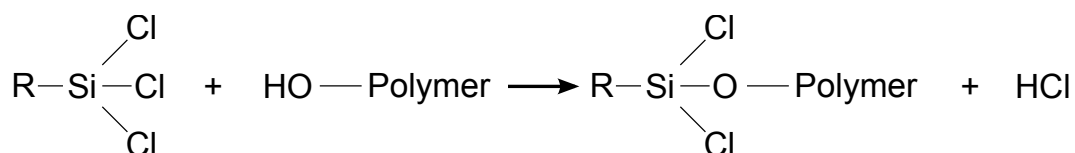


Figure 2.11: Reaction schematic of a -trichlorosilane capped molecule grafting onto PVA.

2.3.1.2 Fluorination hydrophobicity

Given that established methods for grafting onto PVA exist the next stage is to consider which molecules would be best attached. Typically when others have sought to reduce the solubility of a polymer by surface grafting they have looked to fluorine-containing molecules (e.g. Imae *et al.* [5]). C-F bonds are highly stable due principally to the strong electronegativity difference between the fluorine and carbon atoms [76]. Nishino *et al.* [74] reported an increase in the water contact angle

on 98% hydrolysed PVA as a result of a fluorinated surface (changing from $\sim 50^\circ$ to over 100°).

Reisinger *et al.* [77] produced a good review covering the fluorination of many types of polymer, focussing mainly on the synthesis of such polymers. They comment that in general polymers containing fluorine atoms along their backbone have low surface energy values. It can further be said that when considering the fluorination of a polymer there are three options as to where we might spatially place the fluorine atoms. In the main chain itself (e.g. PTFE), chain ends or as polymer side chains [5].

For the specific case of PVA we can consider each of these options for attaching fluorinated groups to the polymer backbone. Fluoroolefins can be added to yield the corresponding PVA fluorinated ethers [77]. In that work the T_g decreased as the fluorination level went up, possibly as a result of the disruption of the hydroxyl hydrogen bonding.

Another option is to carry out fluorination via SF_6 gas under an electrical discharge, under which SF_6 molecules are thought to decompose into various reactive radicals including fluorine atoms and SF_x compounds (where x is less than 6) [77]. Das *et al.* achieved a 4% fluorination after 10 hours of treatment time [78]. They also noticed an improved solvent resistance compared with untreated PVA. However this technique is likely to lead to some bulk modification after long exposure times [77].

Nishino *et al.* carried out fluorination of PVA by grafting on 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PF-decyl) [74]. More recently Xue *et al.* prepared superhydrophobic surfaces on cotton textiles using PF-decyl [79]. They make a good observation in that the majority of studies to-date regarding such fluorination have been on rigid solid substrates, thus possibly limiting the usefulness of the work for considering practical applications on flexible substrates [79].

2.3.1.3 Prior work on silicon

Prior to these polymer-based papers the majority of the published work on fluorinated silanes had been focussed on grafting onto silicon substrates. Ref's [80–82] all consider the deposition of PF-decyl onto Si. Maboudian *et al.* [80] looked at the microstructure of the monolayers formed for the purpose of anti-stiction coatings. They found the PF-decyl monolayer to be $\sim 1.4\text{nm}$ thick. This compares favourably with the 1.5nm reported elsewhere [81]. Bunker *et al.* [81] had a particular focus on tackling the process problems of depositing monolayers. In particular they produced a helpful schematic as to possible options when depositing via the -trichlorosilane group onto a silicon substrate (figure 2.12).

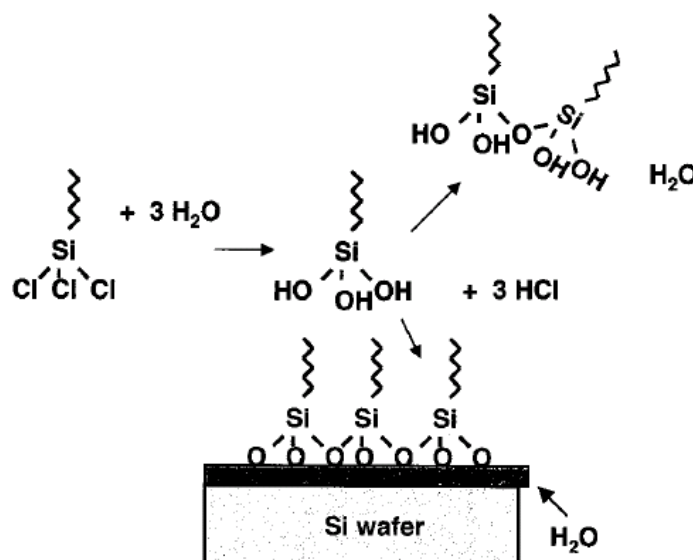


Figure 2.12: Reproduction of figure 1 from [81] showing -trichlorosilane groups aggregating.

Thus for the case of -trichlorosilane capped molecules there is the risk of self-aggregation instead of or as well as deposition. In order to try and manage this Bunker *et al.* trialled various solvent compositions, each of which contained a differing proportion of hydroxyl groups (as in order to attach a -trichlorosilane to a silicon surface it is first necessary to hydrolyse it [80, 81]). Bunker *et al.* found that the key factor in depositing onto silicon is the optimisation of the hydroxyl concentration [81].

Therefore given that -trichlorosilane groups react with hydroxyls their deposition onto PVA should be a favourable reaction (as there are already an abundance of

hydroxyl groups present on the surface).

2.3.1.4 Analysing grafted species

Measuring and detecting the presence of successful graft entities can be performed via several techniques. It is perhaps helpful to split up the analytical tools regarding the field of information which they tend to supply, a good distinction being between chemical and morphological information. In addition, most of the techniques do not tell us conclusively whether the grafted species are covalently or just electrostatically bonded to the surface (excepting perhaps NMR).

FTIR (described in more detail in section 3.7) gives a good qualitative measure of the chemical groups present in a sample, and also quantitative information to a first approximation. An example is given by Lee *et al.* who coated aluminium with fluoro carbon compounds yielding strong C-F peaks around the 1200cm^{-1} region [83].

XPS is an additional means to examine the chemical groups present in a system, and it is well suited to examining grafted samples due to its surface specificity.

NMR has been used by Zhou *et al.* [69] to detect the presence of additional groups on a PVA substrate after the grafting on of succinic anhydride. Subramanyam *et al.* [75] used NMR to prove the attachment of PDMS onto PVA.

For the case of grafting very different groups onto a surface the change in contact angle for a given solvent can be quite large, and is primarily due to the changed chemistry of the surface. (A change in contact angle can be due to other factors though, section 3.5).

AFM is a great technique for examining surface morphology at a small scale. It has been used with good success by many authors to demonstrate a change or lack thereof as a result of modification via grafting.

DSC was also used by Subramanyam *et al.* [75] to investigate the impact on thermal

properties of their modification. As a result of grafting PDMS onto PVA they reported that the T_g peak became broader and that the T_m peak was no longer visible.

Very few authors have commented on the surface stability of grafted species. For the case of grafting onto a non-polymer substrate this is probably less of a concern. However for polymers the opportunity exists for conformational changes to take place which could result in the modified surface layer migrating into the bulk. The concentration gradient would drive such a transition, but this would have to be balanced against the hindrance to conformational changes which exist below the T_g .

2.3.2 Other techniques for surface modification

Treatment with a plasma is a common precursor for graft attachment [84]. A corona discharge has also been previously used, with a good example being in the assistance of PVA desizing [85].

Serizawa *et al.* describe an interesting technique known as “layer-by-layer assembly” (LBL) [86, 87]. Using this technique it is possible to produce ultra-thin layers (10's of Ås), the process relies on electrostatics and the precipitation-out of the polymer above a certain salt concentration [88].

Shim *et al.* worked on eliminating some of the limitations of the layer-by-layer approach, in particular the time-consuming rinsing and drying step between each deposition cycle. They promote a ‘dewetting’ approach and expect their technique to be applicable to most LBL assembly systems [89]. Quinn *et al.* provide further discussion on this technique, and notably they comment on the behaviour of hydrogen-bonded layered films [90].

Of the rarer techniques available Coppée *et al.* managed to nano-structure polymer surfaces partly through controlled heat treatments [91].

2.3.3 Topography

The topography of films can be altered via several methods, however it is the end result of the changed morphology which is of interest. Recently Forbes discussed the influence of super hydro -phobic and -philic films [92]. Lee *et al.* carried out work onto the surface topography of PE and Teflon, and they concluded, “It is now abundantly clear that topography is an important and useful variable in controlling surface properties” [93]. Further discussion is given by Assender *et al.* [94], Wenzel *et al.* [95] and Öner *et al.* [96].

2.4 Water uptake by polymeric materials

The principal aim of the work in this thesis is to increase the solvent resistance of a PVA surface. To do this it is important to establish how a solvent interacts (and for the case of a favourable solvent) dissolves a polymer.

2.4.1 Polymer dissolution mechanisms

The current accepted understanding is that, “The dissolution of a polymer into a solvent involves two transport processes, namely solvent diffusion and chain disentanglement” [97]. Before discussing these two processes it is helpful to define a dissolved polymer as one in which a single polymer chain’s movement is restricted only by the influence of the surrounding solvent molecules, and not by other polymer chains [25] (each molecule can therefore be considered as an isolated chain). And secondly an undissolved (dry and solvent-free) polymer has the limits of motion of a single polymer chain defined by the influence of its neighbours [98]. In between these two limiting cases we have partially dissolved states, as illustrated by figure 2.13.

For a polymer to dissolve the following processes must occur:

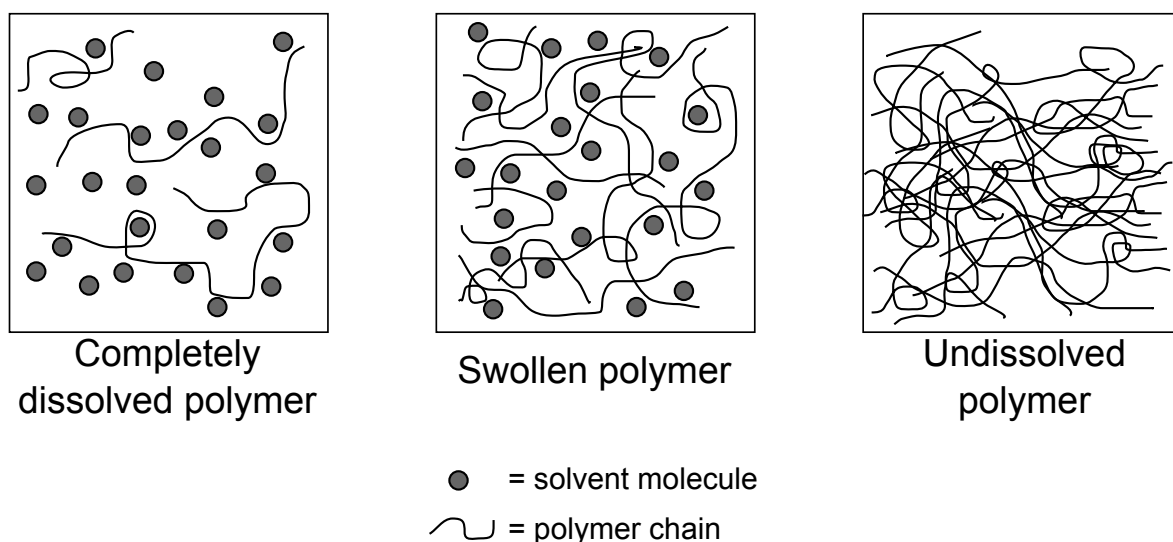


Figure 2.13: Comparison of the various states of polymer dissolution.

- Solvent molecules diffuse into the free volume [97] between the polymer chains.
- These plasticize [97] the chains and help them to move apart.
- A gel layer is formed, where the chains are still partially restricted by neighbours; however there is a significant volume fraction of solvent molecules present in the gel phase.
- The chains gradually disentangle from one another, and diffuse apart via reptation [99–101].
- Individual chains then become free from the bulk material and are free to diffuse through the bulk solvent.
- Eventually all of the chains become free in this manner, rendering the bulk polymer completely dissolved.

It should be pointed out that the above process only applies for amorphous non-chemically cross-linked polymers. Further complications arise due to the presence of cross-links (section 2.4.1.3) or crystals (section 2.4.1.4).

2.4.1.1 Solvent diffusion

If a polymer is to dissolve in a given solvent there must be a chemical potential gradient in the system driving the ingress of solvent molecules [101]. This comprises a combination of the entropy increase upon addition of the solvent to the polymer matrix and any intermolecular forces between the solvent molecules and the polymer chains. Such interactions are those weaker than a covalent bond, namely hydrogen bonds, permanent dipoles and van der Waals interactions. They may act to attract or repel the solvent molecules from the bulk polymer; depending on the specific system (e.g. a polymer containing many polar side-groups is likely to interact favourably with a polar solvent such as water).

2.4.1.2 Chain disentanglement

Once a suitable volume of solvent molecules has entered the polymer chain disentanglement can begin. The principal mechanism proposed for polymer chain migration is that of reptation, and one of the earliest authors to discuss this was Klein [102]. The basic premise of the theory is that, “The [polymer] molecule is constrained to wriggle, snake-like, along its own length, by curvilinear propagation of length defects such as kinks or ‘twists’ along the tube.” And it was De Gennes [98] who first considered the ‘worm-like’ motion of amorphous polymers. The stiffness of the polymer backbone will have an impact on how easily the polymer chains are able to undergo reptation [97].

According to Narasimhan *et al.* we can define the disentanglement rate as, “the ratio between the radius of gyration of the polymer and the reptation time” [101]. We can measure these characteristics using neutron scattering and hence gain an estimate of the disentanglement time.

Disentanglement is also aided by plasticization, which is the penetration of small ‘plasticizer’ molecules into the bulk polymer matrix. These molecules then act as

‘lubricants’ for the polymer chains, allowing them to move more easily [103]. The influence of plasticizers on the dissolution rate of polymer films has been discussed in more detail by Cooper *et al.* [104].

2.4.1.3 Influence of cross-links

For the purpose of this work a ‘cross-link’ will be defined as, ‘a permanent covalent bond between neighbouring polymer chains.’ Other links can exist between polymer chains, such as hydrogen bonds or physical entanglements, but these are weaker in nature.

The most significant impact which covalent cross-links have on the system is that they can prevent total dissolution of the polymer matrix. Upon addition of a solvent to a cross-linked system swelling of the system can still occur (by stretching and twisting of the covalent bonds) however the radius of gyration of the system has now effectively become infinite such that the disentanglement rate becomes negligible.

2.4.1.4 Crystallinity

Hassan *et al.* looked at the dissolution kinetics of semi-crystalline PVA gels [105]. A three stage mechanism in crystal dissolution was proposed, “detachment, diffusion, and disentanglement.”. Figures 2.14, 2.15 & 2.16 illustrate each process.

Hassan *et al.* go on to suggest equation 2.5 for the Gibbs free energy change ΔG_1 of unfolding a segment of chain length l , thickness b and width w from a single crystal.

$$\Delta G_1 = bwl\Delta f - 2bw\sigma_e - 2bl\sigma_s \quad (2.5)$$

Δf indicates the Gibbs free energy difference per unit volume of PVA chains between the crystalline and amorphous phases of PVA, whilst σ_e and σ_s are the free energies per unit area of the end and side surfaces respectively.

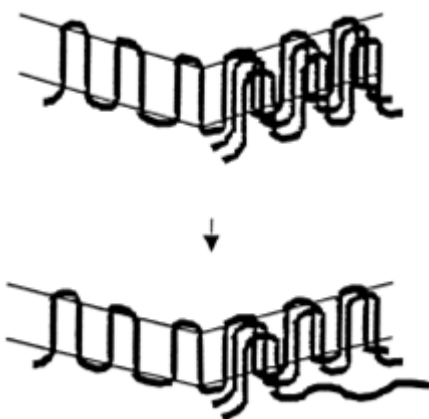


Figure 2.14: Detachment-controlled dissolution (from [105]).

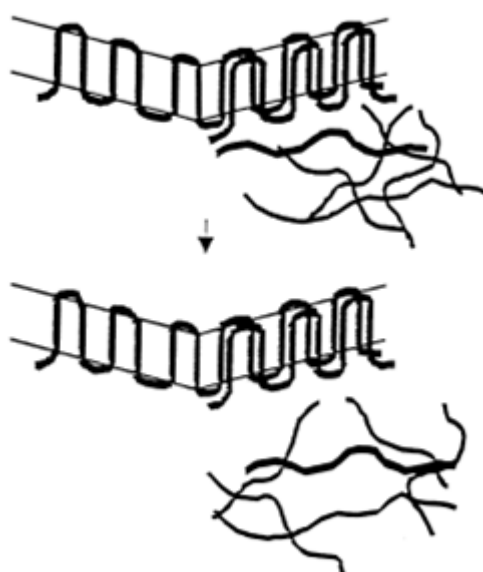


Figure 2.15: Diffusion-controlled dissolution (from [105]).

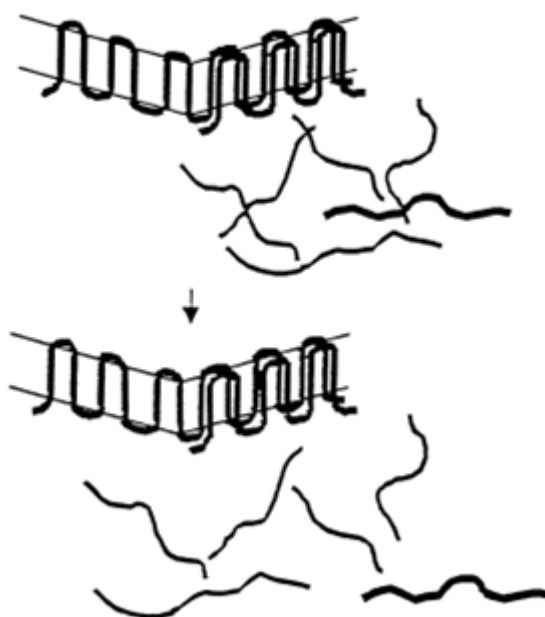


Figure 2.16: Disentanglement-controlled dissolution (from [105]).

Reprinted from: Polymer, 41(18), Hassan, C. M., Ward, J. H. & Peppas, N. A., Modeling of crystal dissolution of poly(vinyl alcohol) gels produced by freezing/thawing processes, 6729-6739. © 2000, with permission from Elsevier.

Thus the presence of crystals adds a prior ‘detachment’ step of the chains from the crystals. This extra stage for crystalline material (*cf.* amorphous) leads to longer dissolution times. The thermodynamics also favour the retention of the crystalline phase [24]. Hence it is sensible to suggest that the greater the crystalline fraction of a sample the greater the resistance to solvent attack [9]. Further discussion of the dissolution mechanism of semi-crystalline PVA has been published by Mallapragada *et al.* [64].

Göpferich described two possible sources of crystallinity change during polymer dissolution. If degradation (that is chain scission) occurs during dissolution then the, “generation of crystallized oligomers and monomers” [106] may take place. He also points out that due to the faster dissolution of amorphous *cf.* crystalline material the overall crystallinity of the remaining solid in the sample will appear to increase during dissolution.

2.5 Control of PVA solubility

Given the fundamental mechanisms underlying dissolution numerous attempts have been made to modify the dissolution behaviour of PVA.

2.5.1 Bulk cross-linking

Bulk polymer cross-linking is a well known process and is the introduction of permanent covalent bonds between polymer chains such that a networked structure is formed [107]. The cross-links act to ‘pin’ the polymer chains, and thus hinder their translational and rotational motion. This is significant as if the chains are unable to move then it will mean that the polymer matrix is less able to accommodate permeation of solvent molecules [6]. Cross-linking also renders a polymer insoluble (though often still able to swell).

There are two main methods by which polymer chains may be cross-linked. Either a ‘cross-linker’ molecule is inserted and used to tie the two chains together, or a ‘sensitizer’ molecule decomposes in a reaction to produce free radicals which then allows the chains to attach directly to one another.

2.5.1.1 ‘Cross-linker’ molecule methods

A reasonable body of work has been carried out to perform the bulk cross-linking of PVA. Typically it is the hydroxyl groups which are attacked [2, 108], and Giménez [108] states that all multifunctional compounds capable of reacting with hydroxyl groups can be used to cross-link PVA (thus dialdehydes, dicarboxylic acids, dianhydrides etc. [2]) and these react by allowing a condensation reaction to occur (figure 2.17).

Several cross-linking schemes have found particular favour. The most common one involves the use of glutaraldehyde. This seems to be a fairly flexible cross-linker, as

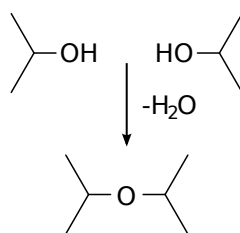


Figure 2.17: Condensation reaction between two hydroxyl groups on neighbouring PVA chains.

many authors have reported success with it [109, 110]. Indeed, glutaraldehyde has been used to cross-link different degrees of hydrolysis PVA [111], it has been used to cross-link during PVA polymer synthesis [112] (to form semi-interpenetrating polymer networks) and also to cross-link whilst fibres of PVA were being electro-spun [113]. The degree of cross-linking can also be varied simply by changing the ratio of PVA to glutaraldehyde [114]. Glutaraldehyde is readily available however its principal drawback is its toxicity (toxic by inhalation).

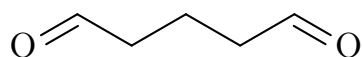


Figure 2.18: Structure of glutaraldehyde.

A non-toxic alternative is the borate ion. Several authors have reported success in using borate to cross-link PVA [115–118]. The proposed cross-link structure is given by Ochiai *et al.* [115] and Sinton discusses the control of inter- over intra- molecular bonding by manipulating the polymer to borate ratio [119].

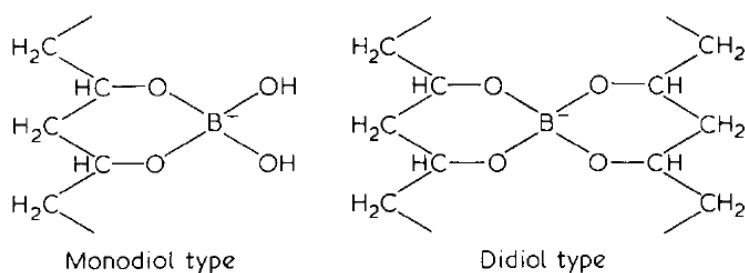


Figure 2.19: Reproduction from [115].

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A third option is to use maleic acid (or anhydride). Maleic acid has been used to successfully cross-link PVA by Gohil *et al.* and they recorded improved resistance to swelling (in water) for the cross-linked films [120]. Yang *et al.* also had success with maleic anhydride [2].

A few other compounds have been used to cross-link PVA, for example Shafee *et al.* [121] used hexamethylene diisocyanate to cross-link PVA, basing their work on the knowledge that isocyanates will react with alcohols to form carbamates (as shown in figure 2.20). Li *et al.* [122] and Guohua *et al.* [123] used formaldehyde as a hydroxyl cross-linker and Gebben *et al.* comment that PVA can be cross-linked with a low M_w dialdehyde such as glyoxal [114].

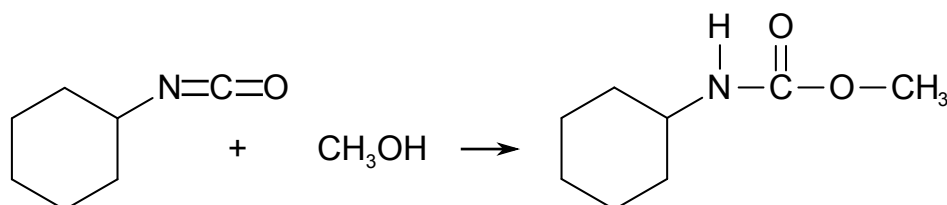


Figure 2.20: Isocyanate and hydroxyl reaction

Some authors have also investigated pseudo-cross-linking of PVA, for example the production of crystals via the freeze-thaw method [3]. However such work will not be discussed further here.

2.5.1.2 ‘Sensitizer’ / free radical methods

An alternative method of cross-linking is to produce free radicals using sensitizer molecules and / or electromagnetic radiation or a plasma discharge. Bhattacharya produced a good overview of methods of radiation used in treating polymers [124]. He helpfully highlights the following common advantages of radiative cross-linking:

- Radiation processes are free from contamination.
- No catalysts are required.
- Chemical initiation is limited by the concentration and purity of the initiator, radiative processes are not.
- Radiation processes are not temperature dependent - i.e. the formation of free radical sites on the polymer is only dependent on the polymer being able to absorb the radiative energy. [124]

There are several types of electromagnetic radiation which can be used to cross-link polymers, each of which will now be discussed briefly.

UV

The general principles of using ultra-violet (UV) radiation to cross-link a polymer are given by Decker [125, 126] and Miranda *et al.* [127]. UV cross-linking has the major advantage that very high polymerization rates can be achieved under intense illumination [126]. It therefore has significant potential for use in an industrial environment where a quick reaction time is likely to be of considerable benefit.

Decker reports that as most monomers are transparent to UV light a photo-initiator is usually required [125]. A photo-initiator is a molecule which undergoes photolysis ("The cleavage of one or more covalent bonds in a molecular entity resulting from absorption of light ..." according to IUPAC), in this case absorbing UV radiation and subsequently generating free radicals [125]. The free radicals then provide the means by which C-H (or other) bonds can be cleaved. The free radical on the photo initiator then combines with an H atom from the polymer, to leave a polymer radical (M•).

Baum pointed out that it is impossible for C-H or C-C bonds to absorb UV radiation in the range $\lambda = 290\text{-}400\text{nm}$ [128]. Thus a photoinitiator is required, and despite the presence of hydroxyl groups this is also the case for PVA. (The bonds and their respective energy present [in fully hydrolysed PVA] are: C-C 348kJmol^{-1} , C-H 413kJmol^{-1} , O-H 366kJmol^{-1}).

Sodium benzoate (figure 2.21) is a common sensitizer which has been used successfully to cross-link PVA. Takakura *et al.* [129] varied the concentration of sodium benzoate in $20\mu\text{m}$ thick PVA and found no increase in cross-link density above 4.0wt% sensitizer. They predicted and observed a straight line correlation between the cross-linked polymer solubility and $1 / \text{sensitizer concentration}$. Takakura *et al.* also commented that cross-linking occurred frequently, whilst main chain scission was negligible [129].

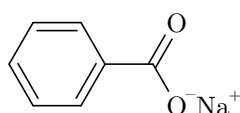


Figure 2.21: Sodium benzoate molecule.

Some success has also been reported by other authors with attempts at cross-linking starch by using sodium benzoate as a photoinitiator [130, 131]. Delville *et al.* helpfully included proposed mechanisms for the photolysis of sodium benzoate [130] as reproduced in figure 2.22.

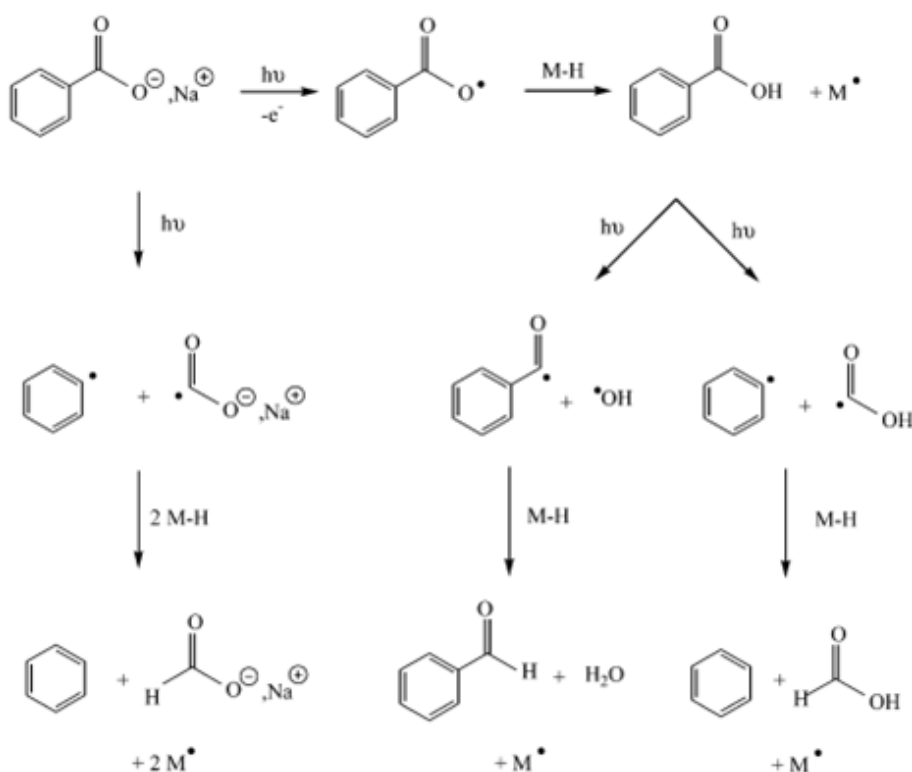


Figure 2.22: Proposed mechanisms of sodium benzoate photolysis, reproduced from [130]. Reprinted from: *Carbohydrate Polymers*, 49(1), Delville, J. et al., Solid state photocrosslinked starch based films: a new family of homogeneous modified starches, 71-81. © 2002, with permission from Elsevier.

γ-rays

Gamma ray radiation (γ -ray) can sometimes be used to cross-link polymers but in addition if the radiation is high enough in energy chain scission (by cleaving C-C bonds) is also possible [132]. For the specific case of treating PVA there are differing views in the literature. Takakura *et al.* commented that when PVA is exposed to ionizing radiation (e.g. γ -rays) no cross-linking takes places, though chain scission (and hence degradation of the polymer properties) does [129]. Moad and Winzor agreed by commenting that both cross-linking and chain scission are possible, though they

state that scission is more likely when vinyl polymers undergo irradiation in air [133]. They also noted that the probability of chain scission might be different between a monomer unit in the middle of a chain and one located near the end [133].

Burillo *et al.* have looked at gamma-ray induced cross-linking of PVA on several occasions. They admit that previous results are not conclusive, but state that on the whole PVA tends to degrade as opposed to cross-link [134]. They also stated that, "...pure PVA is more difficult to be cross-linked than the acetone-containing PVA." [134], although they did not elaborate on why they thought this was the case. Perhaps it is due to differences in the relative stabilities of the acetate and hydroxyl groups under γ -radiation.

In summary whilst cross-linking and chain scission are both possible it appears that chain scission will inevitably result by using γ -radiation, hence it will not be used in this work.

Plasma

The use of plasma treatment to modify polymer surfaces is becoming more common and general information has been provided by Clark *et al.* [135] and Gilliam *et al.* [136]. Typically plasmas are used to ablate or functionalize an inert surface to allow the grafting or deposition of various species.

For the case of PVA Matthews *et al.* used exposure to a helium plasma to ablate the surface [137]. They reported a decrease in the molecular weight of the PVA and attributed this to chain scission. Further evidence of this was the subsequent increase of the solubility of the PVA in methanol. They also observed a film thickness decrease of several micrometres. Rogojanu *et al.* built on this work, proposing several possible radical formation mechanisms along with recording AFM images of the treated surfaces [138].

e-beam

Electron beams have previously been used to cross-link PVA, although the majority of the previous work published has been on cross-linking in the liquid (as opposed to solid) state. Peppas *et al.* claim that an e-beam affects PVA solutions in two ways, firstly by the formation of polymeric radicals and secondly by the formation of $\text{H}\bullet$ and $\text{OH}\bullet$ radicals from the solvent. They claimed that cross-linking of PVA hydrogels was successful in solution, but not for solid samples below their T_g , as a result of the low mobility of the free radicals formed during irradiation [139].

2.5.1.3 Influence of crystallinity

As has been previously mentioned the existence of crystals is generally accepted to hinder dissolution (section 2.4.1.4). The samples prepared in this work typically had an as-cast crystalline fraction of around 40% (see section 6.4.3). The differing ability of crystalline and amorphous material to cross-link has not been widely discussed, though Keller *et al.* cover it briefly in their work [140], stating that though they had evidence to show more cross-linking in the amorphous phase, the exact ability to cross-link crystalline material was more complicated, including (amongst other factors) the local lamellae spacing.

However the ability of cross-linked material to be crystallized has been discussed, with Qian noting that for the case of cross-linked semi-crystalline polymers subsequent crystallization is more difficult [15], whilst Hasimi *et al.* observed this for the specific case of the cross-linking of PVA using glutaraldehyde [109]. Gohil *et al.*'s XRD patterns also suggest this [120].

2.5.1.4 Surface cross-linking

Intentional surface-specific cross-linking of PVA is seldom found in the literature. One example is provided by Li *et al.* who attempted to do so by smearing a layer of 2wt% borax solution onto the film surface [116]. Thus there is considerable scope to

purposefully trial the surface cross-linking of PVA by previously established bulk cross-linking methods.

Chapter 3

Equipment & Methods

3.1 Casting

Typically the polyvinyl alcohol films cast in this work were formed by complete dissolution of PVA powder (by using a magnetic stirring rod) in a suitable solvent at a concentration between 1 and 10wt%. A set amount of the solution was poured onto a clean glass petri dish (~ 100 mm diameter) and the dishes were subsequently left in an oven at 30°C for at least 30 hours (preferably at least 40 hours) for the solvent to evaporate. Next the films were cooled to room temperature and extracted from the petri dishes using a razor blade and a pair of tweezers. The films were kept dry before use.

The drying conditions of 30°C for at least 30 hours were found to be optimum for producing good, consistent films after varying both the drying temperature and time. Packter *et al.* found that the temperature was significant [141], whilst Hermann *et al.* argued that slower drying was more favourable to avoid internal stresses within a film [142].

Distilled water was the most common solvent used, along with DMSO (dimethyl sulphoxide) on occasions. DMSO is considered to be a better solvent (further from the theta condition) for PVA but using a very good solvent allows the chains to un-

ravel more - thus resulting in a bigger change in volume upon solvent evaporation which in turn leads to a bigger degree of internal stress in the cast film [142].

3.2 Spin coating

Spin coating has been used in this work to produce regular, thin, smooth films. The basic principle of spin coating is to deposit a solution onto a substrate rotating at high speed. A limited amount of the solute will be retained on the substrate and the majority of the solvent will be driven off during spinning, hence drying the films very quickly. The schematics of spin coating are illustrated in figure 3.1.

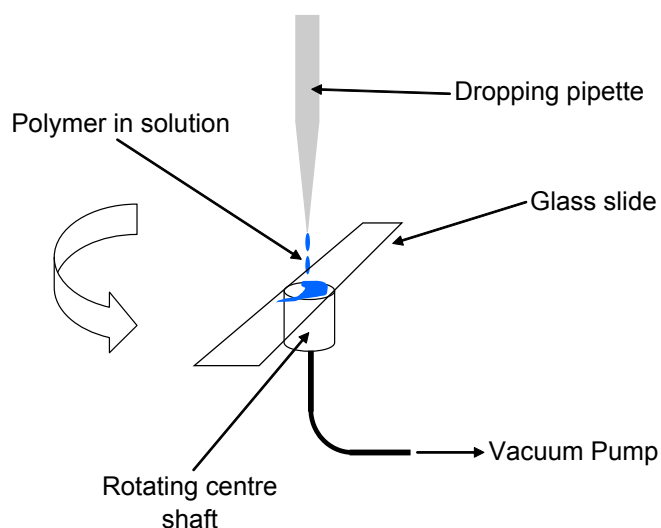


Figure 3.1: Spin coating schematics.

The exact spin coating parameters were established after various trials, and it was found that the solution concentration had the strongest impact on final film thickness. The film thickness also decreased with increasing spin speed, though there was no noticeable change above 1000rpm.

The solvent evaporation rate has been determined elsewhere as strongly influencing the film thickness [143] (particularly at longer times [144]), along with impacting on the film roughness [40] (smoother films with a faster spin speed). Weill *et al.* [145] found that film thickness correlated more strongly to M_w than M_n . Mathematical modelling of film development during spin coating has been performed by

Schubert *et al.* [37] and Flack *et al.* [143]. In summary spin coating is a relatively straightforward and reliable means by which to produce thin polymeric films.

3.3 Liquid water uptake

The liquid water uptake of a polymer involves immersing a sample in distilled water and monitoring the mass increase (as a result of solvent molecule retention) as a function of time. The samples are removed from the solvent at regular time intervals and their mass recorded. Excess adsorbed surface molecules must first be removed as these are not truly absorbed. This is typically done by 'patting' the samples dry with absorbent material before each mass measurement [146, 147]. The method depends on all surfaces of a film being equally permeable and it also assumes that the drying step removes all of the adsorbed molecules and no others.

It is possible to gain an insight of the diffusion characteristics of a solvent through a swelling polymer (see equation 3.1).

3.4 Water vapour uptake

The principal shortcoming of the liquid water uptake test is that it relies on all surfaces of a sample being the same which is of course inappropriate for a sample which has been surface modified on one side only. There were very few examples of pre-existing tests in the literature of a means of assessing the solvent uptake / swelling of a sample as the result of the interaction of one surface only. (One such example is the quartz crystal microbalance [88], but this operated on a size / mass scale inappropriate for most of this work).

As a result of the shortcomings of the liquid water uptake test a new method was developed which involved placing a film on the surface of a beaker, sealing it, and exposing it to a different atmosphere on either side, as shown in figure 3.2. The

humidity was fixed on the treated side of the film by equilibrating with a saturated $\text{NaCl}_{(aq)}$ solution, and the other exposed to the atmosphere. Shafee *et al.* also used saturated salt solutions to control the humidity in an environment for monitoring water uptake of PVA [121]. Chen *et al.* helpfully comment that PVA will readily absorb moisture above an RH of 50% [4]. This further helped in the selection of NaCl which (when in a saturated solution) gives a relative humidity of $75\% \pm 0.5$ [148] varying very little with temperature [148]. Thus a concentration gradient is established, with a relative humidity of $75\% \pm 0.5$ and atmospheric humidity on the bottom and top surfaces respectively.

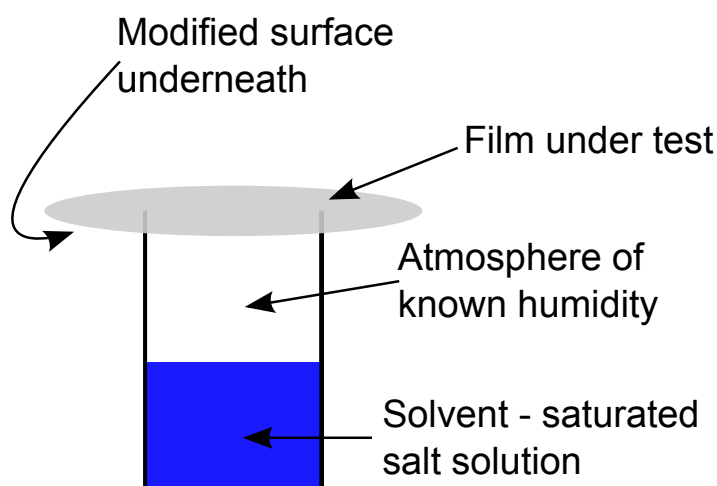


Figure 3.2: Water vapour uptake test method.

At regular time intervals the film was removed and its mass recorded. The films typically showed a few percentage mass increase over a period of several hours as a non-linear function of time. Rapid swelling occurred within the first few hours, before much slower swelling set in after a period of around 24 hours (i.e. the plotted graphs were logarithmic in shape). In addition the films were not always of the same thickness, having a size of $100\mu\text{m} \pm 25\mu\text{m}$. As such the saturated vapour mass was different between samples, so the values were normalised as a fraction of sample mass.

3.4.1 Concentration profile

To understand the concentration profile across a film we can consider a cross-section of untreated material as shown in figure 3.3, whereby a solvent molecule concentration gradient is setup from the bottom to the top surface. We can assume the limits of concentration on each surface of the film to be dictated by the adjacent atmosphere, i.e. 75% RH on the bottom surface and atmospheric on the top surface (figure 3.4). The atmospheric humidity was monitored and was found to average at 43% RH $\pm$ 7%.

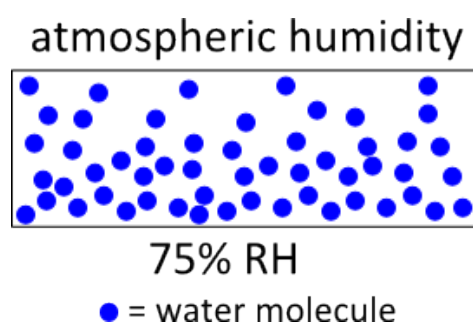


Figure 3.3: Schematic of vapour molecules through a film under test.

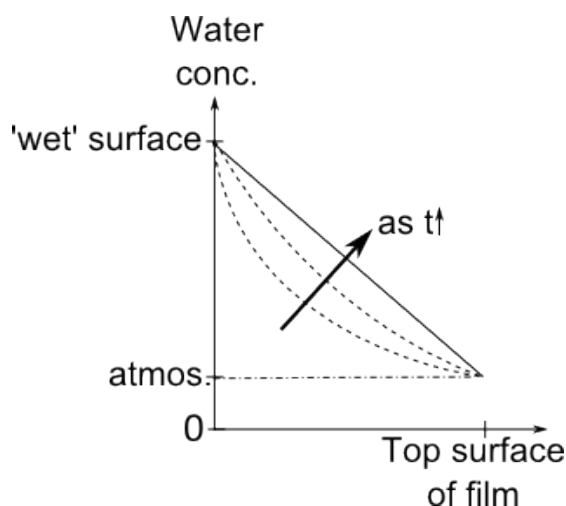


Figure 3.4: Proposed concentration profile for vapour molecules in a film under test.

The concentration will tend towards a straight line (figure 3.4), this is representative of a constant flux through the system. The area of the plot (at steady state, where water vapour uptake rate at the bottom surface = vapour expulsion rate from the top surface) can be calculated from the saturated water vapour uptake mass.

As the bottom surface is treated and made more solvent resistant the concentration plot is likely to vary as shown in figure 3.5.

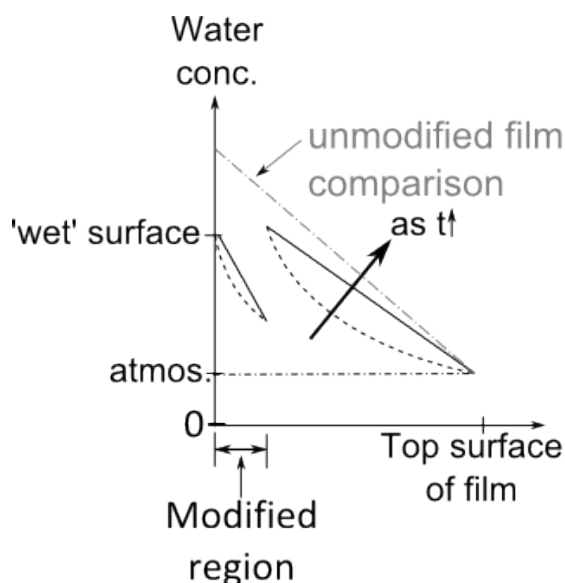


Figure 3.5: Proposed concentration profile for vapour molecules in a modified film under test.

Figure 3.5 is based on the assumption that the saturated water concentration in the modified region of film is less than for the untreated case. As such the level at the surface exposed to 75% humidity will be less than for the untreated case, and there could be a positive concentration gradient at the interface (assuming a sharp interface) between the modified and unmodified material, owing to the greater solubility (and hence stability) of water in unmodified PVA (though the concentration will not reach as great a value at this point as in the case of the unmodified film). Thus the total mass of vapour molecules in the system will be reduced.

The model makes the assumption that the driving force for water transport through the sample is purely a result of the concentration gradient of vapour from one film surface to the other. Secondly it is assumed that the saturated vapour value for a film (the maximum mass of vapour which a given film can hold in this test environment) is linearly proportional to the dry film mass. Thus it is possible to normalise the saturation data for films of differing thickness. It should also be pointed out that in the initial stages of the test the water vapour uptake will be independent of film thickness because no molecules will have permeated to the top side of the film (at which point the rate of uptake will begin to slow).

3.4.2 Diffusion coefficient

To extract diffusion data it is pertinent to begin by attempting to approximate the water vapour uptake test to a more familiar experimental scenario. Equation 3.1 (given by Peppas *et al.* [149] and others) is a typical place to start for bulk degree of swelling experiments.

$$\frac{M_t}{M_\infty} = kt^n \quad (3.1)$$

Where M_t = mass of solvent taken up at a given time, M_∞ = saturated solvent mass uptake of a sample, k = a constant, n = diffusion exponent.

Various types of diffusion have been defined, and these have been correlated to the diffusion exponent n as shown in table 3.1 (produced from [149]).

Diffusion exponent n	Diffusion type
0.5	Case I (Fickian)
$0.5 < 1.0$	Anomalous (Mixed)
1.0	Case II
> 1.0	Super Case II

Table 3.1: List of commonly accepted diffusion types.

The rate limiting step in Fickian diffusion is the solvent molecule mobility [149], whilst for case II diffusion it is the rate of polymer relaxation [150]. This is further backed up by Hansen who comments that for Fickian diffusion the initial mass increase of a sample will be linear with the square root of time, whilst for case II the relationship is linear with time [151].

Equation (3.1) is dependent on the mechanism(s) of diffusion operating in the system. It is independent of the absolute mass uptake but instead relies on the fraction of the mass of the saturated mass absorbed as a function of time. Therefore it is likely to be valid for the case of the surface vapour test described herein.

Trial runs of plain PVA were performed on the water vapour uptake test and the films quickly approached the saturated mass uptake, such that the fourth measurement and following all had $M_t/M_\infty \geq 0.8$. According to Peppas *et al.* equation

3.1 should best be limited to ≤ 0.6 (as it is an approximation of a more complicated formula [149]). Although in the more complicated formula the films are absorbing vapour from both surfaces, whilst in this work they absorb from a single surface. Hence it seemed reasonable to set the approximation to ≤ 0.8 for the calculations performed herein.

Based on three repeat runs for plain 88% hydrolysed PVA (M_w of 85k-124k) n was determined to be 0.7 (1s.f.) and k to be $7 \times 10^{-4} \text{s}^{-0.7}$ (1s.f.). A value of $n=0.7$ implies mixed diffusion, that is a combination of solvent diffusion and 'glassy' front motion limited solvent progress. Hasimi *et al.* reported values of n of between 0.6 and 0.8 [109] which fits with that observed for the unmodified PVA samples in this work.

Peppas *et al.* further go on to state that for the case of Fickian (Case I) diffusion the approximation of equation 3.2 can be made.

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi l^2} \right)^{\frac{1}{2}} \quad (3.2)$$

Considering the parallel of equation 3.2 with 3.1 it is possible to get an idea of the diffusion coefficient, D , of water in PVA. This is done by firstly plotting $\ln(M_t/M_\infty)$ against $\ln t$ (as shown in figure 3.6). By taking logarithms of equation 3.1 the intercept is $\ln k$ (for a plot of the form $y = mx + c$), which when equated with equation 3.2 means the intercept is equal to $\ln(4D/(\pi l^2))$. Thus since the average intercept (from figure 3.6) is -7.4 gives D as $4.8 \times 10^{-12} \text{m}^2 \text{s}^{-1}$.

Various authors have carried out similar work on the diffusion coefficient of water in PVA and similar polymers. Hasimi *et al.* [109] reported a value for D of $1.25 \times 10^{-10} \text{m}^2 \text{s}^{-1}$ of water in PVA, whilst Long *et al.* [152] reported values between $2 \times 10^{-15} \text{m}^2 \text{s}^{-1}$ and $2 \times 10^{-14} \text{m}^2 \text{s}^{-1}$. Thus the recorded value here fits within the boundaries of that recorded elsewhere.

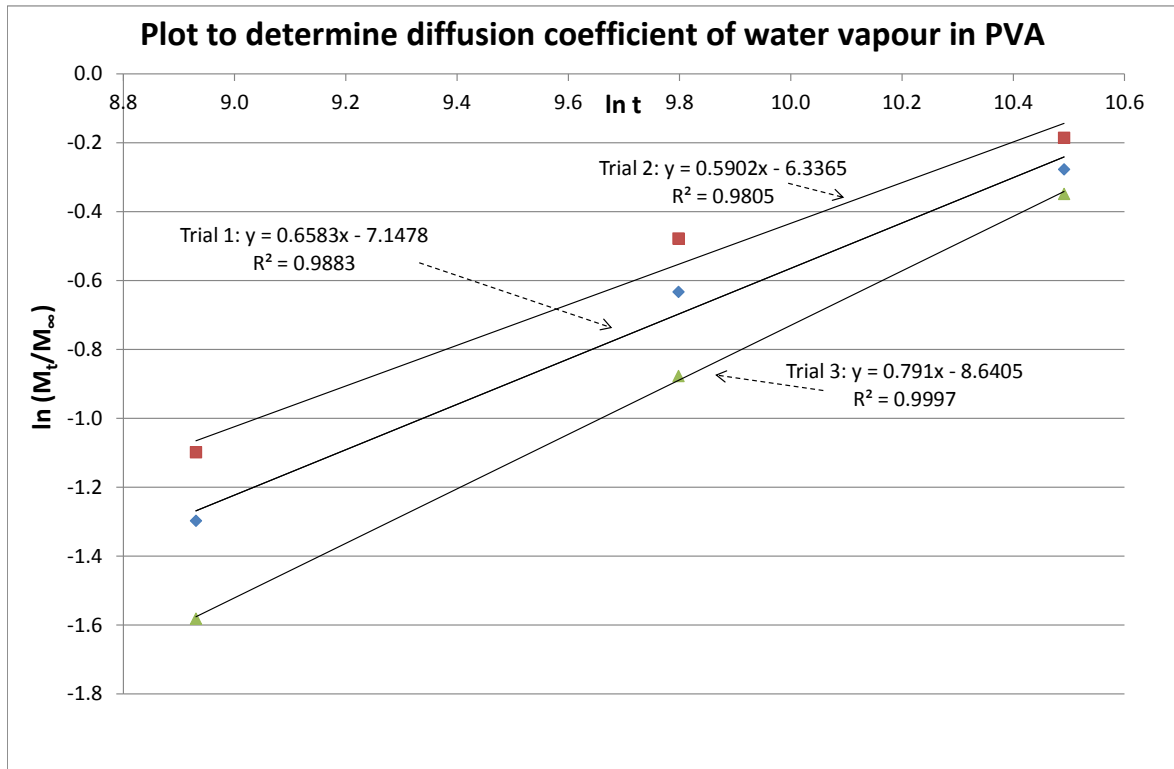


Figure 3.6: Plot of water vapour uptake to determine diffusion coefficient, D .

Errors in the water vapour uptake measurement

The reliability of the surface water vapour uptake test was established by performing trials on plain PVA. For a given atmospheric vapour content the films were found to have a mass gain of within 0.65% of one another at the saturated vapour level. The accuracy of the top pan balance used was $\pm 0.2\text{mg}$ which is negligible considering the mass of the films and vapour involved.

The method is currently limited by its reliability, in that a water vapour uptake difference between samples can only be stated with high confidence if the difference is relatively large.

3.5 Dynamic contact angle analysis

Contact angle analysis has been used frequently during this work as it can yield relevant information from the top 0.5nm or so of a sample's surface [153]. For most systems it is also a non-destructive technique [154, 155]. The contact angle of a liq-

uid on a solid provides valuable information and fundamentally is a comparison of the preference of the system for liquid-liquid interactions or liquid-solid interactions. Typically a predominantly dispersive interaction (between the liquid and substrate) is defined as hydrophobic, and conversely non-dispersive as hydrophilic. Furthermore we can classify the bonds being considered into primary (chemical), quasi-chemical (hydrogen bond), and secondary (van der Waals) [156]. Knowledge of such interactions is especially useful for this work as the non-interaction between a liquid and substrate is being sought via surface modification.

The simplest form of contact angle analysis is via goniometric analysis. This involves depositing a drop on a surface, and (assuming it remains stable) taking a tangent to the drop surface where it meets the surface and then calculating the angle between that and the surface.



Figure 3.7: Contact angles of a liquid drop on a surface.

A horizontal drop gives us one angle, but were we to tilt the surface we would usually see a difference between the two angles (figure 3.7b). At the point at which the drop starts to roll down this titled surface we will get the advancing and the receding contact angles for the leading and trailing edges of the drop respectively. This difference in contact angles is known as contact angle hysteresis. It can be helpful as a starting point to reveal any inhomogeneities on the surface of a sample, and Miyama *et al.* and others list possible causes for contact angle hysteresis:

- Surface roughness [154]
- Surface chemical heterogeneity [154]
- Surface crystallinity variations [157]
- Surface conformational changes [158]

- Surface deformation [154]
- Adsorption and desorption [154]
- Swelling and penetration [154]
- High rotational mobility of macromolecules at the surface [157]

Initially attempts were made to assess the contact angle of various solvents on plain PVA (88% hyd., M_w 85k-124k) using a static goniometer. This proved difficult as using water on a reference plain PVA sample failed to result in a stable drop as the water readily dissolved the surface of the PVA. Secondly for other transparent solvents the digital imaging software failed to distinguish between the drop and the transparent PVA substrate.

As such an alternative method of analysis was sought and a suitable solution proved to be dynamic contact analysis, using the Wilhelmy plate variation. The Wilhelmy plate method was chosen due to its ability to function regardless of sample transparency and glycerol was chosen as a testing liquid due to its structural parallels with water (copious hydrogen bonding), yet unlike water it did not dissolve PVA during the time scale of the tests.

The Wilhelmy plate operates by taking a specimen of a consistent cross-section and suspending it from a microbalance. A beaker sits below this (containing the solvent under analysis) on a controlled movable stage (moveable in the z-axis). The stage is driven upwards such that the solvent makes contact with the film (as illustrated by the simple schematics shown in figure 3.8).

A meniscus is formed around the sample perimeter. As the stage is continually moved upwards the meniscus will likewise move upwards (providing we have an equilibrium situation, whereby the surface is not permanently changed as a result of interacting with the solvent). Given such a state a force balance equation can be produced by resolving the forces parallel to the sample surface:

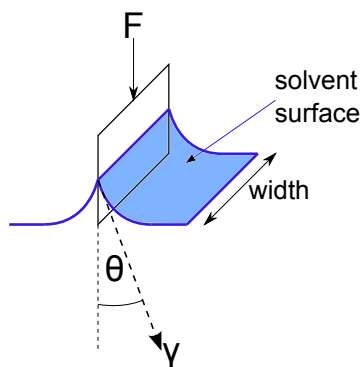


Figure 3.8: Basic schematic of the Wilhelmy plate method (showing a wetting angle of $<90^\circ$).

$$F = mg + P\gamma \cos \theta - g\rho t w d \quad (3.3)$$

Where P = perimeter, γ = liquid-vapour surface tension, θ = contact angle, $-g\rho t w d$ = buoyancy contribution.

At some point the direction of motion of the solvent beaker will be reversed, thus effectively withdrawing the sample from the solvent. At this point the meniscus is typically pinned to the surface and it only begins moving again once the new equilibrium (receding contact angle) has been established. Such a switch in angle is as a result of the system switching from measuring the advancing to the receding angle, and any difference between these angles is specifically a result of dynamic hysteresis [154].

It should be noted at this point that a second type of hysteresis is also possible, namely 'intrinsic' hysteresis. Whilst dynamic hysteresis is as a result of a change in direction of the sample under test, the intrinsic hysteresis is as a result of any surface configuration changes caused as a result of the surface being wetted [154]. Helpfully the Wilhelmy plate method is able to distinguish between the two types - repeat immersion of the same area will show whether intrinsic hysteresis is taking place or not.

A typical data set obtained is shown in figure 3.9. The data is simply a plot of the force downwards on the microbalance (via the sample) vs. immersion depth of the sample into the solvent. The advancing and receding contact angles are determined

by extrapolating the immersion and withdrawal portions of the graph back to the y-axis (at which point the buoyancy contribution is nil and the system can be tared for the force caused as a result of the sample mass) [155].

The typical 'loop' shapes produced via this technique are discussed in more detail by several authors, with Miyama *et al.* [154] giving a particular comment on the shape and position of the loops produced. Weikart *et al.* [155] mention that if a film of solvent adheres to the surface between runs we will likely see a hoop shaped graph (rather than the more typical parallelogram), whilst Martin *et al.* [159] helpfully produced four schematics of the basic limits of plots produced using the Wilhelmy plate technique.

There are additional benefits to this technique. Lander *et al.* [153] made a comparison of various means of analysing the contact angle and concluded that the Wilhelmy plate technique was the best. Particular benefits highlighted are (compared with static goniometry) that operator subjectivity is reduced or eliminated and that a much larger surface area of each specimen is sampled for a given measurement [153].

The typical operating parameters for Dynamic Contact Angle analysis used in this work included a four loop cycle immersion and withdrawal (per sample), beginning by immersing to a depth of 10mm, then retreating to 5mm, then cycling between 15 and 5mm three times before complete withdrawal of the sample. This procedure allowed the repeated wetting of the 5-10mm region four times, 5-15mm region three times, and the initial wetting of dry material in both the first and second cycles. Thus repeat information could easily be obtained from the same sample. Sample sizes were typically 1.5cm across and during all runs sample speed was kept at $40\mu\text{ms}^{-1}$.

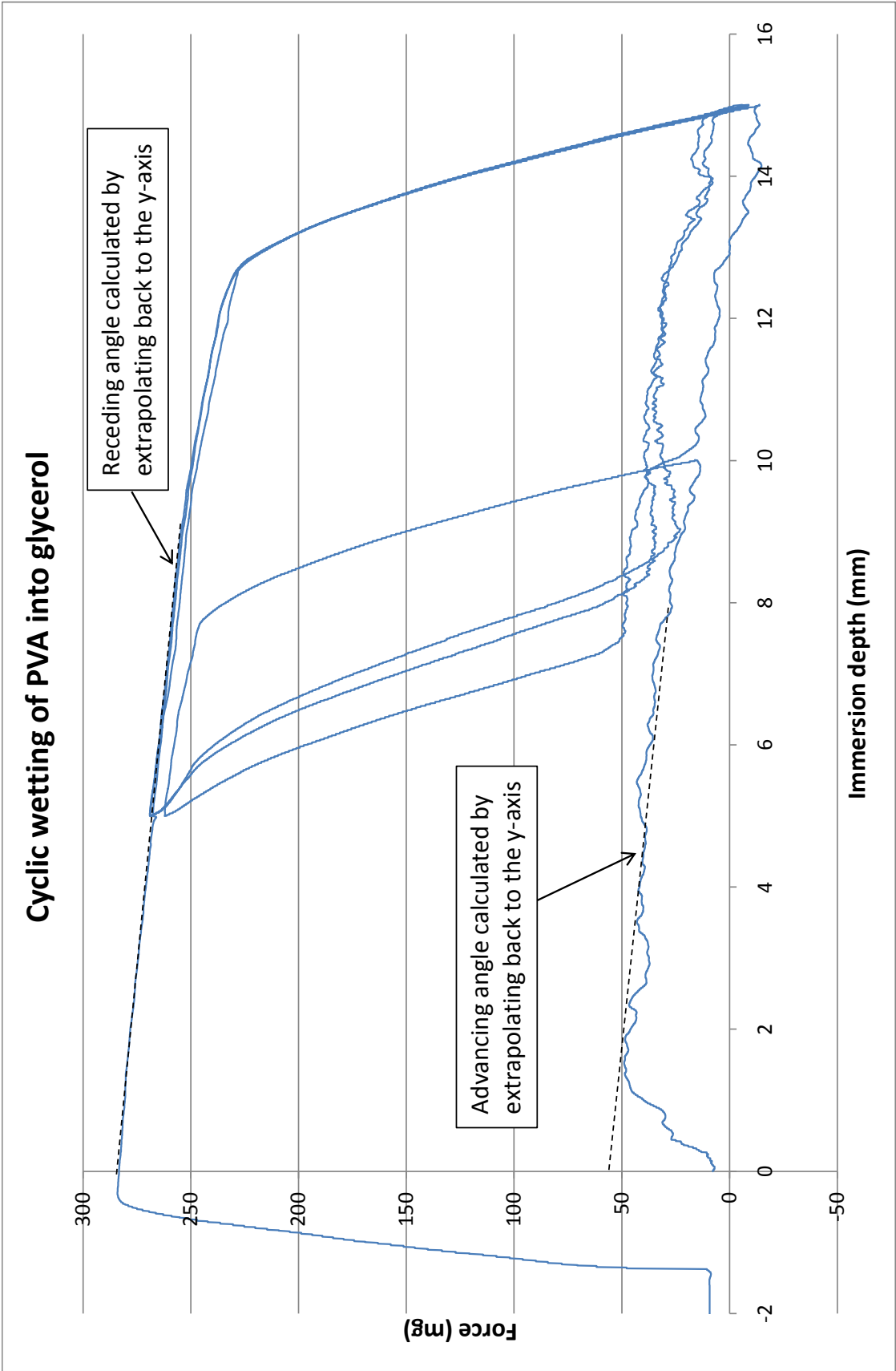
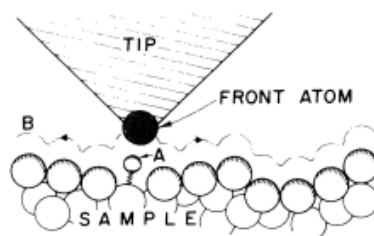


Figure 3.9: Dynamic contact angle data for glycerol on PVA.

3.6 Atomic Force Microscopy

The atomic force microscope (AFM) was invented by Binnig, Quate and Gerber in 1986 [160]. It provides a means of investigating the surface of insulators on an atomic scale [160]. In essence an AFM consists of a small cantilever with one end consisting of a sharp tip (typical tip radius $\sim 10\text{nm}$) whilst the other end is held in a fixed position. A sample is placed on a moveable stage underneath the tip and the stage is then moved in the x- and y- directions to allow an area of the sample to be 'imaged' by the probe. The probe tip interacts with the sample surface through electrostatic interactions between the lowest tip atom (typically 2/3 atoms in practice if the tip is not atomically sharp) and the atoms on the top most layer of the sample surface. In this way the tip is moved up and down according to any surface undulations.

A laser is reflected off the top surface of the cantilever. As the tip's vertical position is changed (due to attraction with or repulsion from the surface) the laser beam reflection is picked up in a slightly different place on the detector, thus allowing the surface to be mapped. The basic operating principle of AFM is shown in figure 3.10.



Reprinted with permission from Binnig, G., Quate, C. F. & Gerber, Ch., *Phys. Rev. Lett.* Vol 56, 930 (1986). © 1986 by the American Physical Society. Available at <http://link.aps.org/doi/10.1103/>

Figure 3.10: Reproduction of figure 1 in [160].

Thus far the topographical contact mode of imaging has been described. Subsequent advancement of the AFM incorporated a non-contact mode and then a tapping mode (principally for softer surfaces where it is possible to damage the surface and / or tip during imaging). For non-contact the tip never touches the surface (i.e. it only interacts with the outermost van der Waals forces), whilst for tapping mode it does. In both cases the tip is oscillated, however the cantilever oscillation amplitude is different in each case (typically $<5\text{nm}$ for non-contact AFM, and ~ 20 to 100nm for tapping mode [161]). This means that for the case of tapping mode the tip is

oscillating with much more energy and so is unlikely to permanently adhere to the surface (which is sometimes a problem when using non-contact mode) [161].

Introducing the oscillation means that several new imaging modes are available including phase imaging, which is a measure of the phase lag in the vibration (comparing the oscillation with which the cantilever is driven with the resulting oscillation as a result of surface interaction). This yields information on chemistry changes on the surface (amongst other things).

In this work AFM was primarily used to give topographical information about the film surfaces. (Other imaging modes were sometimes made use of, including the phase and error imaging feeds.) Two machines were used, and these were a Park Scientific Autoprobe CP (using NSC35/AIBS tips manufactured by MikroMasch) and a Pacific Nanotechnology Nano-R AFM (using P-MCU-SICC-0 tips). In all cases tapping mode images were recorded. For 'soft' polymers such as PVA contact mode imaging is not particularly suitable, as the tips tend to damage the soft surface and they themselves become blunted [161]. However tapping mode is perfectly suitable for materials such as PVA [162].

Typically images were recorded at a frequency of one line per second and a resolution of 256 lines. This gave a good compromise between image quality and speed of acquisition. The optimum image size was found to be $5\mu\text{m}^2$ as the sample began to get damaged below $1\mu\text{m}^2$, above $10\mu\text{m}^2$ the depth of field suffered, again making interpretation more difficult.

The images often needed processing to remove artefacts (such as a polynomial background). All image corrections were performed using the software package 'Gwyddion' (see <http://gwyddion.net/> for details on this software) or WSxM (as detailed by Horcas *et al.* [163]).

A home made heating-stage for the Park Scientific AFM was constructed (by a fellow member of the research group [164]). A strain gauge was mounted onto a thermally insulating substrate (a piece of cork) and connected to a direct current elec-

tricity supply. Two carbon ‘sticky-pads’ were mounted either side of the gauge onto which the sample under test was placed. The system was calibrated by using the stage to melt three materials of known T_m , wood’s metal (70°C), indium/tin alloy (118°C) and indium (156°C).

3.7 Fourier Transform Infra-Red Spectroscopy

Fourier Transform Infra-Red Spectroscopy (FTIR) is a means of chemical analysis of a sample. It operates by probing a sample with a beam of infrared radiation (the infrared spectrum varying roughly from a wavelength of $0.7\mu\text{m}$ to $500\mu\text{m}$). For the purposes of infrared spectroscopy wavelengths are typically quoted in wavenumbers, the unit being number of waves per cm (which will be used throughout this work to agree with convention). The infrared range is typically subdivided into far-infrared (4 to 400cm^{-1}), mid-infrared (400 to $4,000\text{cm}^{-1}$) and near-infrared ($4,000$ to $14,000\text{cm}^{-1}$), with the mid-infrared being the most commonly utilised.

By probing a sample with infrared radiation it is possible for the radiative energy to be absorbed by molecules within the sample, this however only takes place when two conditions are met. Firstly the absorbing molecule must be able to undergo a change in dipole moment and secondly the incoming photon must have enough energy to raise the molecule into the next allowed vibrational state.

Several types of vibration are possible, including symmetrical (ν_1) and anti-symmetric stretching (ν_3), scissoring (ν_2), rocking, wagging and twisting.

The wavenumber at which absorption occurs is at a characteristic value for a given molecule / moiety in a given configuration. This allows a ‘fingerprint’ for a given species to be produced by scanning across a range of wavenumbers (typically the mid-infrared region).

The specifics of Fourier Transform Infra-Red Spectroscopy typically includes the use of a Michelson Interferometer. Essentially this consists of two perpendicular plane

mirrors (one of which is moveable) as shown in figure 3.11. A beamsplitter bisects the planes of the two mirrors such that for a monochromatic incident beam of light 50% of the incident radiation goes to each mirror [165].

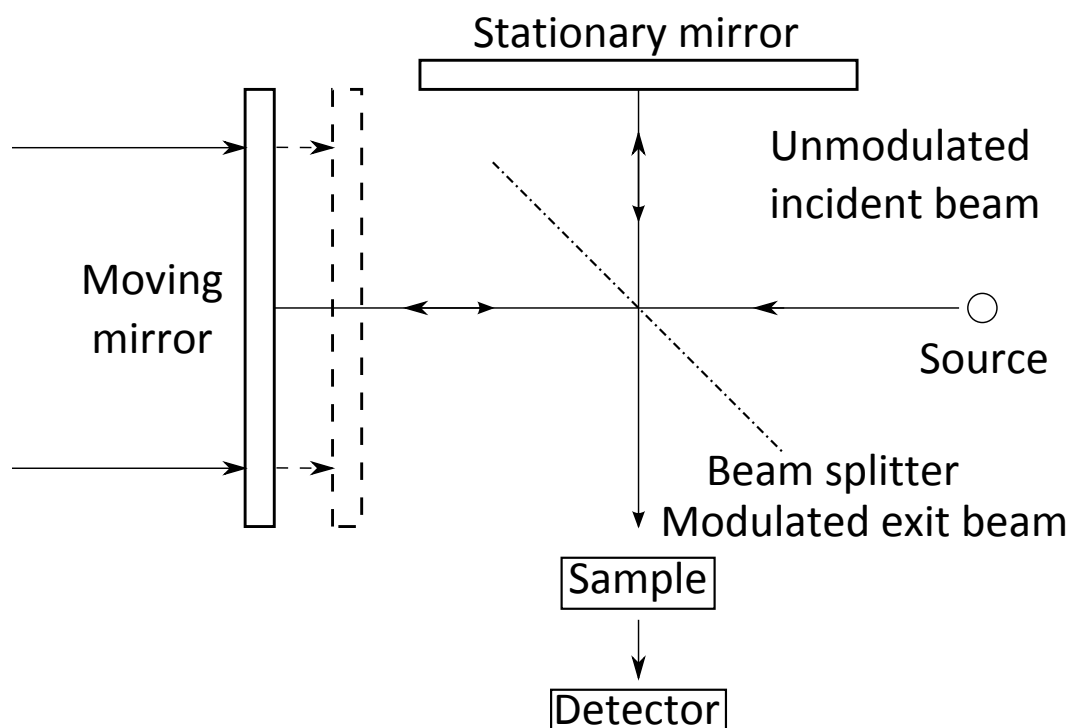


Figure 3.11: Schematics of a Michelson interferometer reproduced from Stuart [165].

Given that there is a difference in length between the two paths interference of the beam takes place and is constructive for a path difference of $(n + \frac{1}{2})\lambda$ [165]. As such varying the position of the moving mirror results in a different combination of wavelengths undergoing constructive and destructive interference. Thus by positioning the mirror in many positions many spectra can be recorded. Such spectra are then collated and a Fourier Transform performed. Such a calculation accounts for the fact that for a given mirror position the intensity of a given wavelength of radiation will vary, thus allowing a spectrum to be quickly built up for many wavelengths in a short period of time.

During operation a reference spectrum is first recorded (with no sample present) to enable the 'background' peaks of the atmosphere to be subtracted from those of the sample. Samples can then either be examined in transmission mode (by placing the sample directly in the line of the beam) or in attenuated total reflectance (ATR) mode.

ATR mode involves placing the sample in contact with a crystal through which the infrared beam is propagated (see figure 3.12). The beam undergoes internal reflection at the surface of the crystal, though a portion escapes and enters the sample (typically the beam amplitude at a depth of $1\mu\text{m}$ is $1/e$ of that at the entry surface [166]). Some of this beam then propagates back along the sample surface to be picked up by the detector. The primary advantages of ATR mode are that it is surface-specific (to a depth of $\sim 1\mu\text{m}$), it is possible to analyse samples which are too thick or strongly absorbing to be run in transmission mode and also the sample requirements and prior preparation are minimal. The primary disadvantage is that the signal obtained is dependent on how good the contact is between the sample and the crystal (thus leading to some uncertainty in the results when comparing samples).

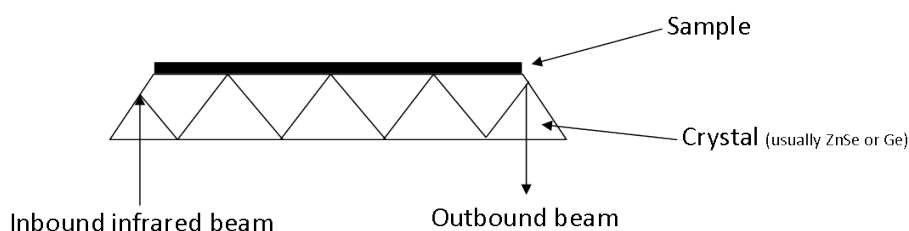


Figure 3.12: Basic principles of operation of the ATR mode of analysis.

It possible to convert between transmission and absorption data by using equation 3.4.

$$A = \log_{10} \frac{P_{in}}{P_{out}} \quad (3.4)$$

Where P_{in} and P_{out} are the power of the beam entering and leaving the sample respectively.

The advantages of FTIR are that it is relatively quick and easy to mount a sample and record a spectrum and it is extremely useful at identifying certain functional groups. It is also possible to use infrared spectroscopy to determine quantitatively the crystallinity of a semi-crystalline sample. This is discussed further in section 6.4.5.

There are several limitations to the FTIR spectroscopy technique. Firstly it is rarely

possible to identify an unknown compound by using FTIR alone, instead it is more sensible to look for specific groups and build up an assessment of a compound with complimentary techniques. Secondly the peak positions for given absorbing groups are not rigidly fixed at a given wavenumber. Peaks can be shifted by any other atoms joined to a particular bond, neighbouring groups and also conjugation. Shifting is usually limited to less than 30cm^{-1} in each direction.

Predominantly in this work ATR mode has been used as it has been the sample surfaces' which have been of most interest. Since relative (rather than absolute) comparisons have usually been made the aforementioned artefacts have not been a concern.

It is often necessary to normalise data between spectra. This is done by selecting bands which will be unchanged by the modification put forward in this work. The spectra were normalised by either shifting the entire spectra up or down (if the baseline [around 2000cm^{-1}] region with 0% absorption was a significant distance away from from absorbance = 0%) and / or multiplied by a factor to make the unchanged bands fit.

Various peaks have previously been used to normalise PVA spectra, including 1427cm^{-1} (attributed to the C-H bending vibration [167, 168]), 1093cm^{-1} (attributed to -CO bonds [168]) and at 854cm^{-1} [64]. In this work the peak around 1423cm^{-1} was used, along with the neighbouring distinct peaks found at 1329cm^{-1} and 1374cm^{-1} - as fitting to all three gave a very high confidence level for comparing spectra.

It is also important to point out common artefacts seen in FTIR spectra, the most common of which is as a result of atmospheric CO_2 , which has two distinct peaks around 2380cm^{-1} . Water vapour should show up as a broad shoulder around 3300cm^{-1} .

A typical spectrum of untreated PVA is shown in figure 3.13. The principal peaks have been labelled primarily according to Finch [8]. Further information is provided by Krimm *et al.* [169] and Peppas [168].

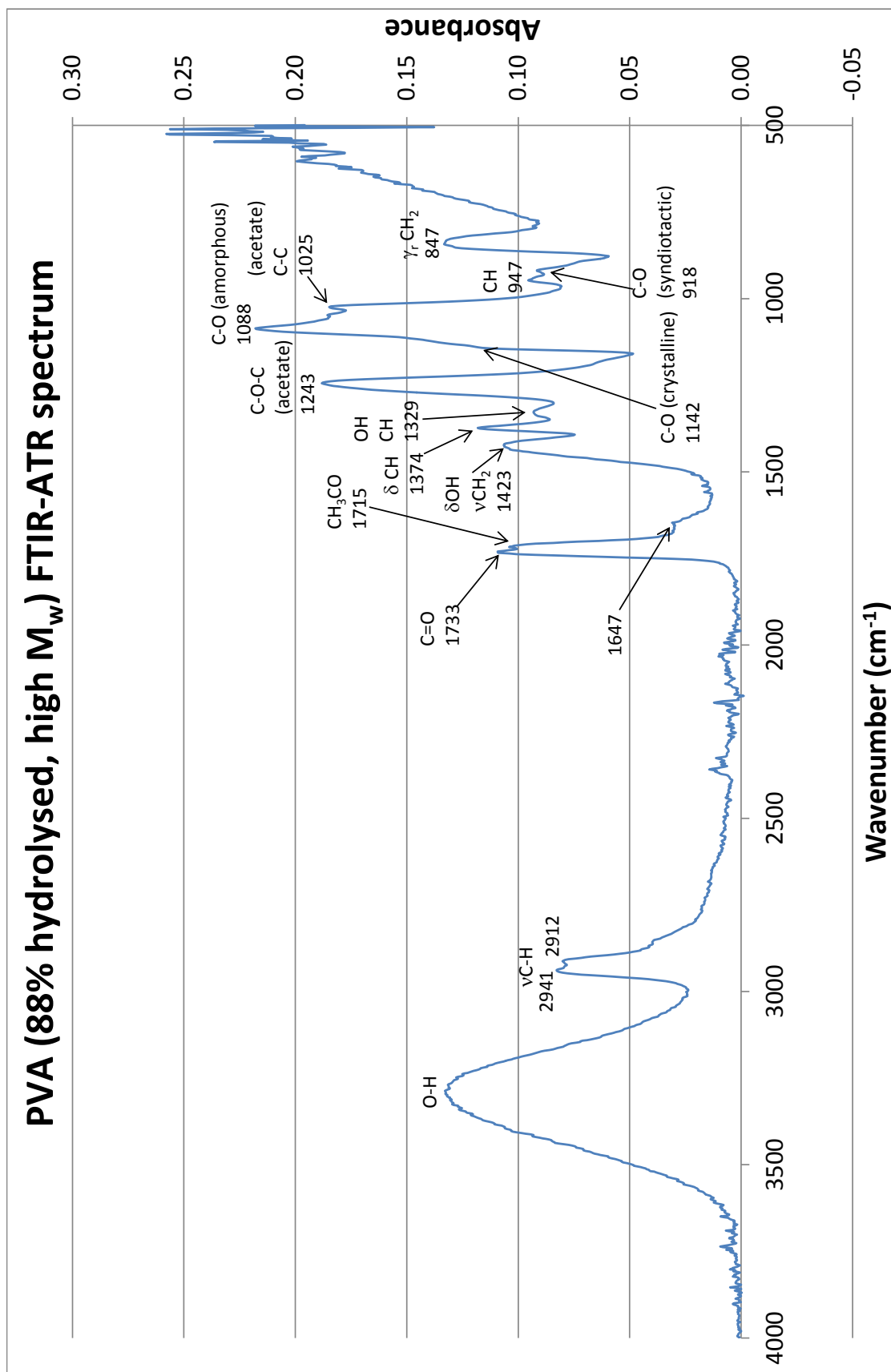


Figure 3.13: FTIR-ATR spectrum of PVA.

Throughout this work the FTIR spectrometer used was a Varian Excalibur FTIR microscope. Background spectra were always taken prior to the first sample in each run. 64 spectra per sample were taken (and co-added) at a resolution of 2cm^{-1} and at a speed of 5Khz. (The other parameters selected were: Filter = 1.2, UDR = 2, Sensitivity = 1, Internal detector = DTGS).

3.8 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) provides a means of determining various thermal properties of polymer samples. The ‘differential microcalorimeter’ was first proposed by Watson *et al.* [170]. In their work a sample of the material under test was heated at a pre-determined rate and the energy required to maintain the heating rate compared with that of a reference sample (typically an aluminium pan). This is in contrast to the previous techniques which attempted to deliver the same energy to a test and reference sample and then measure the resulting temperatures of the two.

By monitoring the energy required to keep heating a sample (or conversely the energy released when cooling a sample) it is possible to record thermal transitions taking place, including the glass transition temperature (T_g), the crystallization temperature (T_c) and the melting temperature (T_m). Gabbott [171] describes how the T_g can be extracted from a DSC trace.

Gabbott goes on to make several suggestions for optimising the experimental setup. Sample encapsulation is said to be key - with poor sample encapsulation being a prime cause of unexpected peaks in the traces [171]. The rate of the scan is also said to be a useful controllable parameter. Given equation 3.5 (reproduced from [171]) it can be seen that increasing the heating rate will increase the signal for a given transition; hence a quick scan can be useful to help show a transition which might otherwise be difficult to detect. (This of course also has the added benefit of reducing the experimental time). The main drawback of a quick scan is that by increasing the

scan rate the resolution of the data is reduced [171].

$$\frac{dH}{dt} = \frac{dH}{dT} \frac{dT}{dt} \quad (3.5)$$

Or alternatively, DSC signal (W/g) = Heat Capacity (J/(K g)) × Scanning Rate (K/s).

Previous examples in the literature of samples of PVA (or PVA -containing samples) analysed by DSC typically scanned samples at 10°C per minute [10, 62, 162, 172, 173]. The focus of most previous work was to use DSC to establish the T_g and T_m of the sample(s) in question.

The values of T_g previously recorded are around 80°C for ~99% hydrolysed [62, 174] and 69°C for ~88% hydrolysed [175].

Coffin *et al.* show that increasing the M_w of PVA leads to a slightly higher T_g [10], this can be explained by Cowie's reasoning which is that a higher M_w results in fewer chain ends per unit volume, thus there is less free volume available and so a higher T_g [24]. Coffin *et al.* [10] and Cowie [9] both claim that increasing the degree of hydrolysis increases the T_g , though the magnitude of increase is much bigger in Cowie's publication (27°C vs. ~5°C).

The DSC used in this work was a Perkin Elmer Diamond DSC running under Pyris v7.0 software. This software was also used for data analysis.

3.9 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a technique by which the type and proportion of each of the elements present in a sample's surface can be determined (excluding hydrogen and helium which are too light to be detected). The principle of operation is that the energetic X-rays interact with electrons present in the orbitals of atoms within the sample surface. If the energy of these is enough such that the

work function of the electrons is overcome they are able to escape from the surface and are picked up by the detector. The energy required to release electrons in this manner is element-specific, thus allowing elemental differentiation. Small shifts will also result from subtly different bonding environments.

The machine used in this work was an ion pumped VG Microtech CLAM 4 MCD analyser system with an unmonochromated Mg X-ray beam. Both wide and narrow (slower scans) have been obtained in this thesis, which were recorded out at 100eV and 20eV respectively. The data obtained was collected using the 'SPECTRA' operating system (version 8) and processed using CasaXPS. Peak areas were measured after satellite subtraction and background subtraction of either a linear background or following methods of Shirley [176].

Most authors agree that it is approximately the top 5nm of a sample which is probed by the beam [53, 84, 135], hence making it a surface-specific technique.

Limitations of XPS include the fact that it can give only the relative (and not absolute) content of chemical elements on a material's surface [177] and the risk of damage to organic materials under high power [178] - indeed, Akhter *et al.* used an X-ray beam to induce degradation on the surface of PVA [179] (though the beam energy was over 1000eV). In addition, the experimental setup necessitates an ultra-high vacuum and the lateral resolution of the beam 'spot' is typically of the order of a few mm's.

3.10 X-ray Diffraction

X-ray diffraction (XRD) is a technique which can be used to help determine the bulk microstructure of a sample. A beam of X-rays is fired at a sample and is subsequently scattered by interaction with the sample electrons. A crystalline arrangement of atoms will produce regular diffracted beams, some of which will constructively interfere according to Bragg's Law (3.6).

$$n\lambda = 2d \sin \theta \quad (3.6)$$

By varying the angle between the sample surface and the inbound X-ray beam any crystalline material will at some point satisfy Bragg's law. Assuming constructive interference a strong signal will then be picked up by the detector. For fully crystalline materials this will appear as a sharp peak at a given beam angle, however for semi-crystalline polymers a much broader peak is typically observed (due to microstructural imperfections in the crystals). Polymeric samples also produce a broad halo in an XRD spectrum and this is as a result of the amorphous material causing diffuse reflections in many directions.

By integrating the peak areas under the peaks and amorphous halos and then considering the relative proportion of each it is possible to calculate the crystalline fraction of a semi-crystalline polymer. The typical sample volume used to produce an XRD spectra is $\sim 1\mu\text{m}$ deep, and 5mm^2 . The principle advantages are that is a non-destructive technique and that sample preparation is minimal. The main disadvantages are that high resolution spectra can take several hours to complete and that for polymeric materials little information can be gleaned about individual crystals.

In this thesis the type of detector used was a Philips θ - 2θ PW1720 X-ray Diffractometer with a copper X-ray source with $K_\alpha = 0.15406\text{nm}$. Typical scan parameters were across the range of 4° to 60° degrees with a 0.02° step size and a step time of one second (which gave a good compromise between resolution and scan rate).

Chapter 4

Chemical Grafting

4.1 Literature recap

The basic principle of grafting is to produce the attachment of an intended atom or molecule onto a substrate's surface. This is typically done via covalent bonding onto a functional group on the surface. Grafting can be achieved by altering the initial monomers before polymerization, or it can be effected once a bulk polymer sample has been produced (see figure 4.1).

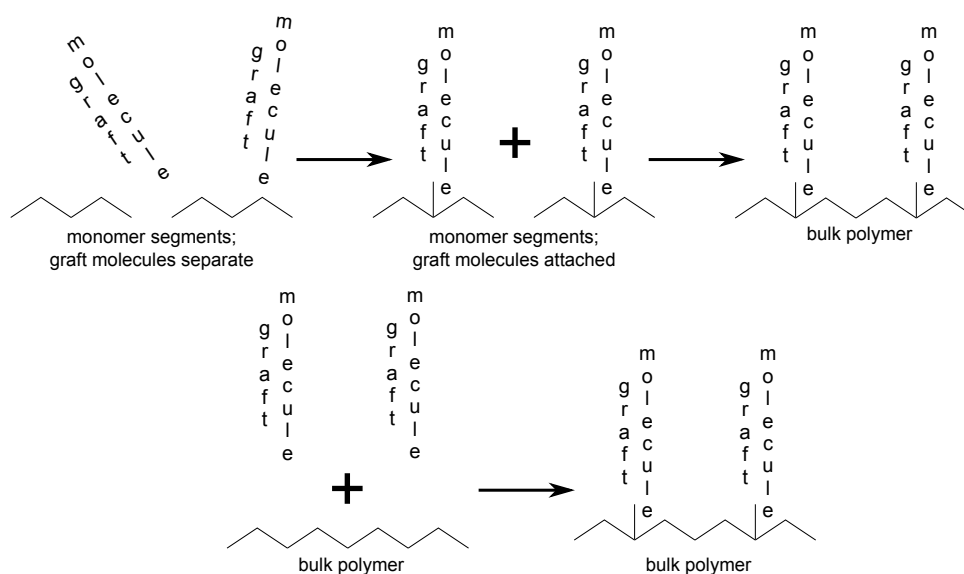


Figure 4.1: Two possible grafting routes.

There are several instances of previous grafting of chemical groups onto PVA. The majority of the work published to date has been on fully, or near fully hydrolysed material. Examples of grafting onto PVA performed to date are included in the literature review in section 2.3.1.

Since the aim of this work has been to decrease the interaction of the PVA surface with water whilst retaining the bulk properties grafting moieties onto the surface is a natural route to pursue.

4.2 Carbene modification

4.2.1 Hypothesis

An interesting species which can be utilised for grafting is that of carbene molecules. Carbene molecules are organic molecules with the general formula $R-C-R'$ (such that the carbon atom has two unpaired and non-bonded valence electrons) [180]. Moloney *et al.* [181] sought to make use of the reactivity of carbene molecules with typical bonds found in polymers (such as C-H, O-H and N-H). They anticipated that given the affinity of carbene groups for these bonds insertion onto polymer chains would be relatively straightforward.

The additional benefit of their method is that generally C-H bonds are not particularly useful for grafting onto, as whilst they are abundant they are not particularly reactive. However the chemistry set forth by Moloney *et al.* is able to react with them thus making use of their presence. Also the method only requires mild reaction conditions and inexpensive reagents.

4.2.2 Method

Based on the novel and recent (2005) method previously set out [181] (where attachment to silica, PE, PTFE were successfully performed) the coating of PVA with carbene molecules was attempted (and to the best of the author's knowledge this was the first time that this method had been trialled on PVA). Thus it gave the dual benefit of establishing whether it would be successful on a PVA substrate along with potentially furthering the understanding of the 'carbene' deposition method. Phenylpyridyl diazomethane was selected, principally because it contained a nitrogen atom it would be easier to detect a successful insertion via XPS.

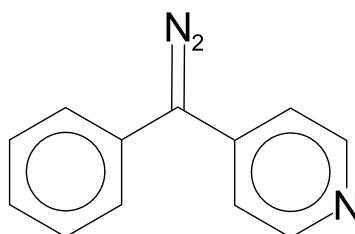


Figure 4.2: Phenylpyridyl diazomethane grafted onto PVA via the double-bond to the N atom.

A solution cast PVA film was prepared and a solution of 10wt% phenylpyridyl diazomethane in toluene made up. 0.05ml of this solution was then deposited onto 2cm² samples of dry PVA film. The coating reaction was then left to proceed overnight, following by drying in air, heating at 128°C for five minutes and then washing in toluene to remove excess unreacted diazomethane molecules.

There are a few limitations with this method. A higher temperature than 128°C would have been preferred as a greater amount of thermal energy would have resulted in the generation of more reactive carbene species for attachment onto the surface. However PVA begins to degrade rapidly above 150°C, thus a compromise was needed. Secondly the solvent had to be chosen carefully, toluene was selected as it was found not to swell or dissolve PVA or cause it to adhere to the glass Petri dish upon heating, however it should be noted that Moloney *et al.*'s preferred choice

of solvent is ether as this is more volatile and thus easier to remove.

4.2.3 Results

4.2.3.1 XPS

The treated films were then analysed using XPS. Initially wide sweeps were taken followed by slower, more focussed spectra around the C1s, N1s and O1s peaks to help clarify their relative atomic percentages. The results obtained are shown in figures 4.3 & 4.4.

We can use these results to calculate the surface coverage of PVA with the phenylpyridyl diazomethane. The key elemental percentages (obtained via the 'CASAXPS' software) are as follows:

Element	Non-coated sample	Coated sample
C	65.56 at%	66.30 at%
O	31.45 at%	24.51 at%
N	0.00 at%	3.28 at%

Table 4.1: Summary of XPS data for non-coated and coated PVA.

If the attached molecule is as in figure 4.5, then there are one nitrogen and twelve carbon atoms per attached molecule. Therefore if we were to only analyse the attached molecule we would expect (table 4.2):

Element	Concentration
C	92.3at%
O	0.0at%
N	7.69at%

Table 4.2: Atomic concentrations in just the attached carbene molecule.

The coated sample actually gave 3.28 at%N, therefore $3.28/7.69 = 42.65\%$ coverage. (Where 7.69 at% is the amount of nitrogen in the carbene groups only, hence only 42.65% of the atoms sampled in the XPS data belong to carbene groups).

This figure is somewhat limited in usefulness as the exact sample depth of the XPS is not known for certain. If it is assumed that only the top layer of material is sampled

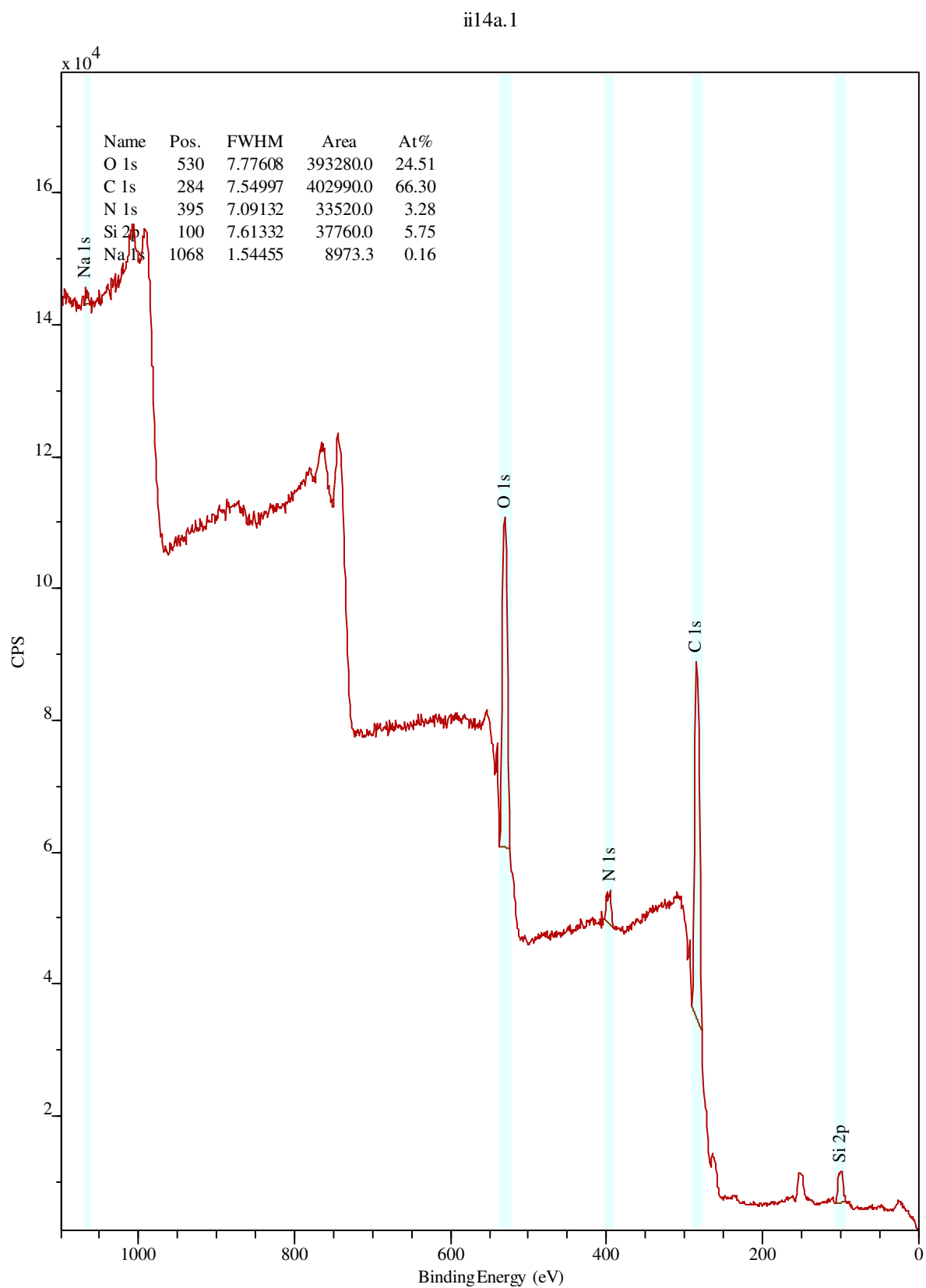


Figure 4.3: XPS spectrum of carbene modified PVA.

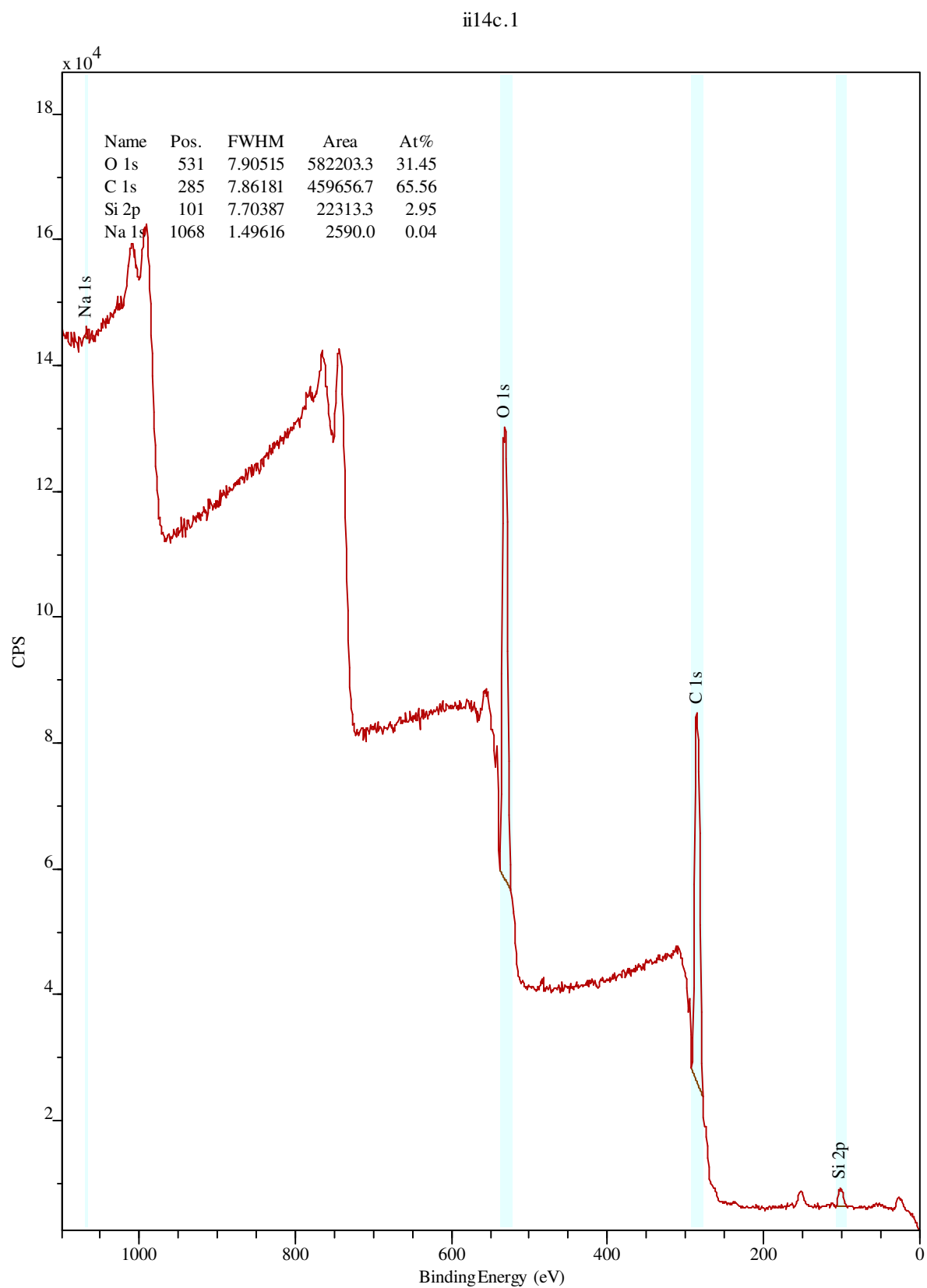


Figure 4.4: XPS spectrum of unmodified (control) PVA.

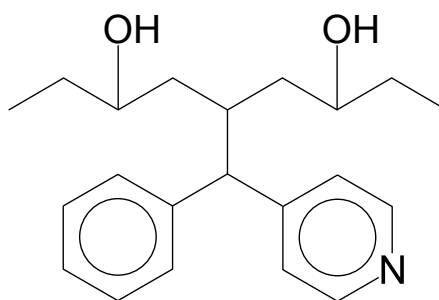


Figure 4.5: An attached phenylpyridyl diazomethane molecule.

then 42.65% can be said to be the coverage to a first approximation. However if the depth sampled is more than this then the coverage will actually be higher, i.e. 42.65% is a lower bound figure.

This conclusion is valid if the graft molecules are only present on the top most layer of the sample. Unfortunately XPS provides no information as to whether this is the case, nor does it tell us of the conformation of the attached molecules (they could lie in or out of the plane for example), or whether they are covalently or electrostatically attached to the surface.

4.2.3.2 FTIR

FTIR-ATR spectra were taken of the modified sample as shown in figure 4.6. The spectra have been normalised by fitting the peaks at 1329cm^{-1} (OH, CH) and 1423cm^{-1} (OH, CH_2) as these are believed to have been unaffected by the presence of the carbene molecules. A difference around 1602cm^{-1} would be expected as a result of the presence of the aromatic rings. Figure 4.6 hints at such a difference (with a very slight peak in the treated sample at a wavenumber just below 1602cm^{-1}).

4.2.3.3 AFM

AFM images were recorded and representative topographical information produced can be seen in figures 4.7 & 4.8. It can be seen that there appears to be some topographical change as a result of the modification. It is possible that agglomerates of

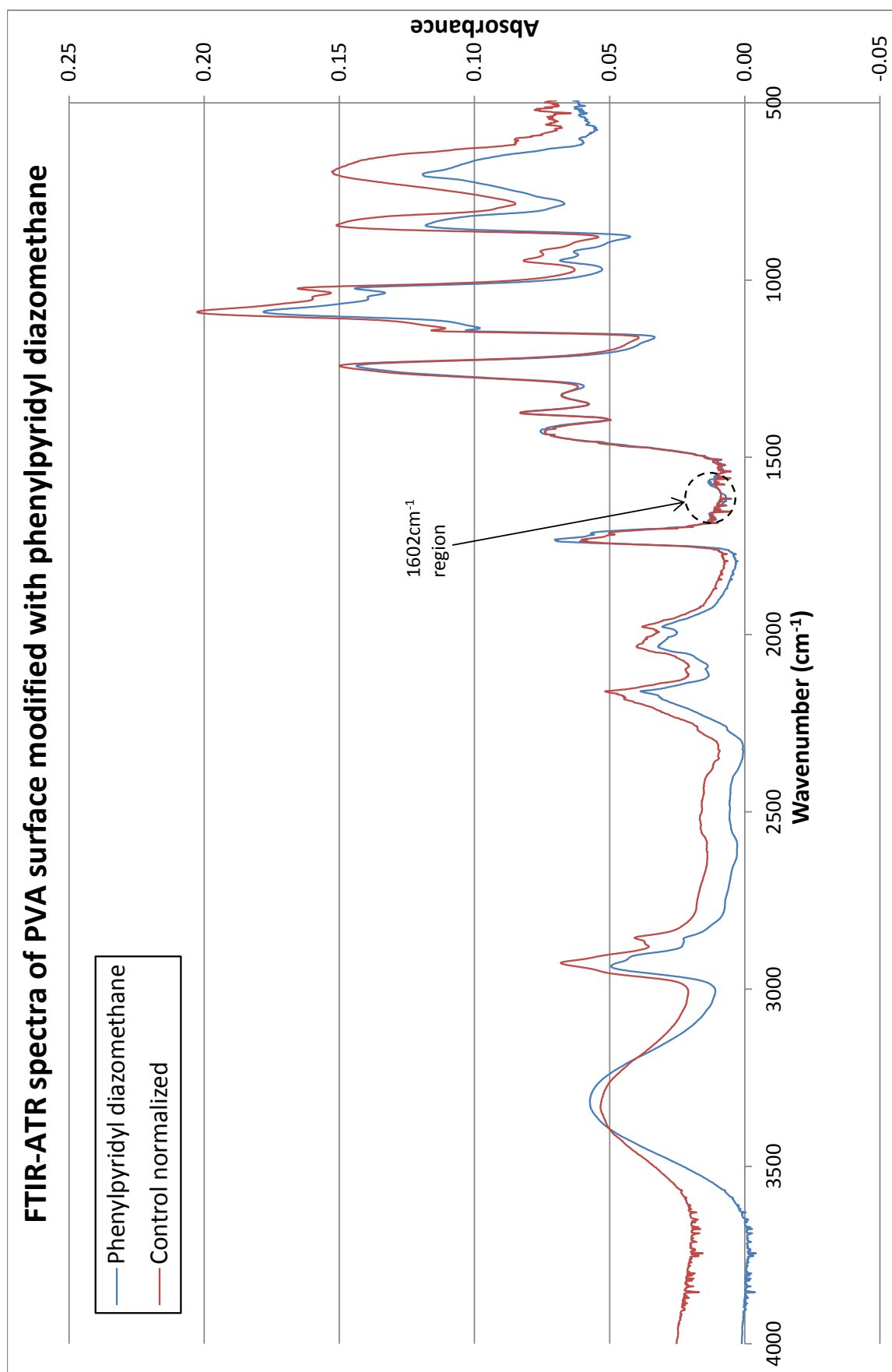


Figure 4.6: FTIR-ATR spectra of modified and control samples of PVA.

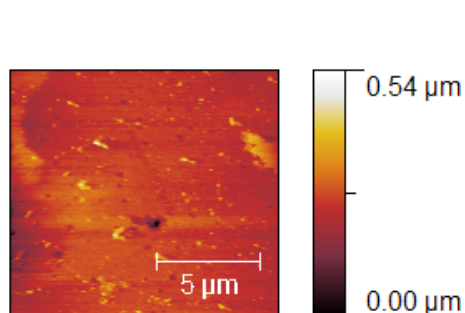


Figure 4.7: Topographical AFM image of PVA treated with phenylpyridyl diazomethane.

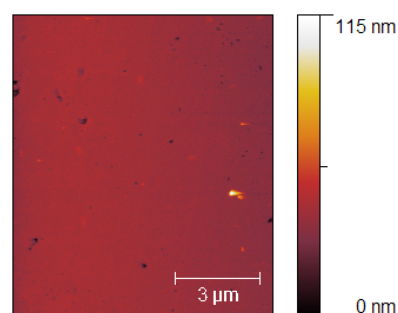


Figure 4.8: Control - PVA subjected to same solvents and heat treatment, but no carbene present.

some form have arranged on the surface. This would explain differing RMS roughness values for the two images, which are 33.8nm and 4.0nm for the treated and untreated films respectively. If there are agglomerates they must be as a result of the carbene molecules, as this is the only difference between the samples.

Therefore we can hypothesize two possible arrangements of groups on the sample surface. Firstly the substrate could be coated completely and then excess carbene molecules have agglomerated on top of that. Or alternatively the carbene molecules could have begun to agglomerate as soon as the deposition began, thus leaving certain areas of the film uncoated.

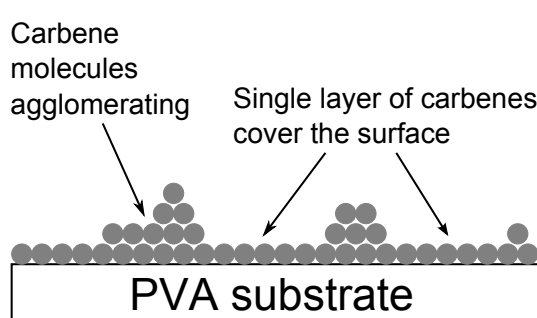


Figure 4.9: First coating possibility for carbene deposition.

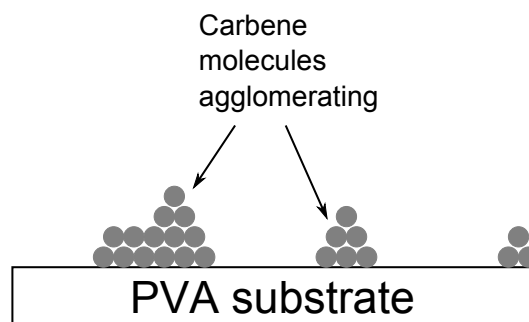


Figure 4.10: Second coating possibility for carbene deposition.

The XPS sample spot size was around 5mm in diameter which is many orders of magnitude bigger than the area analysed via AFM. Since the agglomerates cover only a small portion of the surface (figure 4.7) the area analysed will incorporate both the background and the protrusions present on the surface. Thus if figure 4.10 is correct then the level of carbene recorded will be very low, however a figure of 42.65% was obtained thus suggesting 4.9 is more likely.

4.3 Silane-based modification

4.3.1 Hypothesis

A further grafting route considered in this work has been the grafting of fluorine-containing chains, for example, 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PF-decyl).

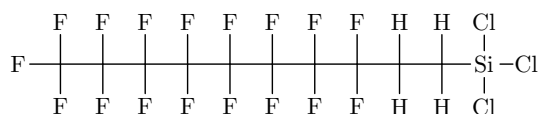


Figure 4.11: Structure of 1H,1H,2H,2H-perfluorodecyltrichlorosilane.

The intention is to couple these groups onto the surface by anchoring on through the trichlorosilane end group, to give a structure as in figure 4.12.

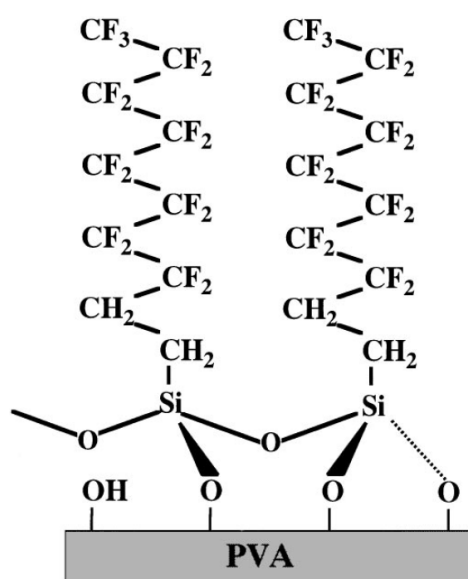


Figure 4.12: Reproduction of figure 8 from [74].

Fluorinated compounds were chosen as a result of their suitability in meeting the technical need of hydrophobicity and good solvent resistance as previously discussed in 2.3.1.2.

4.3.2 Method

Based principally on the encouraging work of Nishino *et al.* [74] it was decided to attempt to coat 87-89% hyd. PVA with PF-decyl (Nishino *et al.* used 98-99% hydrolysed PVA, with a molecular weight of approximately 80,700). They carried out the attachment by immersing their samples into a solution of PF-decyl and butanone at room temperature varying both the immersion time and the concentration of the PF-decyl solution.

They concluded that a fluorination reagent concentration of greater than 50wt% was needed to ensure complete substrate coverage, along with an immersion time of at least two days (given that no improvements in advancing and receding contact angles were observed upon increasing either the concentration or the immersion time beyond two days). The authors also undertook AFM and XPS analysis of their samples.

This relatively straightforward method was utilised to study the fluorination of 87-89% hydrolysed PVA in a similar manner. Since the material was slightly different a check was first made to confirm that the 87-89% hydrolysed PVA was not soluble in butanone, and after 90 minutes immersion the mass of the film had not changed (to the nearest mg).

Initially the reaction was trialled in a petri dish, however an abundance of off-white precipitate was formed on the surface of the film. It is believed that exposure to atmospheric water vapour caused the PF-decyl molecules to bond to each other and form micelles / agglomerates.

Thus the experimental procedure was modified such that the reaction was carried out in an inert and dry atmosphere. The first modification was to use a desiccator purged with nitrogen gas and with silica beads present. However this also failed to stop the copious amounts of precipitate forming.

Trials were subsequently run in a glove box and this worked much more satisfac-

torily. The glove box was purged with nitrogen (and the entrance chamber was purged with nitrogen gas three times before opening it into the main chamber). The films were placed in petri dishes and held down using carbon sticky pads. Solutions of PF-decyl and butanone were then mixed thoroughly before being poured onto the films. The petri dishes, films and solutions were left undisturbed in the glove box for a period of at least two days.

After this time the films were removed from the petri dishes, rinsed in butanone to remove any excess adsorbed PF-decyl and dried in a fume hood until their masses had stabilised.

In order to investigate the role of grafting, chain length and fluorination, this method was repeated in order to coat PVA using 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PF-octyl) and n-decyltrichlorosilane (n-decyl) in a similar manner.

In all trials a concentration of 25wt% silane agent was used. This was in order to help reduce the copious amount of precipitate formed in earlier trials (although a small amount of precipitate was still observed).

4.3.3 Results

4.3.3.1 Mass change of treated films

The average percentage mass change of the treated films after drying to steady state in a fume hood is shown in table 4.3.

Graft molecule	Average mass change	Error
PF-decyl	28%	$\pm 11\%$
PF-octyl	12%	$\pm 1\%$
n-decyl	6%	$\pm 2\%$

Table 4.3: Average mass change of coated films

For this work it appears that the PF-decyl deposits the most material, followed by the PF-octyl. A possible explanation for this is that the longer length of the PF-decyl

molecules leads to increased electrostatic forces between the excess molecules and micelles left on the surface. Thus they are more difficult to remove during the rinsing step. It is also possible that the PF-decyl molecules have a greater propensity to self cross-link and form micelles. Quite why this would be so remains to be determined.

Nishino *et al.* did not report the mass change of their material after grafting [74], nor did the other authors cited earlier who worked on depositing such compounds onto silicon.

4.3.3.2 Liquid water uptake

Since the films were treated on all sides it was decided to assess their level of solubility in water. Three samples of each film were cut out and swollen in 30 mls of distilled water as described in section 3.3. The results obtained are shown in figure 4.13.

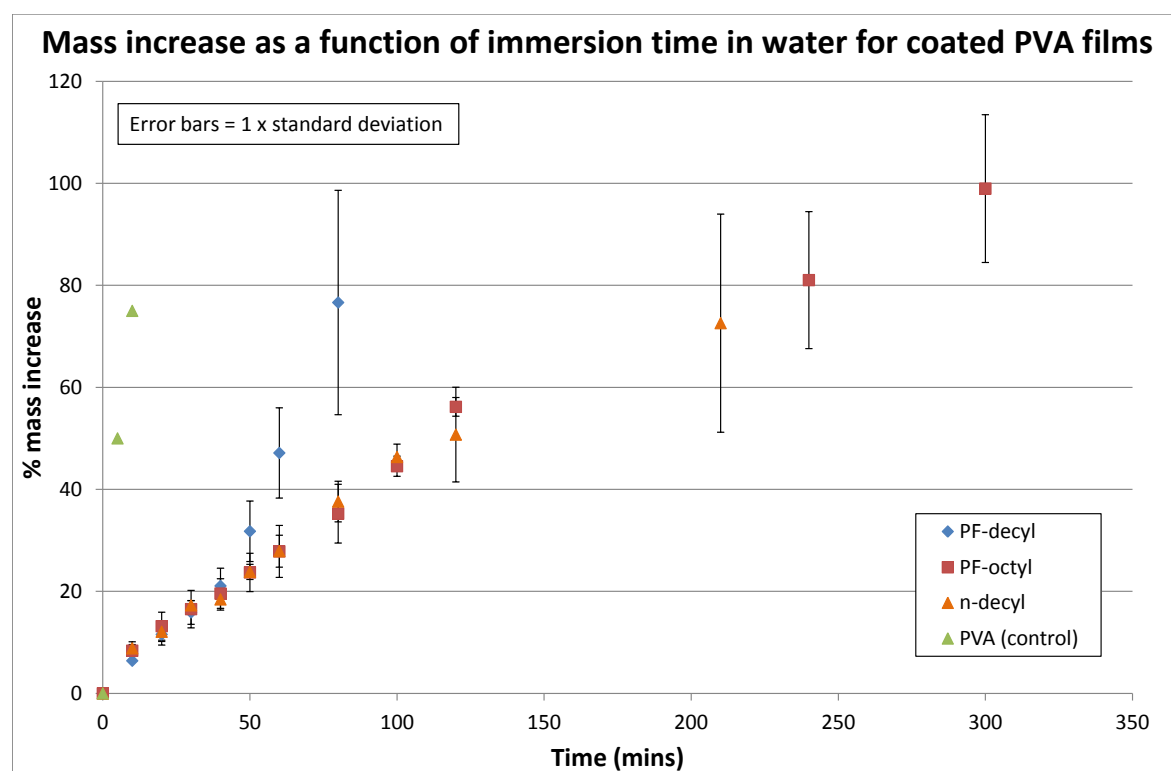


Figure 4.13: Liquid water uptake of PVA coated with PF-decyl, PF-octyl & n-decyl.

The reliability of the data can be seen by the error bars, which only start to become substantial at longer time periods. That is excepting the PF-decyl coated material, which beyond 80 minutes has error bars which become very substantial (spanning the range of 60 to 160% mass increase - this was as a result of the films having fragmented into several pieces by this point). Overall though the data implies a consistent enough coverage to give the same macro length-scale water resistance throughout.

Interestingly the n-decyl coated (ten non-fluorinated carbon atoms present) performs as well as the PF-octyl (six fluorinated carbons), thus implying that the mechanism of water resistance is predominantly dependent on the removal of the -OH groups, and that fluorination perhaps makes only a secondary difference.

The bulk water uptake can also be compared with that obtained by previous authors. Nishino *et al.* reported a mass increase of around 100% after 200 minutes in similarly modified PVA [74]. The mass uptake recorded in this work compares favourably, not having reached 100% after 200 minutes (barring the PF-decyl coated samples). This is perhaps a little surprising as Nishino *et al.* used a higher concentration of PF-decyltrichlorosilane agent, along with modifying an already more hydrophobic sample (98% hydrolysed). Thus the treatment procedure shows good promise.

However it should be noted that grafting onto 87-89% hydrolysed PVA in this way has not led to a complete prevention of water uptake (when immersed in pure water) which might be required for some applications. Water uptake has most definitely been hindered, but not entirely prevented. Thus several questions now arise, namely: are the samples completely covered with the intended compounds, secondly what is the microstructure of that deposit and finally what exactly is it which hinders water uptake? These are discussed later in section 4.4.2.

4.3.3.3 Water vapour uptake

Samples of each of the coated films were swollen over a saturated salt solution of NaCl three times each and the solvent uptake recorded. The average data recorded is shown in figure 4.14. Error bars ($\pm 1 \times$ standard deviation) for the data shown in figure 4.14 are shown in figures 4.16 to 4.19.

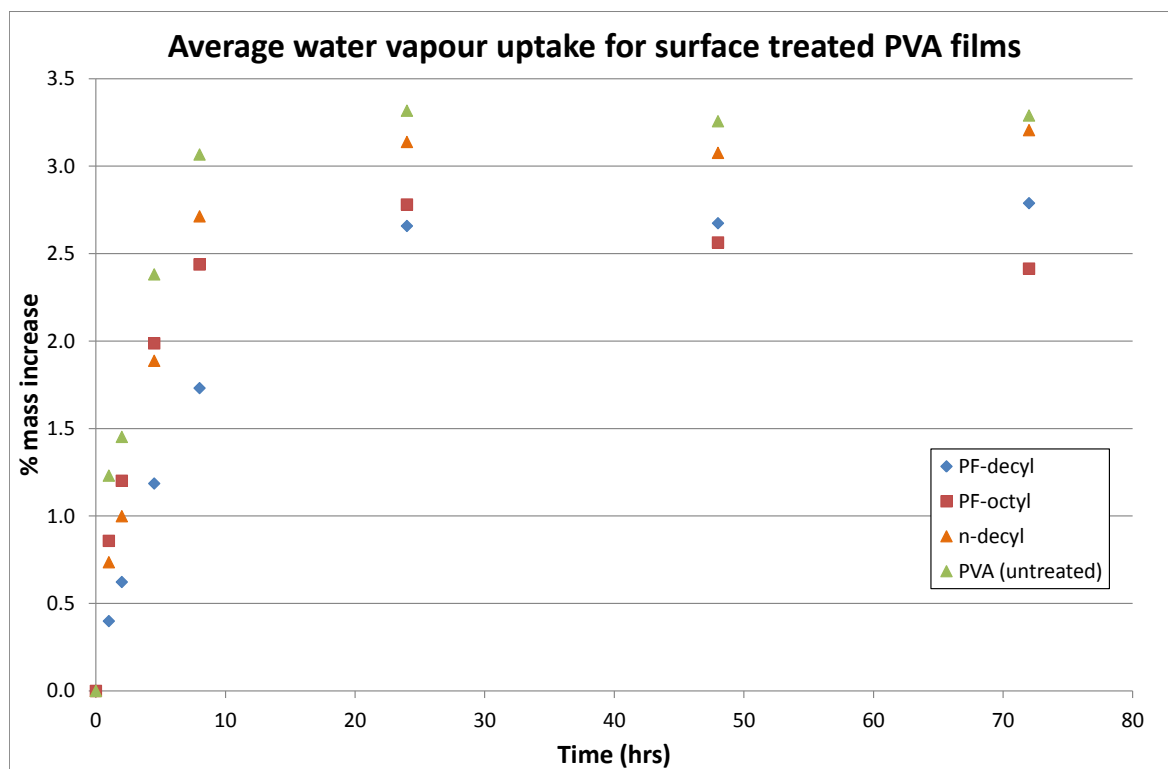


Figure 4.14: Average water vapour uptake data for grafted films.

With this test method the samples all appear to perform to a similar level, with perhaps the tentative conclusion that the fluorine containing samples take up marginally less vapour than the untreated PVA control and n-decyl coated samples.

Considering the initial data points (within the first 24 hours) it is possible to get an indication of the kinetics of water vapour uptake (using the absolute mass uptake as shown in figure 4.15). The PF-decyl coated has the most resistance to initial vapour uptake; the PF-octyl and n-decyl are comparable to one another (though the PF-octyl shows an improvement at 4.5 and 8 hours) followed by the control sample which has the least resistance to initial water vapour uptake. Table 4.4 shows the initial uptake values. It can be seen that after one hour the PF-decyl coated has taken up

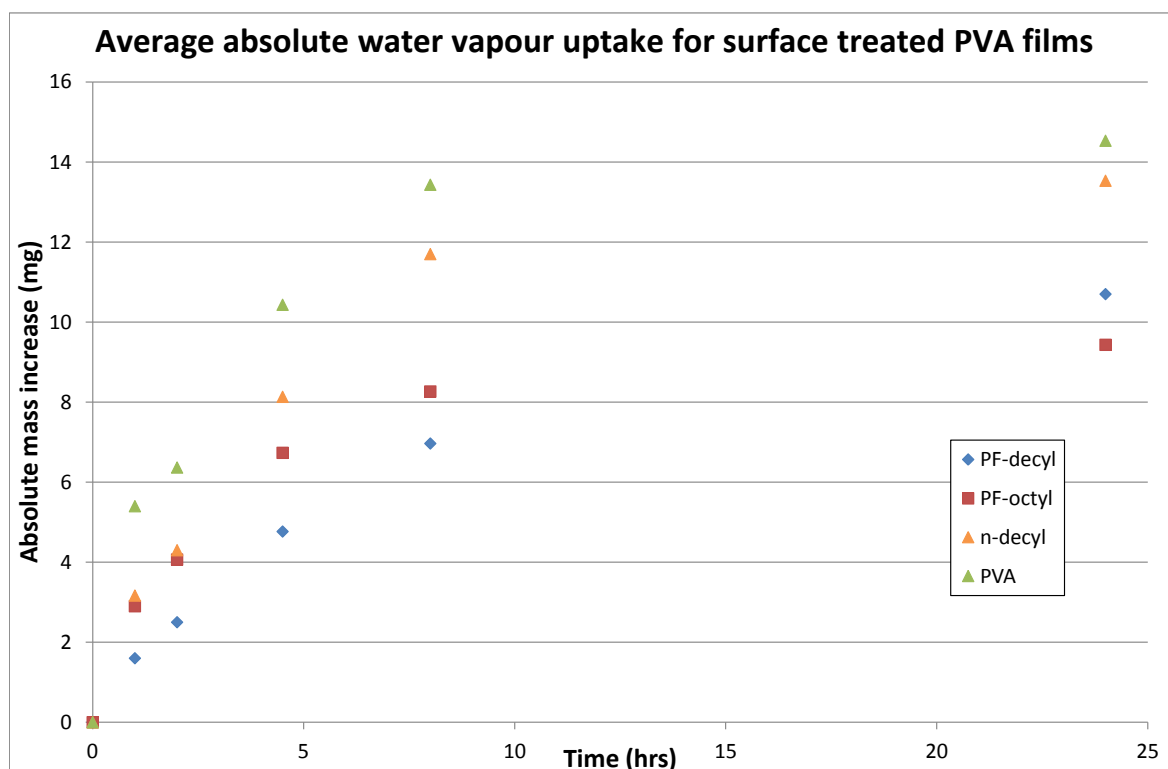


Figure 4.15: Average water vapour uptake data for grafted films.

only around half the water vapour of the other two treated films. After eight hours this figure has increased to roughly two thirds. Beyond twenty four hours the mass uptake values remain constant for all of the films.

Time (hrs)	Grafting material and absolute mass increase (mg)			
	PF-decyl	PF-octyl	n-decyl	Uncoated PVA
1.0	1.6	2.9	3.2	5.4
2.0	2.5	4.1	4.3	6.4
4.5	4.8	6.7	8.1	10.4
8.0	7.0	8.3	11.7	13.4
24.0	10.7	9.4	13.5	14.5

Table 4.4: Summary of early water vapour uptake measurements.

It is worth briefly comparing the liquid water uptake and water vapour data (figures 4.13 and 4.14). For immersion in liquid water the films absorb H_2O reasonably quickly, to the extent that their mass is doubled within a period of several hours. But for the water vapour uptake H_2O is taken up much slower, equilibrating at a film mass increase level of only about 2-3% after 24 hours. In both cases we have the same molecules entering the film, however their concentration is vastly different, being roughly three orders of magnitude greater for the case of a liquid over the vapour. Thus to a first approximation this concentration difference can be said to

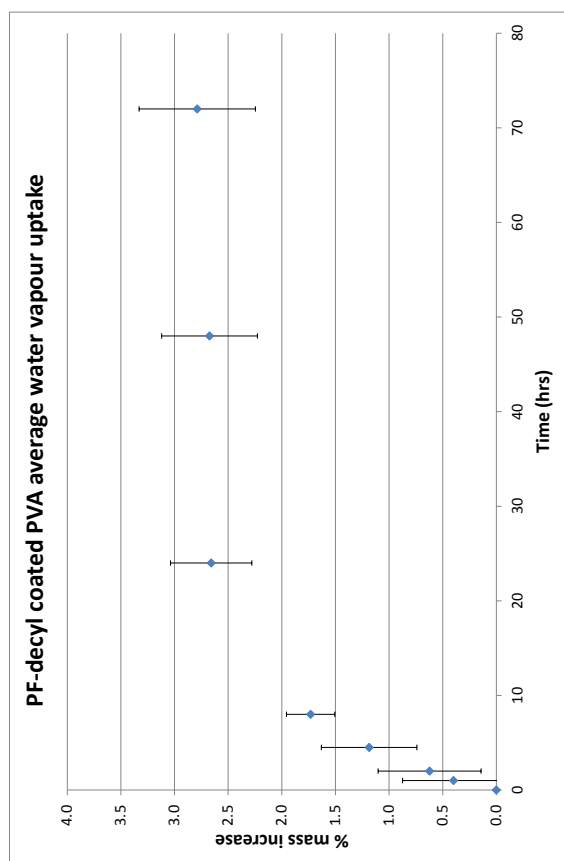


Figure 4.16: Water vapour uptake test PF-decyl coated PVA

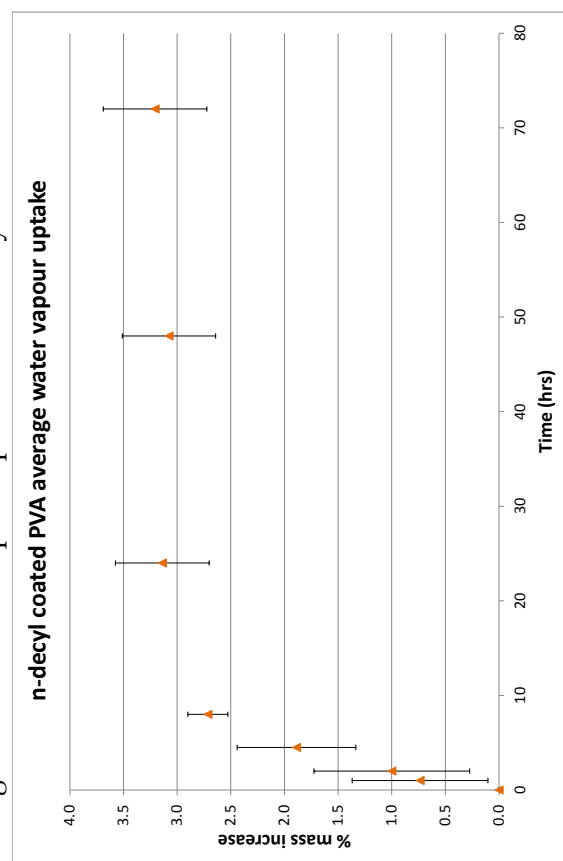


Figure 4.18: Water vapour uptake test n-decyl coated PVA

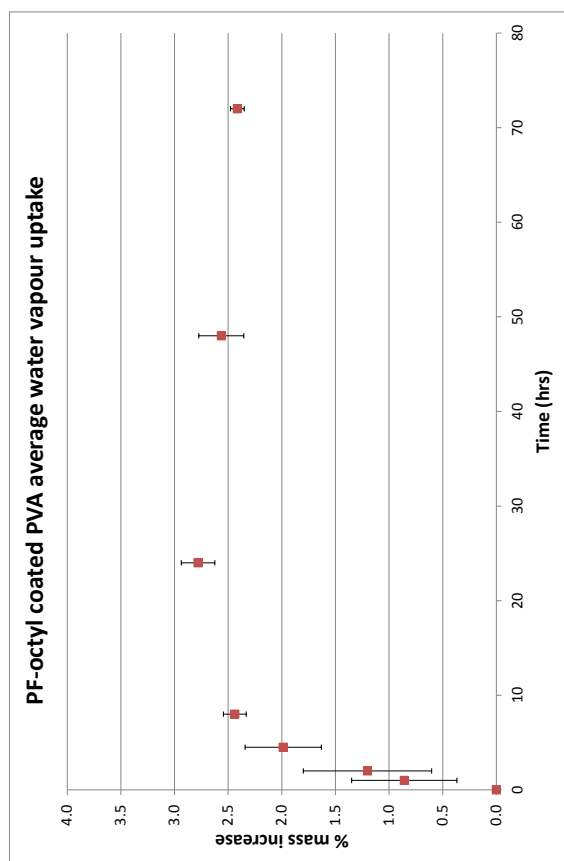


Figure 4.17: Water vapour uptake test PF-octyl coated PVA

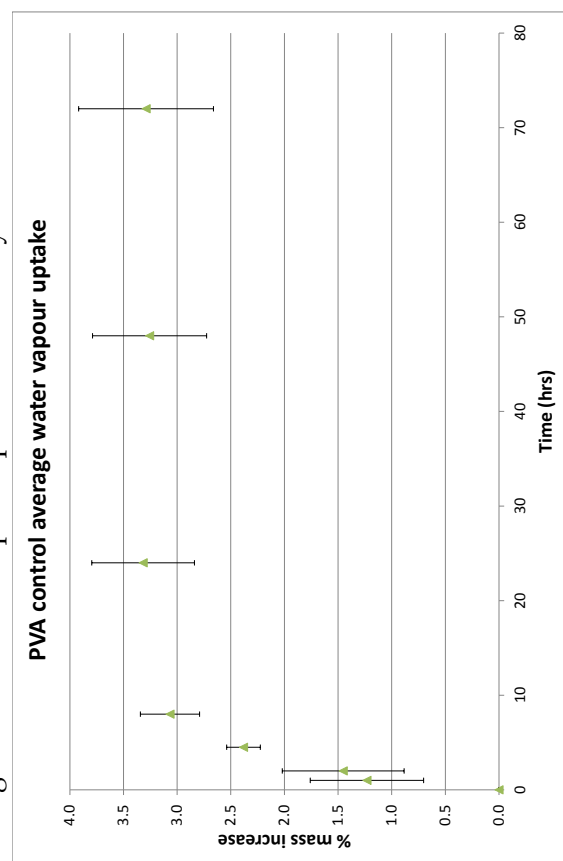


Figure 4.19: Water vapour uptake test for uncoated PVA

account for the difference in uptake rate.

Diffusion calculations

As outlined in section 3.4 the water vapour uptake method can be used to give an indication of the diffusion of water through a thin film. The model proposed there was for a film modified on one side, however the data shown in this section is for films treated on both sides. Therefore the model needs altering slightly. The driving force for solvent vapour through the film will still exist (owing to the different humidities on either side). However for films treated on both sides there is the additional constraint of a barrier to solvent leaving the film, thus the concentration profile is likely to be altered as shown in figure 4.20.

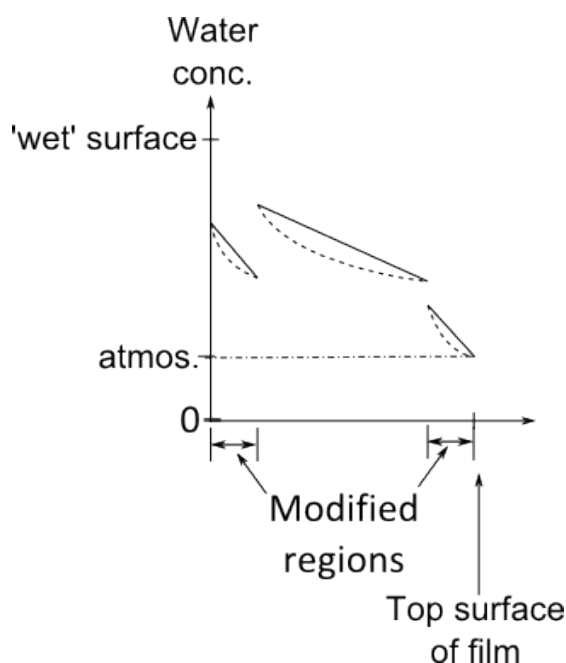


Figure 4.20: Vapour concentration profile for a film treated on both sides, as before the data points tend to straight lines as time increases.

The diffusion exponents have been calculated for the treated films according to the method set out in section 3.4.2 as shown in figure 4.21, yielding values of PF-decyl (0.72), PF-octyl (0.56) and n-decyl (0.63) (all to 2s.f.) which compare with ~ 0.7 for untreated PVA, implying that the PF-octyl coated has the most Fickian-like diffusion profile (though the figures all imply a mixed motion of diffusion - i.e. limited by both solvent diffusion and polymer relaxation to some extent). Without further testing

however it is difficult to draw any further conclusions, and also the fact that we have modified the film on both sides (to give the concentration profile of figure 4.20) has not been accounted for.

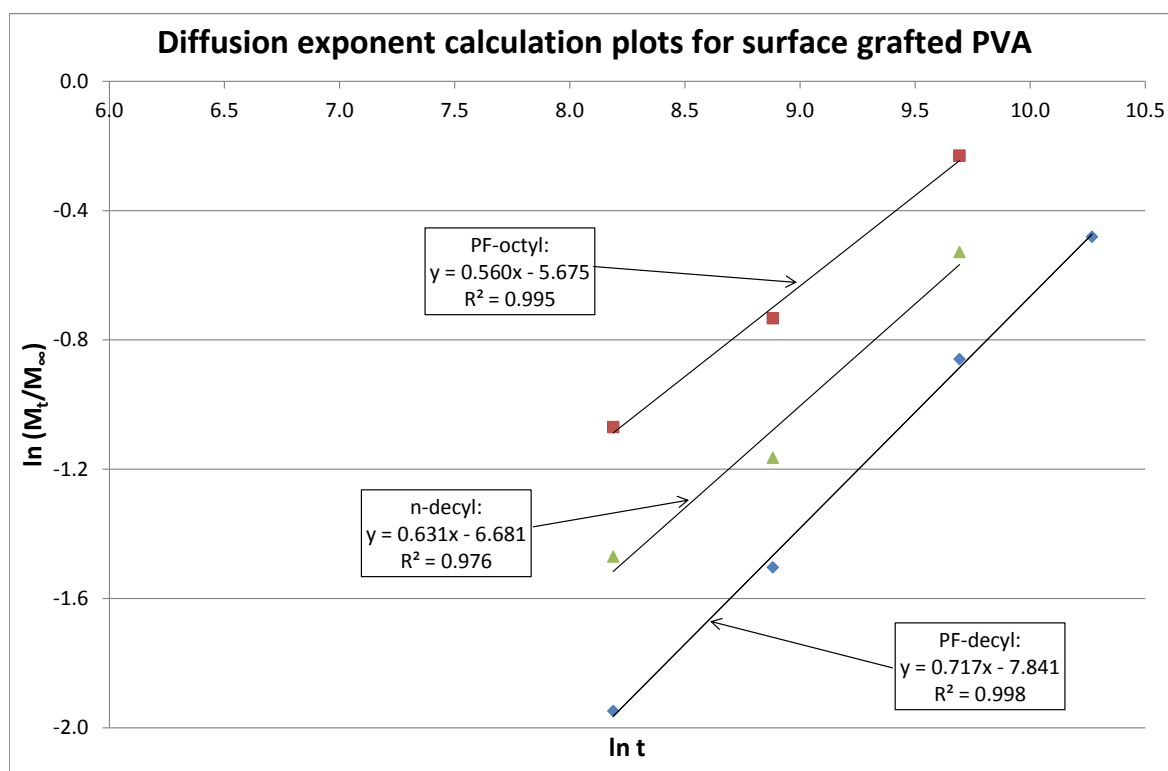


Figure 4.21: Plot of water vapour uptake to determine diffusion exponents, n , for grafted samples.

4.3.3.4 Infrared spectroscopy

Infrared spectroscopy (described more fully in section 3.7) was chosen to confirm the presence of the graft molecules via chemical analysis. The spectrometer was operated in ATR mode. As previously mentioned this analyses the surface of the sample only, thus it was ideally suited to this work (however it is limited in that it samples roughly the whole top $1\mu\text{m}$ of a sample). A reference spectrum of 88% hydrolysed PVA is shown in figure 4.22 and the majority of the peaks have been labelled according to Finch [8].

Spectra were taken of the treated samples, and they are shown in figures 4.23, 4.24 and 4.25.

Considering firstly the two fluorine containing samples, namely PVA coated with

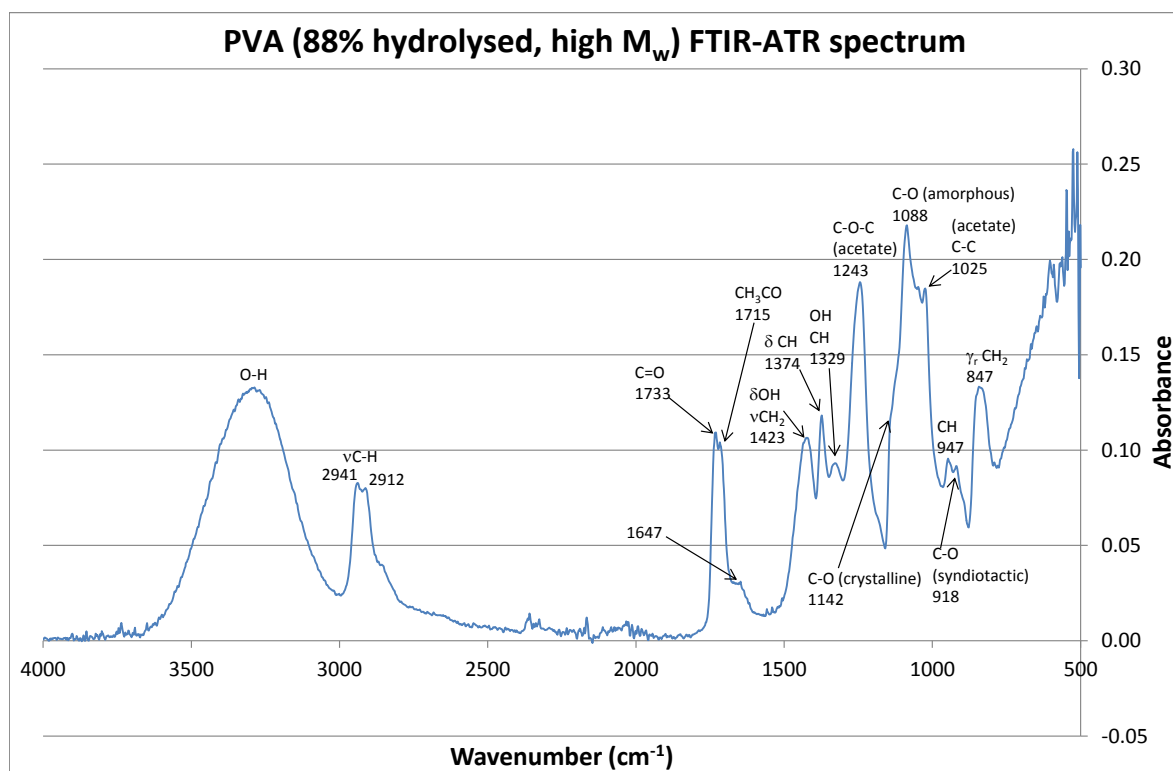


Figure 4.22: FTIR-ATR spectrum of untreated PVA.

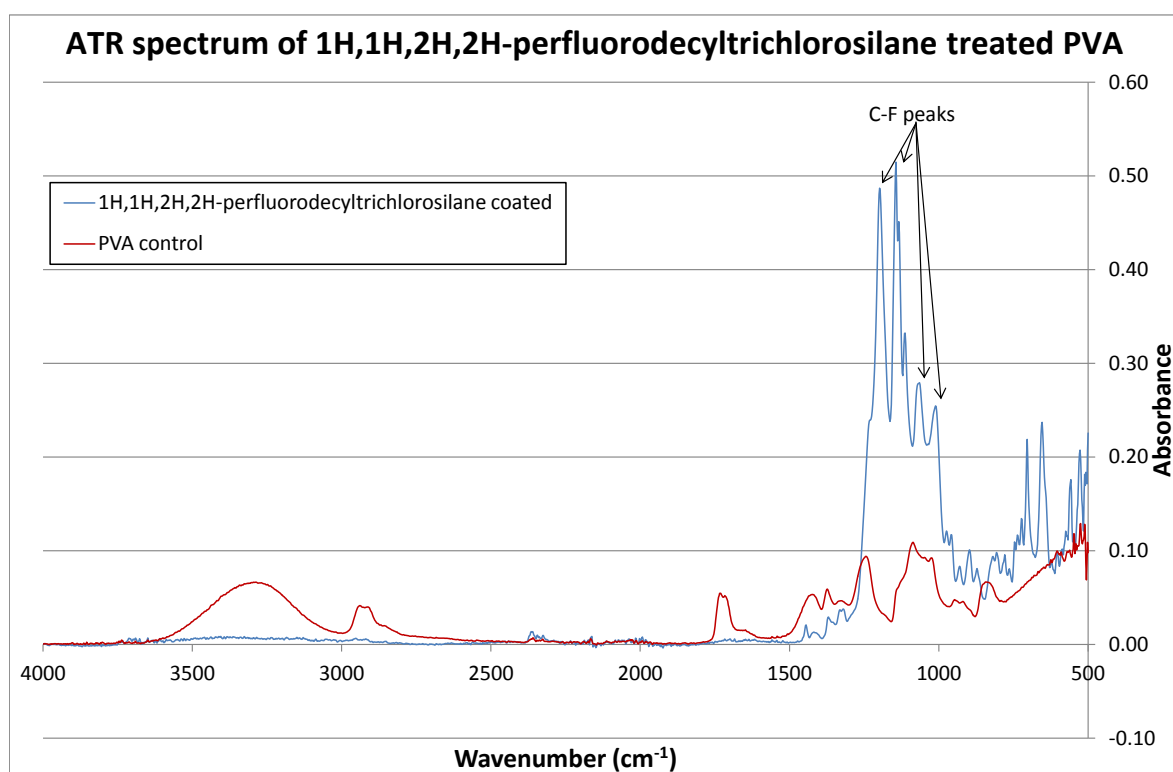


Figure 4.23: ATR spectrum of PVA coated with PF-decyl.

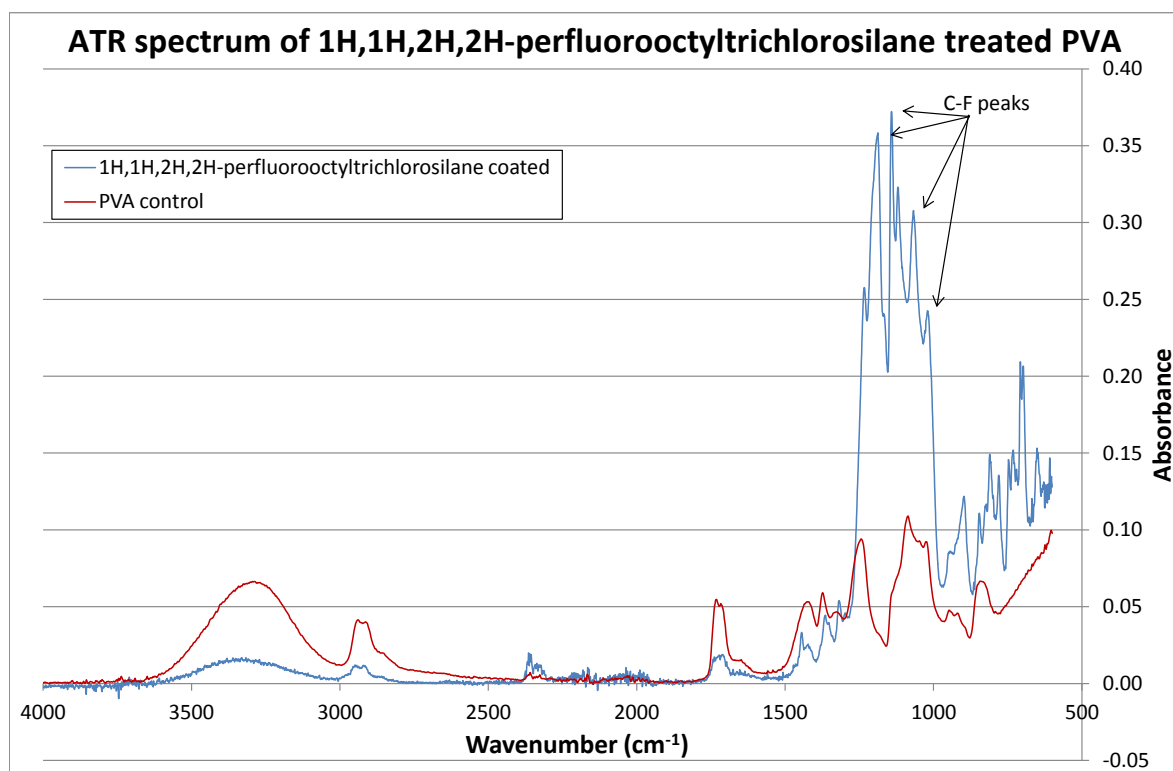


Figure 4.24: ATR spectrum of PVA coated with PF-octyl.

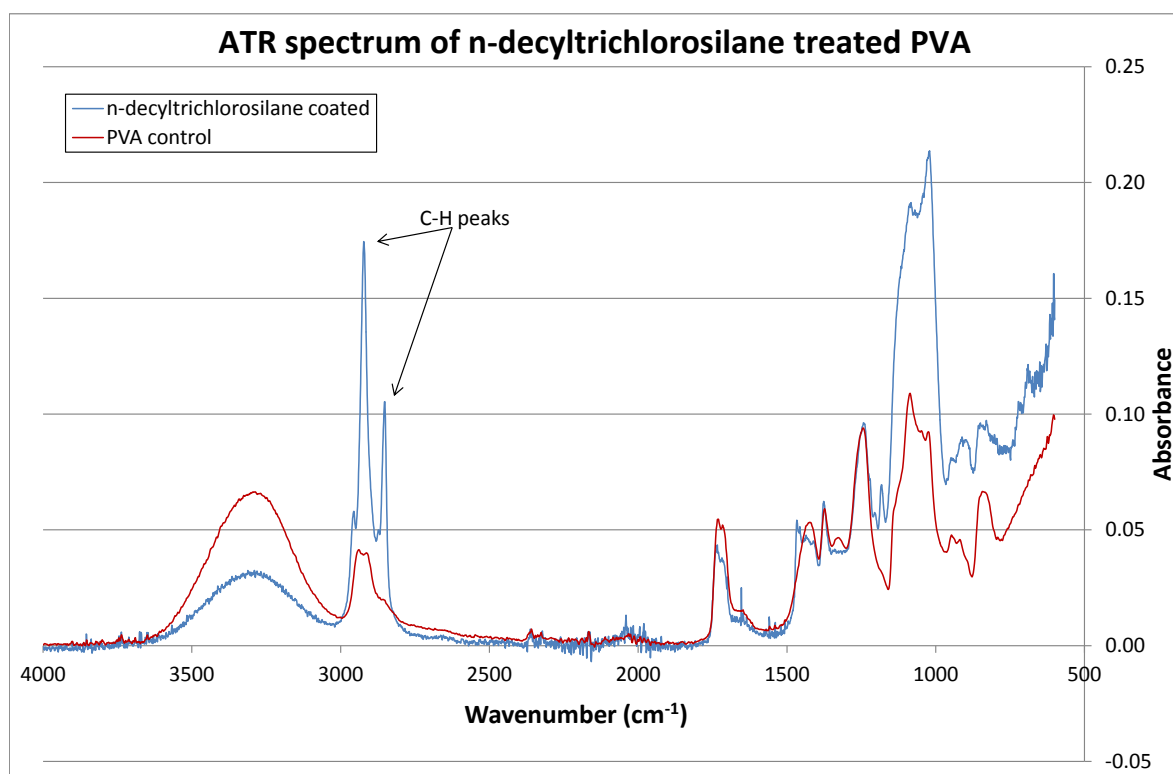


Figure 4.25: ATR spectrum of PVA coated with n-decyl.

PF-decyl and PF-octyl (figures 4.23 & 4.24). The presence of C-F bands confirms that the fluorinated molecules are present on the surface, however this technique is not able to elucidate whether or not the molecules are covalently bonded onto the surface, or simply adsorbed.

In both cases the C-F peaks absorb the infrared beam very strongly due to the large induced dipole in the C-F bond. However the presence of the fluorine seems to have diminished some of the underlying PVA peaks, for example the broad hydroxyl peak centred around 3270cm^{-1} , the CH_3CO peak at $\sim 1710\text{cm}^{-1}$ and the CH_2 peak at $\sim 820\text{cm}^{-1}$. This can easily be accounted for when considering the excess material on the samples' surfaces, as to a first approximation using the data in table 4.3 the films are all likely to have the equivalent mass of at least $1\mu\text{m}$ worth of new material deposited on top. Thus given the sample depth of around $1\mu\text{m}$ we are only really imaging the grafted material, and very little of the PVA substrate. The relationship between graft material thickness and the intensity of underlying PVA spectrum intensity is perhaps best seen for the broad hydroxyl peak (3270cm^{-1}), which decreases in strength from the uncoated PVA through to the PF-decyl coated accordingly.

Fr  chette *et al.* [178] & Hsu [182] *et al.* agree that it is extremely difficult to assign specific bands to specific C-F bond vibrations, principally because vibrational modes tend to be delocalized throughout an entire perfluorinated chain, hence assignment to a particular group will prove difficult [178].

The n-decyl coated spectrum meanwhile is noticeably different. In figure 4.25 a very strong absorption occurred at 2922cm^{-1} and 2852cm^{-1} , this was not the case for the fluorinated samples. This peak is likely due to the additional CH_2 and new CH_3 moieties on the surface.

The second noticeable difference is that the peaks at 1020cm^{-1} (C-C) and 1088cm^{-1} (C-O amorphous) are much stronger than in plain PVA. We would anticipate a strengthening of the C-C peaks due to the presence of the n-decyl chains on the

surface. However the enhanced C-O peak is a little surprising and requires further investigation to establish its cause.

Si-O bonds have an infrared absorption in the range 1000cm^{-1} to 1300cm^{-1} [183], however for the case of the perfluorinated samples these peaks are shielded by the C-F absorptions. There is a hint of a peak in the n-decyl data (1025cm^{-1}) but this is ambiguous as such a peak overlaps with the PVA C-C (acetate) peak.

Imaging IR spectroscopy

The spectrometer (Varian Excalibur FTIR microscope) was subsequently operated using the UMA600 microscopy accessory. This allowed imaging mode spectra of the samples to be undertaken. The 'number of pixels aggregated' was set to one, and sixteen 'tiles' were 'stapled' together. Each tile was $88\mu\text{m}^2$ ($9.381\mu\text{m} \times 9.381\mu\text{m}$) and comprised the average of 32 scans between the wavenumbers 4000 and 900cm^{-1} (the limit of the detector being 900cm^{-1} in this mode). The Lancer FPGA detector was used, and it had a spatial resolution of $5.5\mu\text{m}$. Example images obtained are shown in figures 4.26, 4.27 & 4.28 (using absorption bands characteristic of each graft molecule).

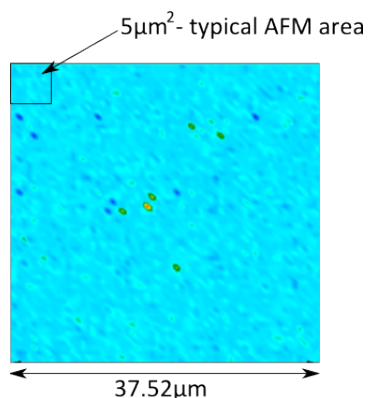


Figure 4.26: Example PF-decyl image IR data taken at 1132cm^{-1} .

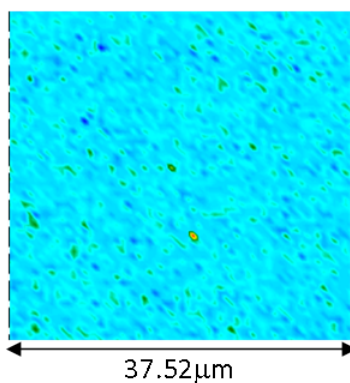


Figure 4.27: Example PF-octyl image IR data taken at 1163cm^{-1} .

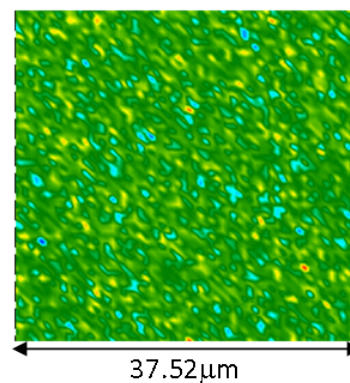


Figure 4.28: Example n-decyl image IR data taken at 2922cm^{-1} .

Considering this data (and other images not shown here) it can be seen that there is no obvious 'patchiness' across the sample surfaces. There are however local variations in the recorded intensity for each band, these are no more than around $2\mu\text{m}$

across but these do correspond with protrusions / agglomerates present in the AFM images as shown in figures 4.29 thru 4.34.

4.3.3.5 Atomic Force Microscopy

The following AFM images were recorded on a Pacific Nanotechnology Nano-R AFM in close-contact mode unless otherwise stated. Tapping mode AFM was used, as the samples proved too soft to be imageable in contact mode. Topography, phase and error channels were all collected. For further details on atomic force microscopy see section 3.6. Representative images collected are shown in figures 4.29 to 4.34.

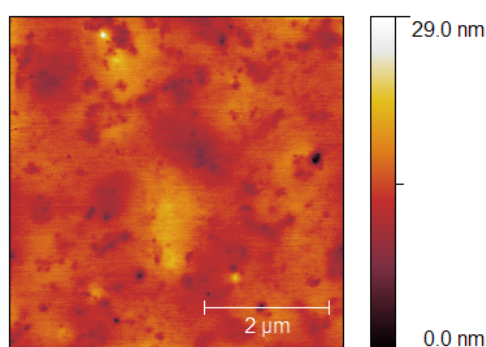


Figure 4.29: Topographical AFM image of PVA treated with PF-decyl.

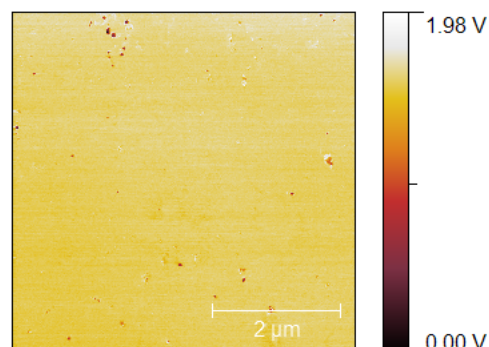


Figure 4.30: Corresponding phase AFM image of PVA treated with PF-decyl.

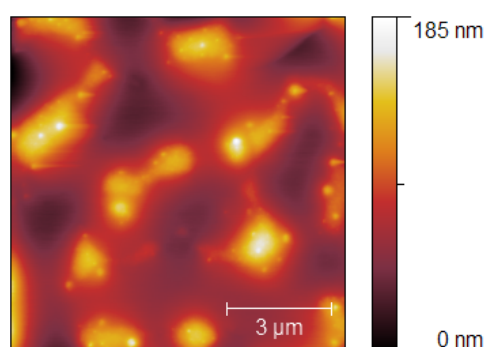


Figure 4.31: Topographical AFM image of PVA treated with PF-octyl.

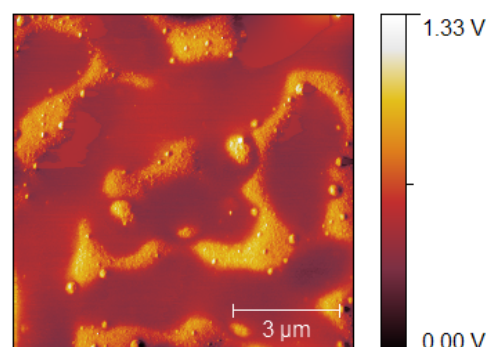


Figure 4.32: Corresponding phase AFM image of PVA treated with PF-octyl.

Both the topography and phase images are useful in elucidating the surface microstructure and the phase images in particular are helpful as they show differences in the viscoelasticity of the tip contact - this may reflect a chemical change in the

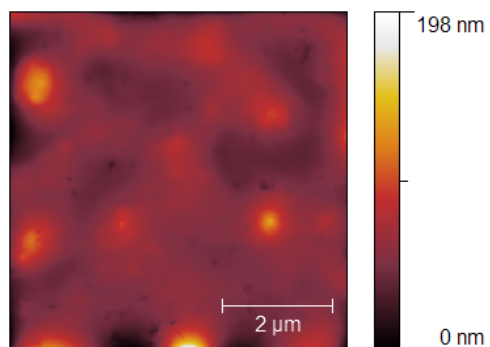


Figure 4.33: Topographical AFM image of PVA treated with n-decyl.

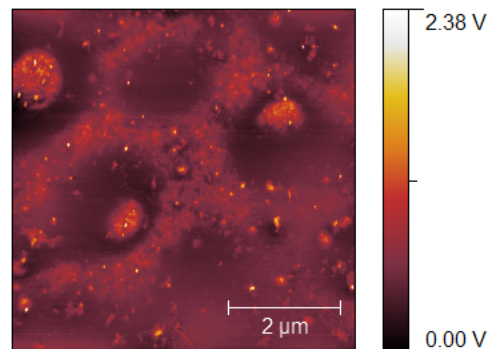


Figure 4.34: Corresponding phase AFM image of PVA treated with n-decyl.

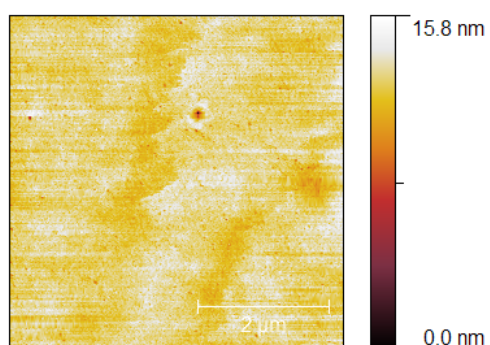


Figure 4.35: Topographical AFM image of untreated PVA.

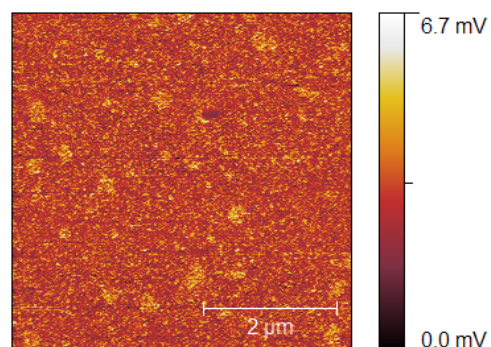


Figure 4.36: Corresponding phase AFM image of untreated PVA.

surface, although phase images can also be influenced by other factors (including the topography). (NB - it should be noted that it was non-trivial to obtain images on free-standing films, small segments were extracted and taped down to keep them as flat as possible - only then was imaging sometimes successful).

Considering each of the topographical images, it can be seen that there are raised areas on each of the samples. These are possibly evidence of the excess precipitation of material onto the surface (which was also observed macroscopically in the early experimental runs). The surface of the PF-decyl coated seems smoother; this is due to the partly to the area chosen for imaging - other areas were rougher but were more difficult to image as clearly.

The phase images are even more interesting, as the PF-decyl image (fig 4.30) shows almost no contrast, implying that the surface has been fully coated within this area of the sample.

The PF-octyl and n-decyl coated phase images appear to show much more structure. The 'higher' (lighter colour) material is most likely due to silane agglomerates on the surface, and this idea will be discussed more fully in section 4.4.2.

Both the PF-decyl and n-decyl images suggest relatively rounded or 'smoother' protrusions on the surface. The PF-octyl image suggests the same for the most part, excepting the highest (brightest) areas, where there are spherical precipitates with a diameter of $0.2\mu\text{m}$ or less which appear to have quite sharp sides.

4.3.3.6 Contact angle

Contact angle analysis has been undertaken in order to yield further information on the solvent-surface interaction. There is very little published work on the contact angle of various solvents on 87-89% hydrolysed PVA, however some of that which has been published is shown in table 4.5.

Several authors have measured the contact angle of -trichlorosilane based molecules

Source	Material	Solvent	Contact angle	Other comments
Nishino <i>et al.</i> [74]	PVA (98% hyd, M_w 80,700)	water	70° adv. 25° rec.	Static contact angle
Serizawa <i>et al.</i> [86]	PVA (M_n 88k; deg. hyd. not stated)	NaCl _(aq)	45°	
EP 1 731 551 A1	PVA (deg. hyd. and M_w not stated)	water	45°	
Kim <i>et al.</i> [1]	PVA (Various M_n and deg. hyd.)	i-octane and cyclohexane surrounding a water droplet	80-95°	Angles increased with deg. hyd.
Nguyen <i>et al.</i> [184]	PVA onto PET (various deg. hyd. and M_w s)	water	11-65°	Inverse air bubble method; contact angle increased with deg. hyd.
Sionkowska <i>et al.</i> [185]	PVA (90% hyd. M_w not given)	diiodomethane, glycerol	51° 62°	Goniometer
Tretinnikov <i>et al.</i> [157]	PVA (deg. hyd. and M_w not stated)	water	59.5° adv. 17.9° rec.	Wilhelmy plate

Table 4.5: Summary of published contact angle data of various solvents on PVA.

after their deposition onto silicon substrates. A summary of published data is presented in table 4.6.

As discussed previously the Wilhelmy plate test method was preferred in this work and the exact procedure used as detailed in section 3.5 based on a method by Miyama *et al.* [154]. Representative results obtained are shown in figures 4.37 to 4.42 and a summary of the contact angles obtained are given in table 4.7.

The PF-decyl coated refused to enter into any of the solvents trialled (hence the PF-decyl plot is not shown here). Instead the film moved to the side further and further as the stage (and hence the solvent sample contact line) was raised. Therefore although no angle can be quoted it can be said that the hydrophobicity of the films was beyond that which the machine was capable of testing.

Some of the other films also had difficulty entering the solvents, the PF-octyl coated would not enter glycerol on the first immersion cycle, but it did on the second and subsequent cycles. Both the PF-octyl and n-decyl coated initially moved sideways

Source	Material	Solvent	Contact angle	Other comments
Xue <i>et al.</i> [79]	PF-decyl deposited onto silica nano particles	water	153°	Static drop
Bunker <i>et al.</i> [81]	PF-decyl	water	110-120°	Static drop
Srinivasan <i>et al.</i> [82]	PF-decyl	water	115°	Static drop
Fr�chet�te <i>et al.</i> [178]	PF-decyl onto Si	water	110°	Static goniometer
Despotopoulou <i>et al.</i> [186]	OTS (octadecyl-trichlorosilane) onto Si	water	112° adv.	Static drop
Parikh <i>et al.</i> [187]	OTS (octadecyl-trichlorosilane) onto Si	water	114°	Static drop

Table 4.6: Summary of published contact angle data of water on -trichlorosilane treated surfaces.

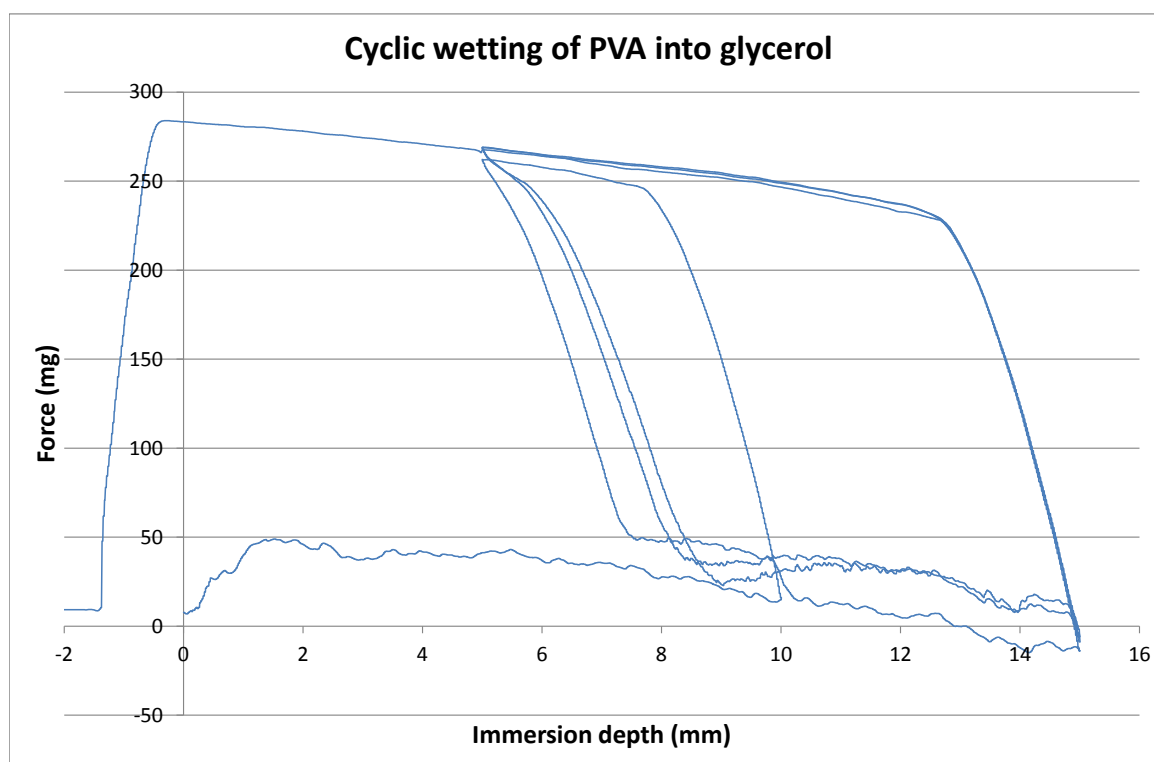


Figure 4.37: Wilhelmy plate data for contact angle of glycerol on untreated PVA.

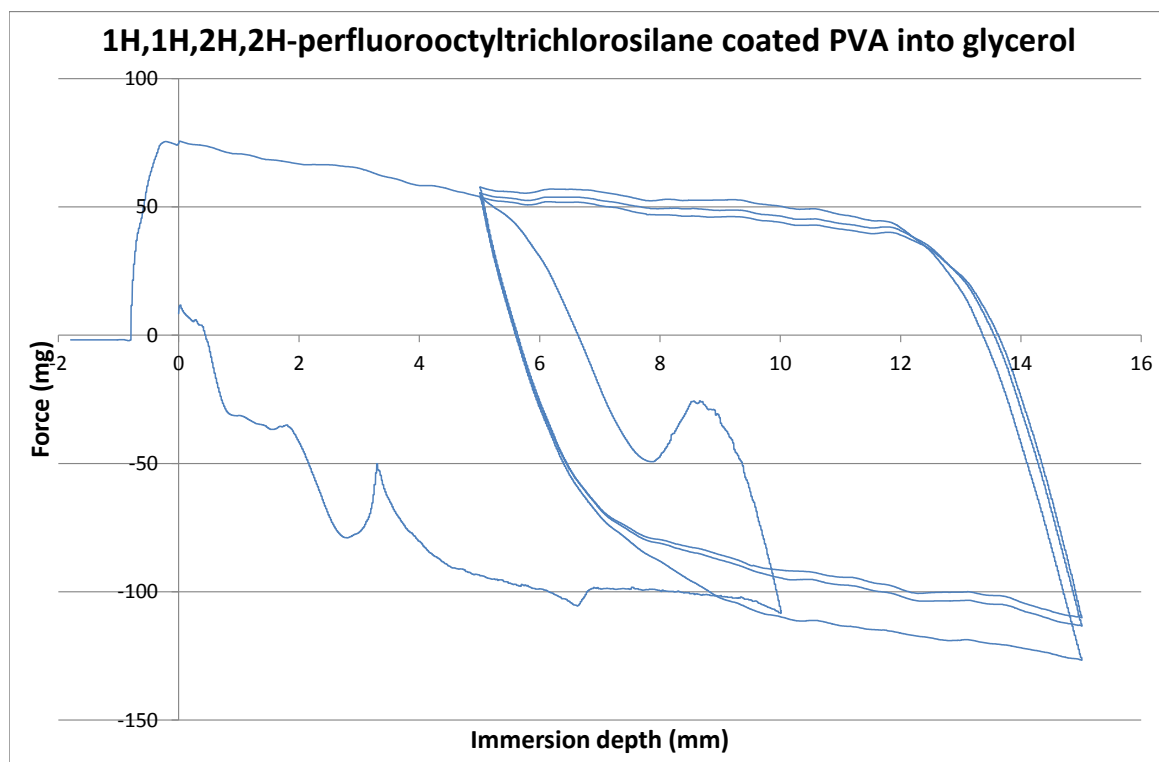


Figure 4.38: Wilhelmy plate data for contact angle of glycerol on PVA treated with PF-octyl.

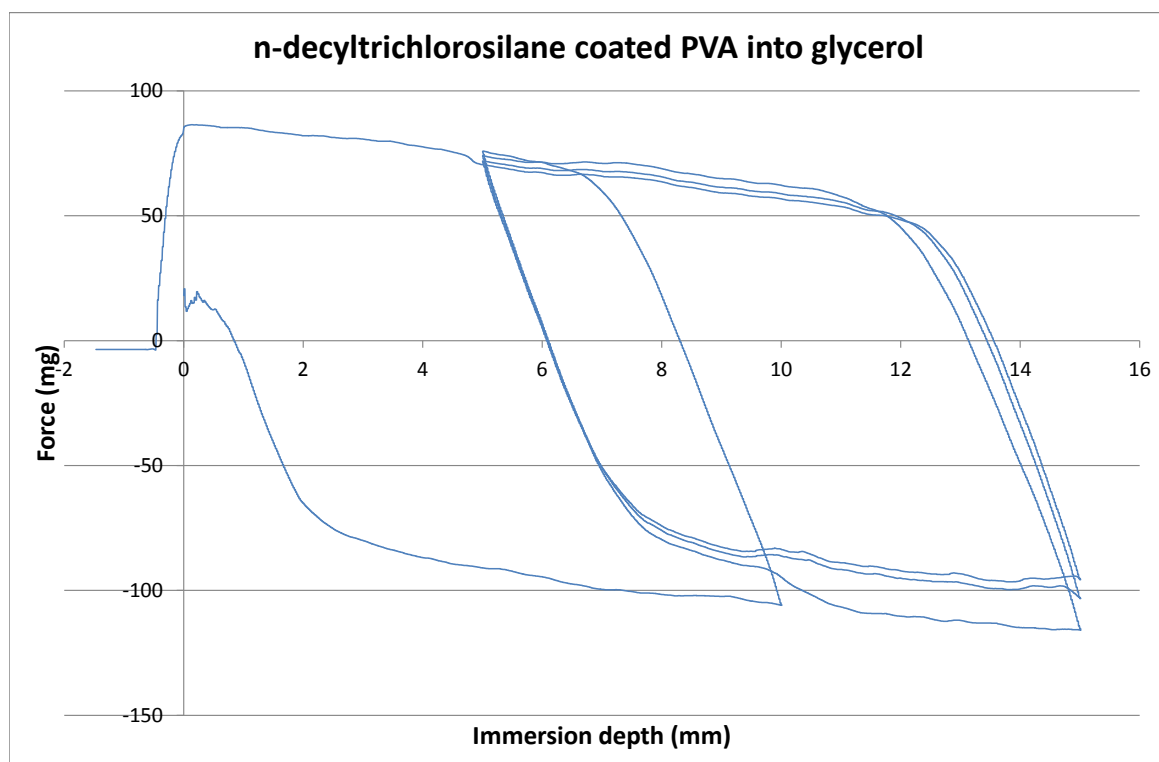


Figure 4.39: Wilhelmy plate data for contact angle of glycerol on PVA treated with n-decyl.

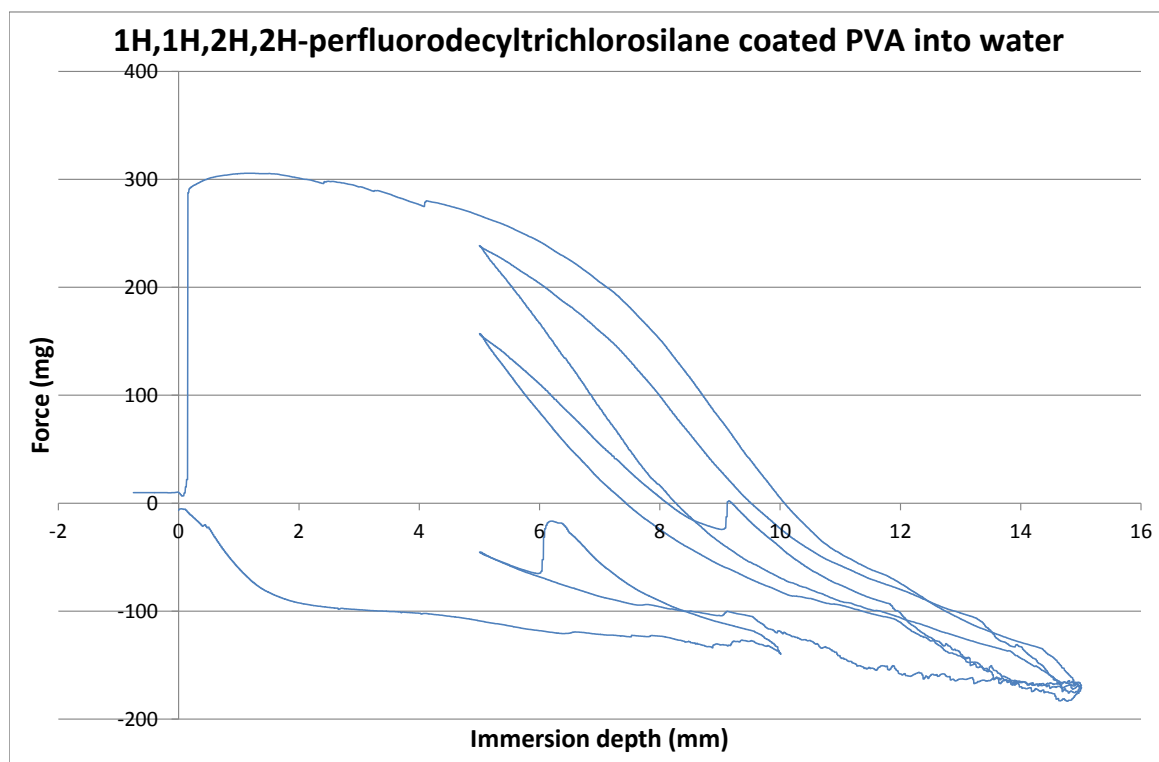


Figure 4.40: Wilhelmy plate data for contact angle of water on PVA treated with PF-decyl.

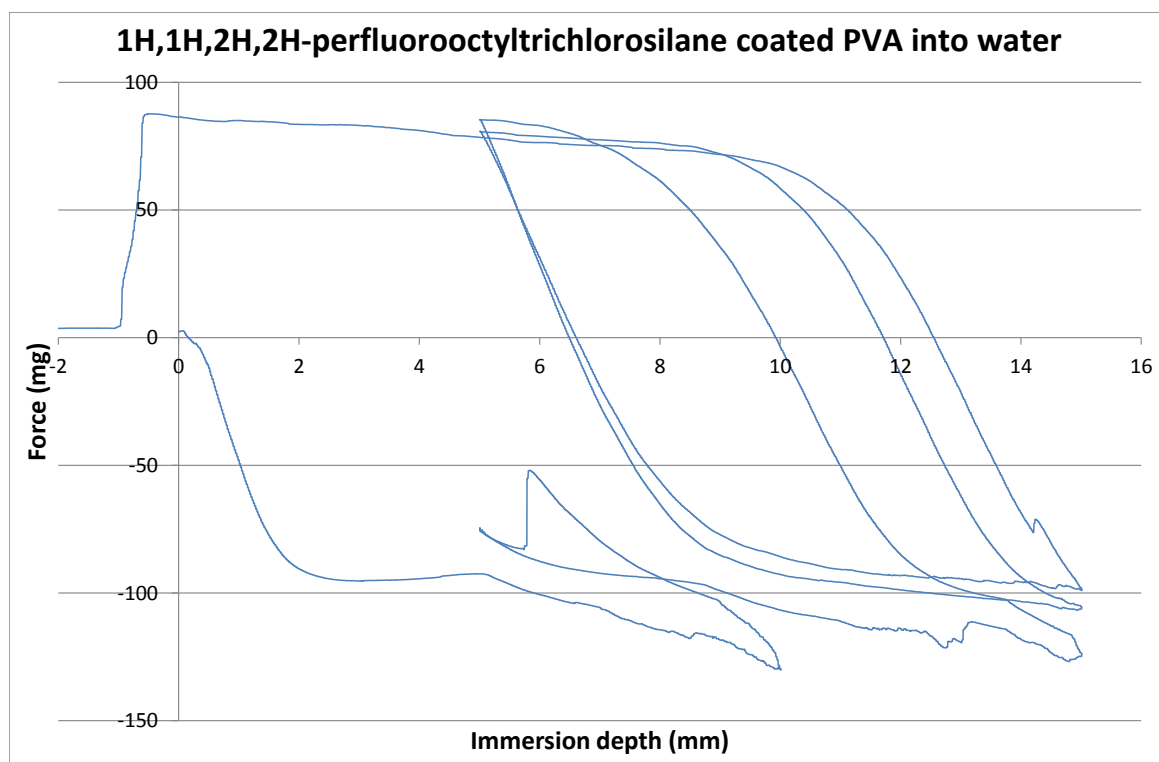


Figure 4.41: Wilhelmy plate data for contact angle of water on PVA treated with PF-octyl

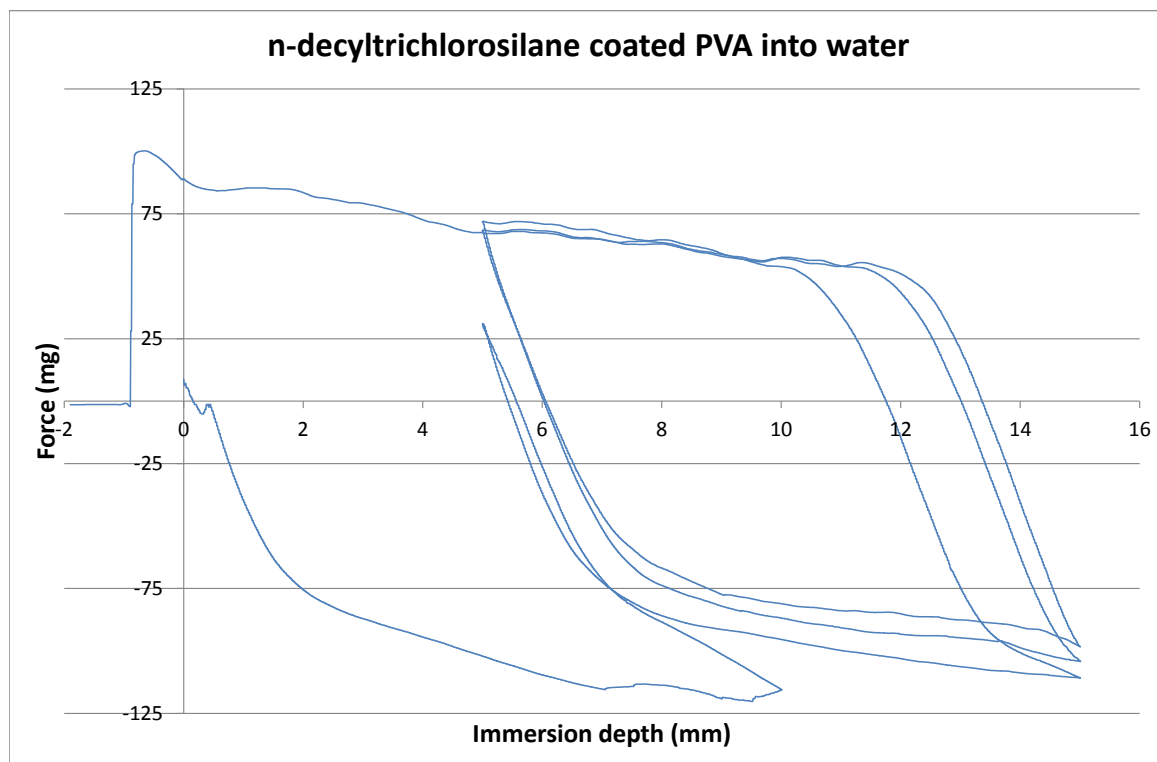


Figure 4.42: Wilhelmy plate data for contact angle of water on PVA treated with n-decyl

Material	Solvent	Avg. advancing	Avg. receding
Plain PVA	Glycerol	$75^{\circ} \pm 5^{\circ}$	0°
PVA coated with PF-decyl	Glycerol	Did not immerse	n/a
PVA coated with PF-octyl	Glycerol	$107^{\circ} \pm 5^{\circ}$	$70^{\circ} \pm 1^{\circ}$
PVA coated with n-decyl	Glycerol	$108^{\circ} \pm 2^{\circ}$	$62^{\circ} \pm 3^{\circ}$
Plain PVA	Water	Fully soluble (0°)	0°
PVA coated with PF-decyl	Water	Did not immerse	n/a
PVA coated with PF-octyl	Water	$110^{\circ} \pm 2^{\circ}$	$60^{\circ} \pm 4^{\circ}$
PVA coated with n-decyl	Water	$111^{\circ} \pm 1^{\circ}$	$65^{\circ} \pm 5^{\circ}$

Table 4.7: Summary of dynamic contact angle data obtained.

for the water trials. The PF-octyl entered towards the end of the first withdrawal and the n-decyl entered during the second immersion cycle. Areas on the graphs where the immersion and withdrawal curves trace one another almost exactly (i.e. no hysteresis) are as a result of the sample sweeping across the surface and not entering the solvent.

To the best of the author's knowledge no published data contains the advancing contact angle of glycerol on PVA. It is tricky to relate this to a water contact angle due to the lack of a well defined contact angle for water on 88% hydrolysed PVA. However it is a useful reference value to allow comparisons with the coated PVA samples to be made.

Considering the coated samples' interactions with glycerol it can be seen that all samples have an increased contact angle, with both the PF-octyl and n-decyl fairing similarly (around 108° advancing and between 60 and 70° receding) and the PF-decyl proving even more hydrophobic. This is a noticeable improvement, especially that of the receding contact angle which means that glycerol is unable to fully wet the surface after initial contact (unlike for the case of the uncoated PVA).

A favourable comparison exists between the PF-octyl and n-decyl data for wetting with glycerol. Not only are the contact angles very similar to each other, but the shape and size of the repeat loops are also the same (i.e. the width and height of the loops, and the distance taken over which dynamic hysteresis occurs). This suggests that the mechanism of resistance to the solvent is the same in both cases. Furthermore as the loops trace over each other in a repeatable manner re-wetting of the same area is not causing surface degradation.

However the data for PF-octyl and n-decyl wetted by water reveals a difference between the two samples. Both again have very similar contact angles along with the height and width of the repeat wetting loops. The difference is that for the case of PF-octyl the withdrawal portion of the loops seem to shift along the x-axis as the repeat cycles continue. This implies that the dynamic hysteresis is initially taking a

far greater distance of sample surface to complete. If this is the case then it could be a result of the liquid-solid meniscus line not being completely pinned during the direction reversal process. However it appears to become more stable as the trials proceed thus implying the surface has been changed marginally by the interaction with the solvent. It is difficult to draw any more substantial conclusion than this with the data available.

4.3.3.7 DSC

DSC has been described in section 3.8. Samples were scanned at ($100^{\circ}\text{Cmin}^{-1}$), quenched to room temperature and then scanned again at $100^{\circ}\text{Cmin}^{-1}$ to investigate the stability of the graft molecules on the surface along with any change in T_g , as shown in figures 4.43 and 4.44.

(NB - the first heat T_g for the PF-decyl coated was a little ambiguous, thus an approximate estimate has been made from the data.)

Graft molecule	First-heat T_g	Second-heat T_g
none (plain PVA)	41°C	44°C
PF-decyl	$\sim 40^{\circ}\text{C}$	44°C
PF-octyl	44°C	56°C
n-decyl	40°C	57°C

Table 4.8: T_g of modified films extracted from figures 4.43 and 4.44.

The results must be treated with some caution, as the first heating cycle often produces ambiguous results due to initial poor thermal contact between the sample and the pan before the sample ‘softens’ to produce good contact. Nonetheless the second heating cycle T_g values are particularly interesting, showing that for the case of PF-octyl and n-decyl the T_g is raised by around 10°C over that of the plain PVA, whereas it is unaffected for the PF-decyl coated film.

Very few authors have published a T_g value for 87-89% hydrolysed PVA. One of the few examples is by Marten, where he states that for 87-89% hydrolysed material the T_g is 58°C [9], although no method is given as to how this value was obtained. The T_g values recorded for the untreated samples were lower than Marten’s figure of 58°C [9], this could potentially be due to a different method used to determine the T_g or the sample had different properties (e.g. M_w) as Marten did not specify either.

DSC first heat traces for PVA treated with various graft molecules

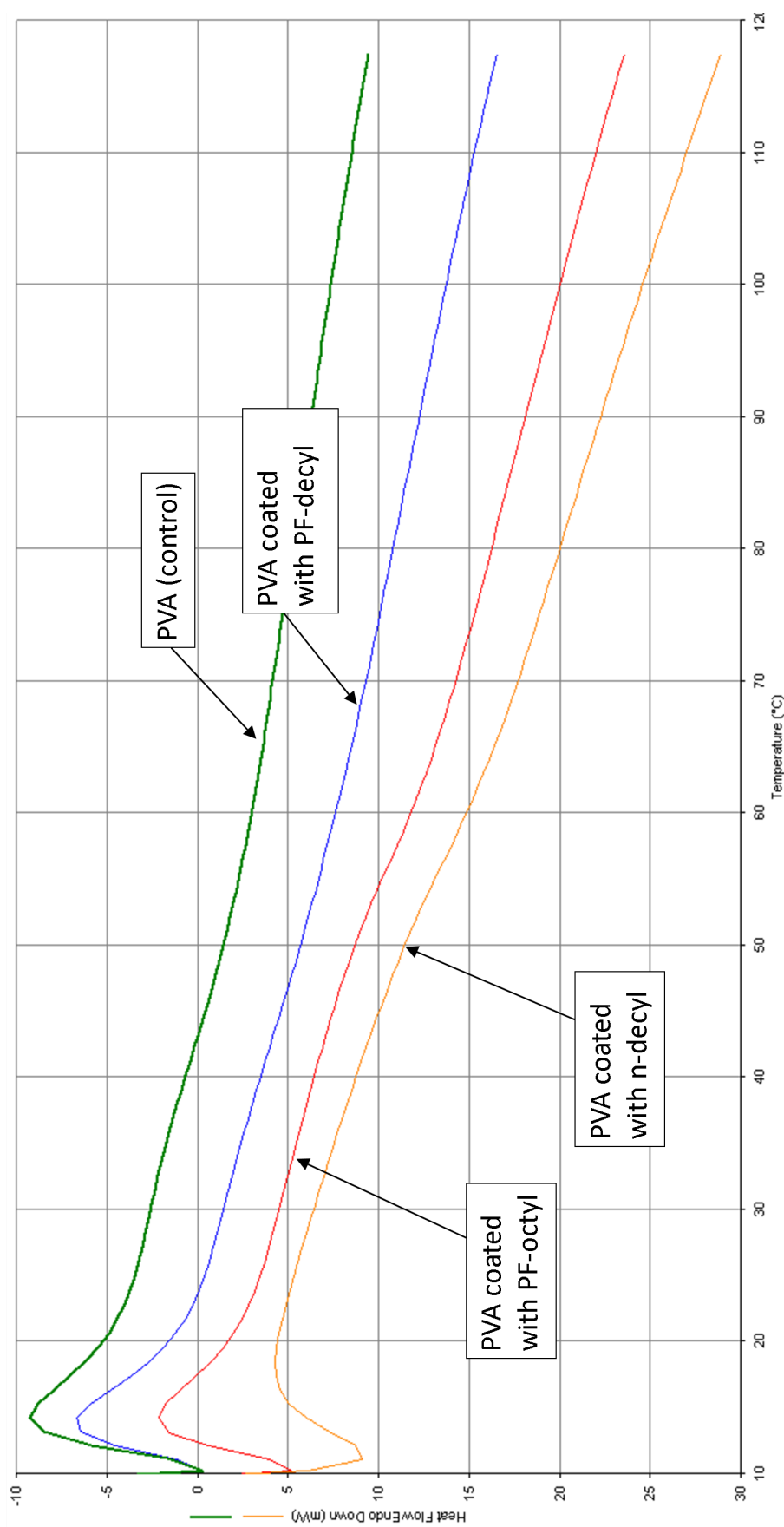


Figure 4.43: DSC scan for PVA with various species grafted onto the surface.

DSC second heat traces for PVA treated with various graft molecules

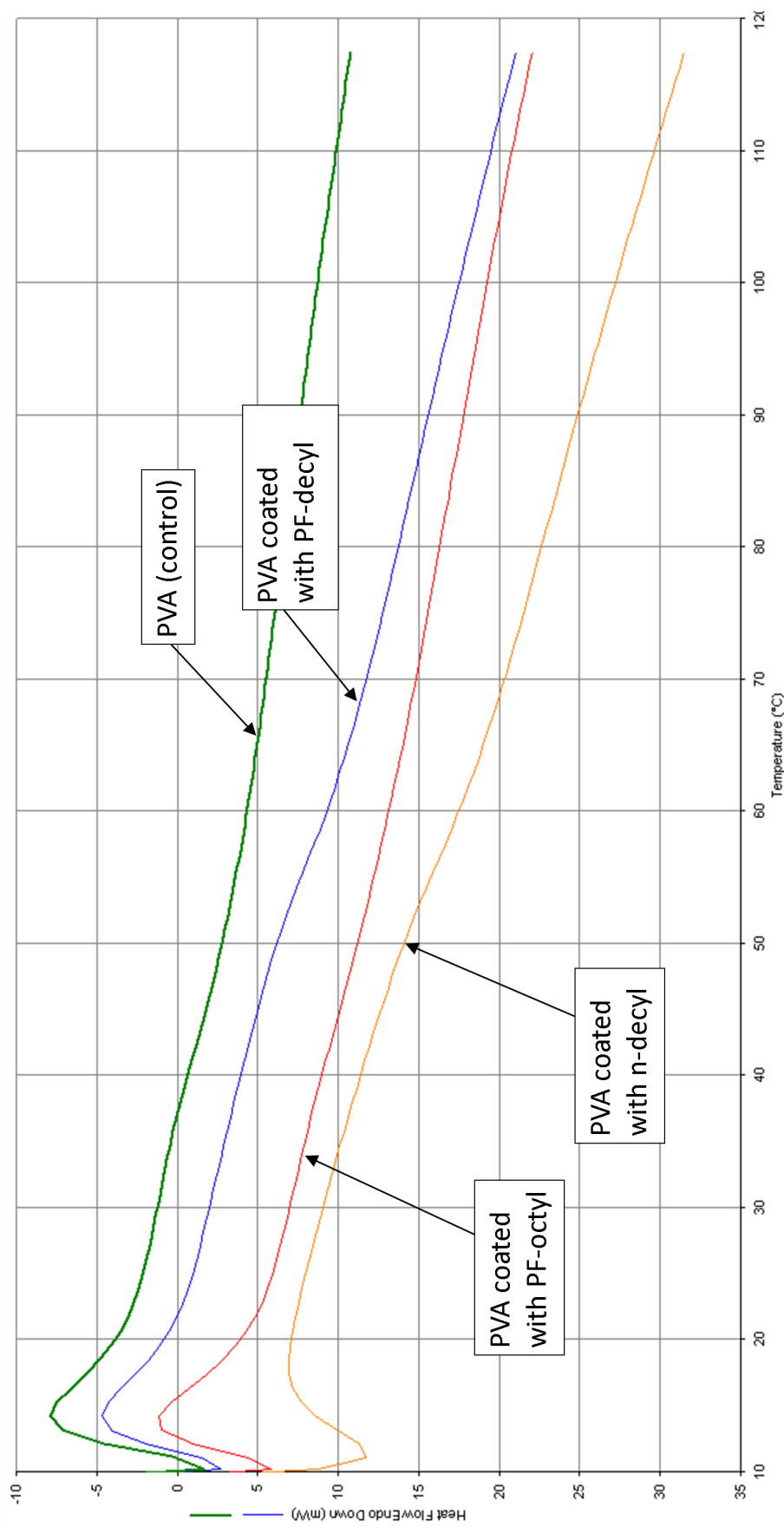


Figure 4.44: DSC scan (second heat) for PVA with various species grafted onto the surface.

4.4 Discussion

4.4.1 Carbene modified

From the data presented in this chapter it can be seen that both 'carbene modification' and coating with -trichlorosilane based compounds are viable methods to modify the surface of a polyvinyl alcohol film. Considering firstly the case of carbene modified surfaces, XPS has shown that aromatic groups were present on the modified surface, supporting the work of Moloney *et al.* [181].

AFM analysis has given an indication of the resulting surface topography which was somewhat roughened as a result of the treatment, with the suggestion of agglomerates of coating material forming on the sample surface. Two topographical options were presented (figures 4.9 and 4.10), and based on the data recorded it seems likely that good surface coverage of the substrate exists.

Owing to a lack of personnel in the collaborating group it was not possible to pursue this strand of work further; as such the attachment of other compounds and the resulting water resistance properties of the coated films was not assessed.

4.4.2 Fluorine modified

Modifying PVA via this method proved particularly successful, with both physical and chemical analysis providing evidence for deposition. Of particular note is the magnitude of improvement of the surface solvent resistance. Bulk dissolution rates fell by an order of magnitude (see for example figure 4.13) and water and glycerol contact angles showed a dramatic increase (from full wetting [0°] to over 100°, see table 4.7).

It is sensible to begin by considering the explicit impact on solubility resistance of the films. The first striking conclusion from the data is that the PF-octyl and n-decyl

coated films seem to perform as well as one another. For immersion of such films in water the data shows these films to be indistinguishable (figure 4.13). The recorded contact angles for interaction with water and glycerol are extremely close to one another (table 4.9).

Material	Solvent	Avg. advancing	Avg. receding
PVA coated with PF-octyl	Glycerol	$107^{\circ} \pm 5^{\circ}$	$70^{\circ} \pm 1^{\circ}$
PVA coated with n-decyl	Glycerol	$108^{\circ} \pm 2^{\circ}$	$62^{\circ} \pm 3^{\circ}$
PVA coated with PF-octyl	Water	$110^{\circ} \pm 2^{\circ}$	$60^{\circ} \pm 4^{\circ}$
PVA coated with n-decyl	Water	$111^{\circ} \pm 1^{\circ}$	$65^{\circ} \pm 5^{\circ}$

Table 4.9: Reproduction of a portion of table 4.7.

The two grafting molecules are structured as shown in figures 4.45 and 4.46.

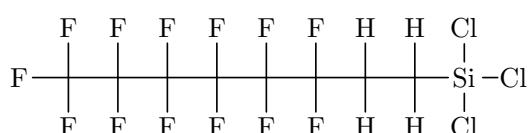


Figure 4.45: Structure of PF-octyl

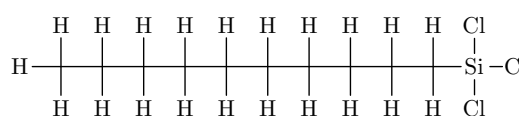


Figure 4.46: Structure of n-decyl

One might assume that the presence of the fluorine atoms is leading to the solvent resistance (owing to the well-documented water resistance of fluorine-containing compounds). If so one would anticipate the n-decyl coated material to perform worse than a similar fluorine containing sample. But as the data shows this is not the case, as such it can be concluded that the presence of the fluorine atoms is not the primary cause of solvent resistance.

The two compounds attached to the PVA substrate in the same way (via the -trichlorosilane linkage onto hydroxyl groups on the surface, see figure 4.12). As such it can be said that the grafted molecules 'remove' hydroxyl groups from the polymer surface and given that it is these groups with which water or glycerol can form a hydrogen bond removing them means there is less capacity for bonding with a hydrophilic solvent to take place.

An alternative explanation is that we have effectively made the surface like that of PTFE or PE (with CF_3 or CH_3 groups as the top most layer). The contact angles for water on PTFE are 140° (advancing) and 97° (receding) and on PE are 108° (advancing) and 87° (receding) (Wilhelmy plate method, Gotoh *et al.* [188]). These angles

are similar to those obtained in this work, but not identical - so clearly the surface microstructure is not quite that of true PTFE or PE.

We must also consider the difference in results between the PF-decyl grafted and PF-octyl grafted. Based on their molecular structures one would assume them to behave very similarly, with perhaps a slight increased hydrophobicity from the longer chain PF-decyl grafted. However the results do not show this, with the liquid water uptake data in particular showing a noticeably different performance to the other graft species. The DSC results (table 4.8) also hint at a phase separation).

One possible explanation is that the PF-decyl phase separates from the PVA owing to its very high hydrophobicity. Thus once the treated surface region has been breached by water the pure PVA underneath is then exposed to the water molecules. However for the other samples if there is no phase separation then there will likely be a greater depth over which some graft molecules are present - thus increasing the fragmentation time in the liquid water uptake test.

To test this theory depth profiling would need to be undertaken, possibly via cross-sectioning and then performing an EDX (Energy-dispersive X-ray spectroscopy) analysis in an SEM (recording the fluorine atom level). In addition a wider range of perfluorinated graft molecule lengths could be attached and the subsequent solvent resistance assessed.

A common feature of the AFM images (shown in section 4.3.3.5) is that there are agglomerates / precipitates on the sample surfaces. These are most likely a result of the -trichlorosilane end groups coupling to one another (either as a result of the target PVA surface being fully covered or spontaneously due to the experimental conditions). Bunker *et al.* have also observed this whilst depositing PF-decyl onto silicon, as shown in figure 4.47.

They attributed the formation of such precipitates to micelle formation. In particular they proposed that inverse micelles are likely to exist (where the hydrophilic head groups surround a water droplet and are at the centre of a micelle) [81]. Thus there is

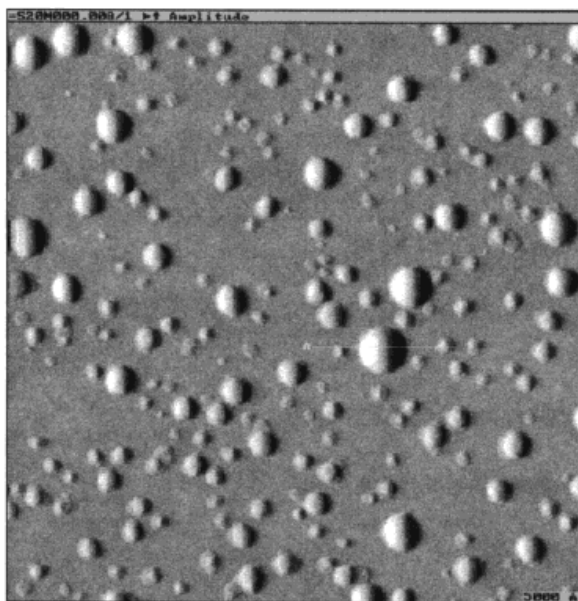


Figure 4.47: Figure 7a reproduced from [81].

the implied necessity for the presence of a water molecule to allow micelle formation to occur.

The grafting in this work was carried out in a dry glove box purged with nitrogen in order to keep the moisture level as low as possible. However it is of course still possible that there was some residual vapour present. Also the residual moisture level of the butanone was unknown (the butanone used was ACS reagent grade, >99.0% obtained from Sigma-Aldrich). This is important to note as Maboudian *et al.* comment that covalent bonds between the -trichlorosilane groups can take place if there is too much water present [80]. They commented that such coalescence often manifests itself as particulates, though they did not mention any typical length scale of such particulates [80].

Thus it is reasonable to conclude that some level of cross-linking between the -trichlorosilane groups has occurred in this work. According to this data the form of the polymerization does include micelle-like objects (see especially the small spherical precipitates in figure 4.32). However it is believed that such deposits are on top of a background layer of deposited material. This is backed up by the good water resistance, consistent contact angles upon repeat readings and the chemical analysis using FTIR. A similar conclusion was reached by Banga *et al.* who deposited

n-octadecyltrichlorosilane onto glass and silicon [189].

Brzoska *et al.* commented on the irreproducibility of grafting moieties onto a sample surface via the -trichlorosilane group [190]. In an attempt to establish the cause of such irreproducibility they investigated the influence of deposition temperature, studying n-alkyltrichlorosilanes of different lengths. They determined that a critical temperature exists, below which ordered structures are formed during deposition, whilst above which disorder was observed. They stated that the order-disorder switching temperature is an intrinsic property of the silane molecules themselves, and as such should be independent of the substrate being coated.

In their work ordered depositions were characterised by low surface tensions and low (less than 1°) contact angle hysteresis values (using the sessile drop test method), implying a very homogeneous surface microstructure. Unfortunately though Brzoska *et al.* gave no indication as to the surface morphology of their films [190]. They went on to report a switching temperature of 10°C for n-decyltrichlorosilane. This is significant as given that the experimentation in this work has been carried out at room temperature it can be expected that even though a deposition has occurred it is likely to be disordered (if Brzoska *et al.* are correct [190]).

Following on from this it is helpful to consider briefly the chain conformation of the deposited molecules. Hsu *et al.* studied the conformation of perfluoro-n-alkane molecules [182]. They noted firstly that E_g , the energy gap between trans and gauche formations, is approximately twice as big for the case of C-F in perfluoro molecules as C-H in n-alkanes [182]. Thus it can be assumed that chains containing a high number of CF_2 units are likely to be relatively linear, however for a CF_2 backbone the angle between successive C-C bonds is not 180° , so a helical arrangement of the molecule is most common [182]. (For n-alkanes however the trans angle is 180°). Hence the exact molecular picture on the surface (ordered or disordered) is not entirely clear.

Considering together the results in sections 4.3.3.2 and 4.3.3.3 reveals a few discrep-

ancies in the data. Firstly, for the case of the liquid water uptake test all samples show a great improvement over the untreated PVA, however for the water vapour uptake test only the fluorinated samples show an improvement. Secondly, in the water vapour uptake test the magnitude of improvement over the control is very limited, this is in contrast to the liquid water uptake test where a marked improvement is observed. It is perhaps possible that the presence of a bulk liquid water environment allows conformational changes of the attached groups, such that they take on an even more hydrophobic arrangement. Such a change might take much longer in the case of the vapour uptake test as the lower concentration of hydrophilic molecules means there is less driving force for conformational change.

A final point to consider (which is difficult to determine from the data presented herein) is whether we actually have covalent attachment of the molecules onto the surface or not. The possibility of agglomeration across the -trichlorosilane groups has been discussed, however this assumes that underneath any precipitates a layer of molecules had attached to the surface. It is this attachment which is assumed to be via covalent bonds, but it would need further verification to be certain. If instead it is van-der-Waals bonds holding the molecules in place then there is the risk of migration / detachment of the molecules with time. This is important to note when storage / a long-term application of the modified films is considered.

To conclude the discussion on silane based grafts it is good to take note of Bunker *et al.*'s [81] comment that silane-based coating processes are known to be irreproducible, and can be influenced by, "temperature, the solvent and its water content, coupling agent concentration, surface preparation, and even the container the substrates are coated." [81]

4.5 Further work

4.5.1 Carbene modification

Given the initial successful attachment it would make sense to continue the work by depositing other (purposely hydrophobic) groups onto the surface of PVA, on samples large enough to allow a comparison with the fluorinated samples shown here. It would also be of interest to assess the long term stability of the attached groups on the surface.

4.5.2 Fluorination modification

As mentioned previously a switching temperature is thought to exist for the arrangement of -trichlorosilane based molecules. Given that this is likely to be between 0°C and room temperature for the samples used in this work an obvious experiment would be to trial the same grafting procedure at 0°C. To a first approximation this would allow the surface topography and solvent interaction behaviour to be determined as a function of surface configuration.

The impact of graft molecule length has been discussed briefly here, however further investigations of different length attachments would be useful to determine the optimum graft length. Longer molecules have the capability to coil / lie on the surface, thus covering a greater proportion of the surface for a given amount of grafting compound. However considering very short molecules it is possible that the attachment density would be higher (less steric hindrance due to other graft molecules).

It would be especially helpful to rigorously determine the depth of material modified. Given that infrared spectroscopy shows the presence of the graft molecules extremely clearly a development of this technique might prove fruitful. Variable angle IR spectroscopy gives a way of controlling the sample depth of a given film.

The question of the bonding type between the deposited molecules and the PVA substrate still remains unanswered. One test which might be of assistance is to perform thermogravimetric analysis (TGA) on the samples. Any material not covalently bonded to the surface is likely to escape from the surface at a lower temperature than something which is covalently bonded and will show up as such on the plot of mass loss vs. temp.

It would also be of interest to attempt the work presented here on 99+% or fully hydrolysed PVA, to assess the impact of the presence of acetate groups.

Chapter 5

Surface cross-linking

5.1 Literature recap

The cross-linking of polymers is a well-established process (discussed more fully in section 2.5.1). In essence it means the introduction of permanent covalent bonds between independent polymer chains, and this is the definition which will be used for the duration of this chapter. The introduction of enough permanent covalent bonds between chains renders a polymer insoluble, although it may still swell (conformational changes between the cross-link points to accommodate solvent molecules) when immersed in certain solvents.

5.2 UV-induced surface cross-linking

5.2.1 Hypothesis

As discussed in section 2.5.1.2 ultra-violet radiation is a suitable means to induce cross-links (whilst avoiding degradation) in PVA. In addition if one is able to control the cross-linking process well enough it should be possible to induce cross-linking in only the surface region of a target film.

5.2.2 Method

PVA films (88% hydrolysed) were solution cast from water, although sodium benzoate powder (the sensitizer) was mixed in with the PVA powder (at 5wt% w.r.t. PVA) during the dissolution step. The films were then formed by casting in glass petri dishes for 48hrs at 30°C.

A Stratalinker® UV Crosslinker 2400 was used for the UV-exposure of the samples with the bulbs emitting UV light with $\lambda = 254\text{nm}$. The power of the system was measured using a photodetector and was found to stabilise at 2.5mWcm^{-2} for samples 3cm away from the bulbs.

Takakura *et al.* [129] used a similar system in their work, recording an intensity of 6×10^{-9} einsteins. $\text{cm}^{-2}\text{s}^{-1}$ ($= 2.83\text{mWcm}^{-2}$) for PVA films which were $20\mu\text{m}$ thick and were placed at a distance of 3cm from the UV source.

5.2.3 Results

5.2.3.1 UV spectrometer

A Hitachi U-3210 Spectrophotometer was used to monitor the UV absorption properties of treated films at 254nm. Various thickness PVA films were cast, with and without sensitizer molecules. The reported UV transmission at a wavelength of 254nm can be seen in figures 5.1 and 5.2.

In agreement with that noted elsewhere there is a striking difference in absorbency as a result of the presence of sodium benzoate molecules. The absorption of a film containing sodium benzoate has been monitored as a function of UV beam exposure time, yielding the results shown in figure 5.3. It can be seen that initially there is a low level of absorption, and that only upon 'activation' of the sensitizer does the absorption increase (up to ~ 0.115). This gradually falls back to the initial absorption value after a period of around 12 hours exposure. This suggests that some

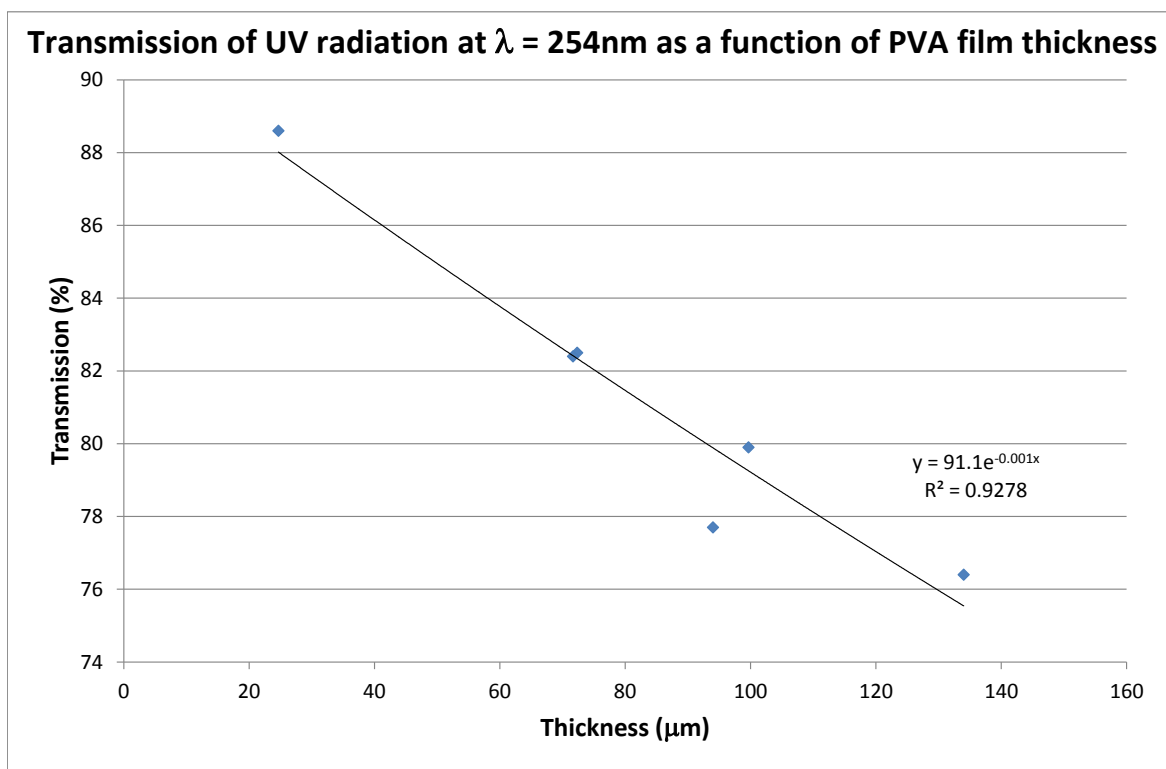


Figure 5.1: UV transmission as a function of PVA thickness (no sensitizer).

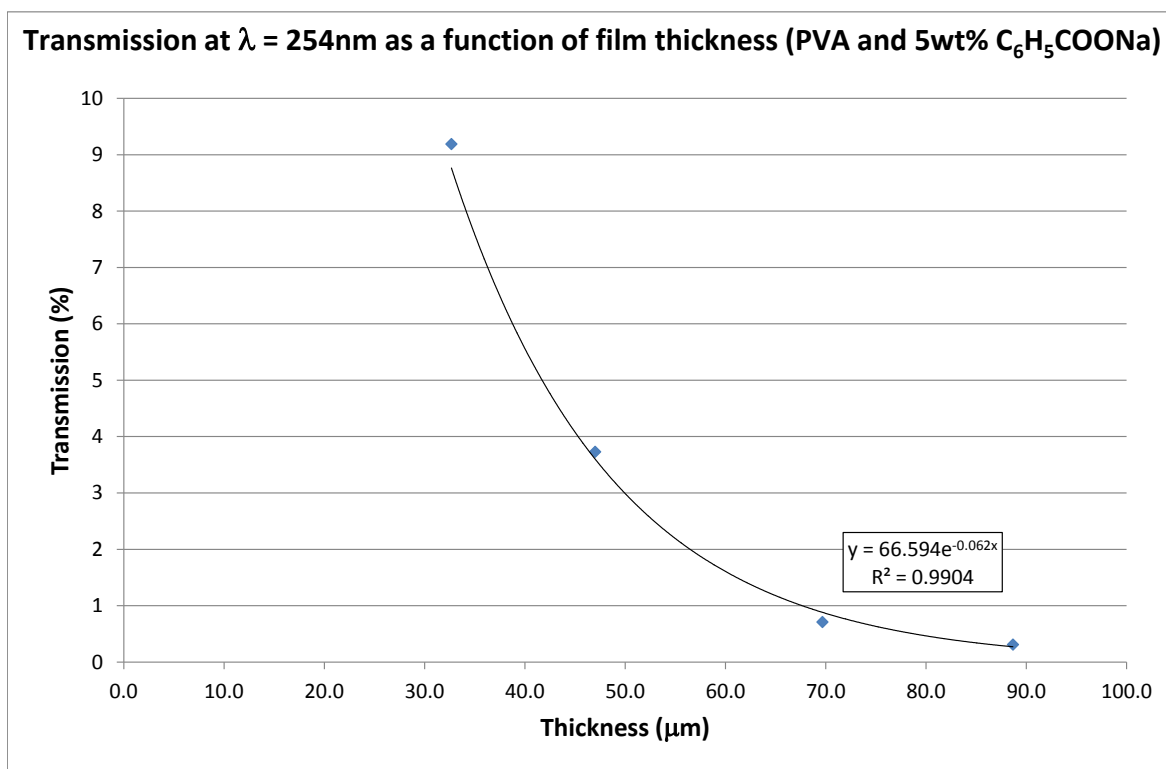


Figure 5.2: UV transmission as a function of PVA thickness (sensitizer present).

sensitizer molecules are 'consumed' (reacted) but not all - else the absorption should be reduced to that of plain PVA (0.056). Alternatively the reaction product could be absorbing UV radiation.

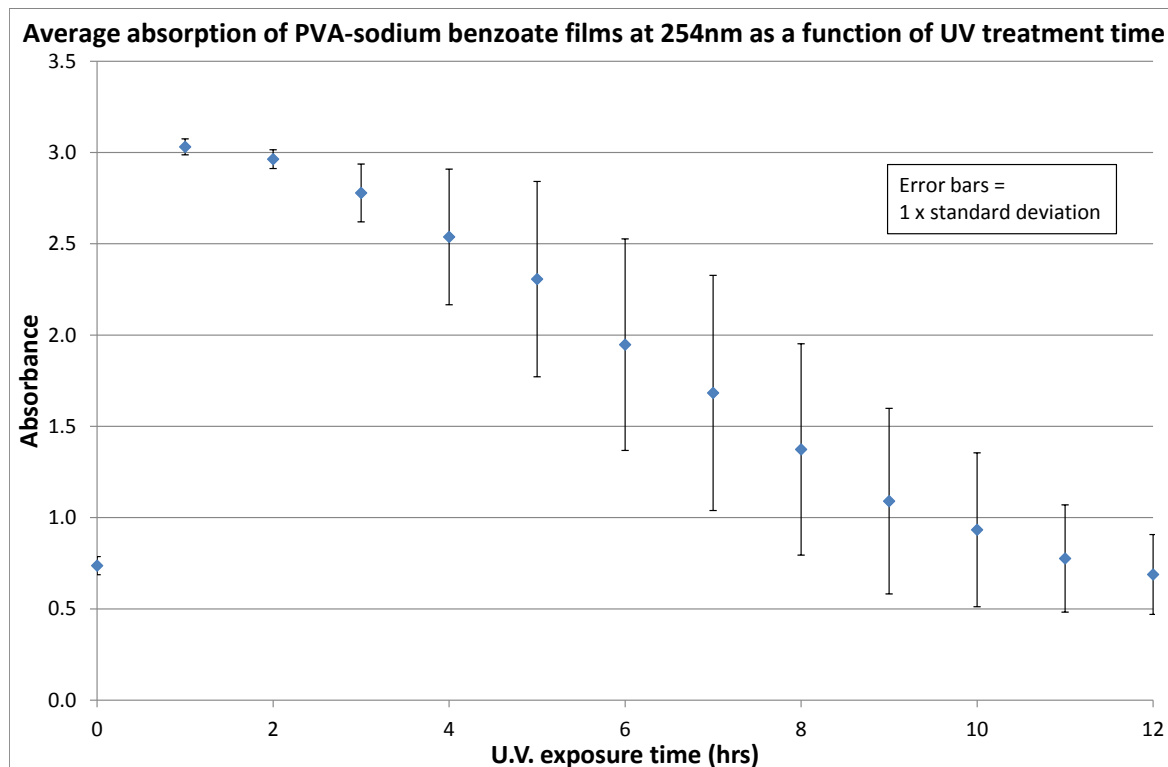


Figure 5.3: Absorption at 254nm of PVA with sodium benzoate at 5wt% as a function of UV exposure time.

5.2.3.2 Liquid water uptake

Samples treated on both sides were immersed in water, in the hope of them having been rendered insoluble. Liquid water uptake data for films exposed to UV for differing lengths of time is shown in figures 5.4 and 5.5.

In all cases a large fraction of each film tested was still soluble. The films initially took on water (by swelling) and then lost mass - this was due to the films fragmenting at swelling times of 20 minutes and above. However in every trial a fraction of the material remained insoluble (always in the form of a 'curled up' gel-like species). Hence some of the film has been rendered insoluble via cross-linking, but that overall fraction of cross-linked material is small.

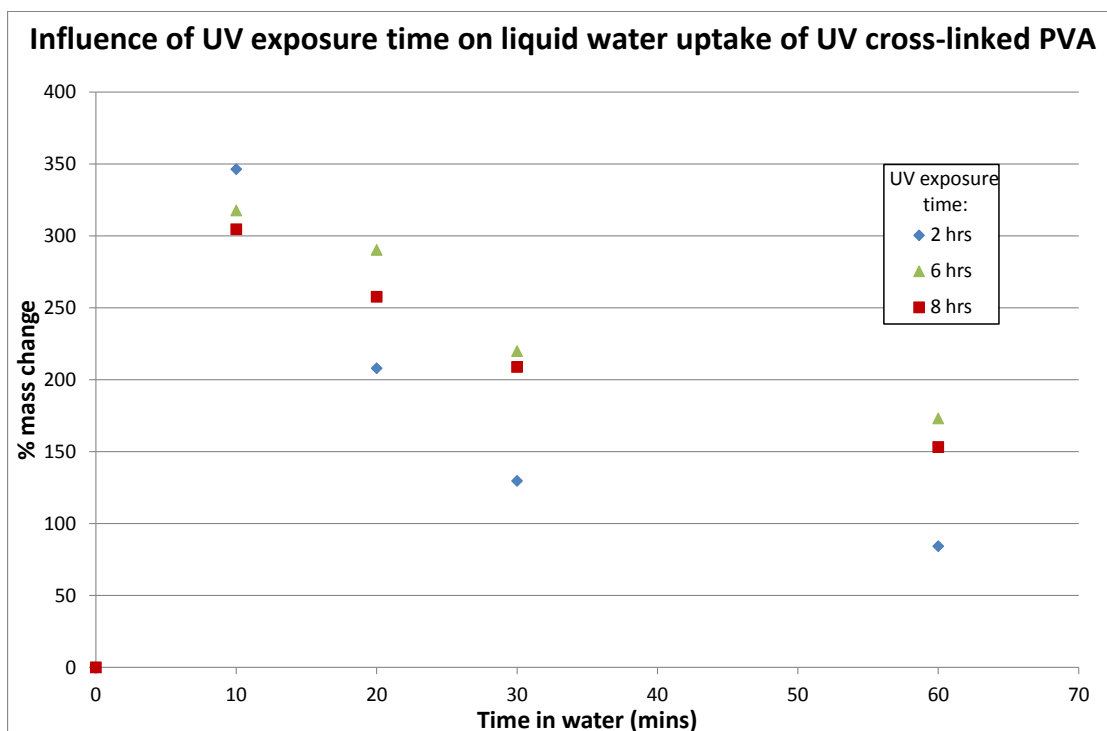


Figure 5.4: Influence of UV cross-linking on liquid water uptake behaviour

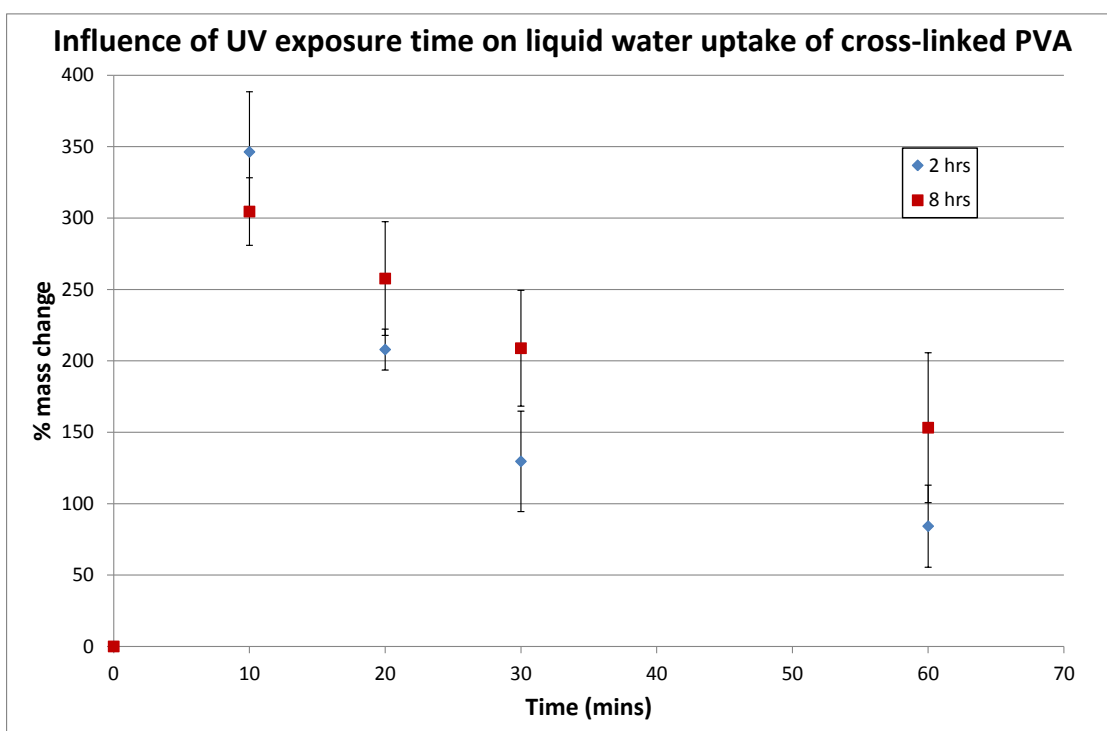


Figure 5.5: Influence of UV cross-linking on liquid water uptake behaviour (with error bars = $\pm 1 \times$ standard deviation)

A thin film ($\sim 30\mu\text{m}$) was cross-linked on both sides for eight hours in an attempt to totally cross-link the structure. However upon immersion in water the film took up water in the same manner as figure 5.4; thus implying that the cross-linking was not complete.

5.2.3.3 Water vapour uptake

Water vapour uptake test data of the films (treated on one side only) are shown in figure 5.6. It appears that the samples perform worse with regards water vapour uptake when compared with untreated PVA (equilibrating at around an 8wt% mass gain compared with 4wt%). This can partly be explained by the introduction of the hygroscopic sensitizer molecules, where the solvent uptake of a film containing sensitizer (but without UV exposure) is almost as much. However there is clearly a negative effect from exposing the films to UV and / or inducing cross-linking as the treated films pick up even more vapour.

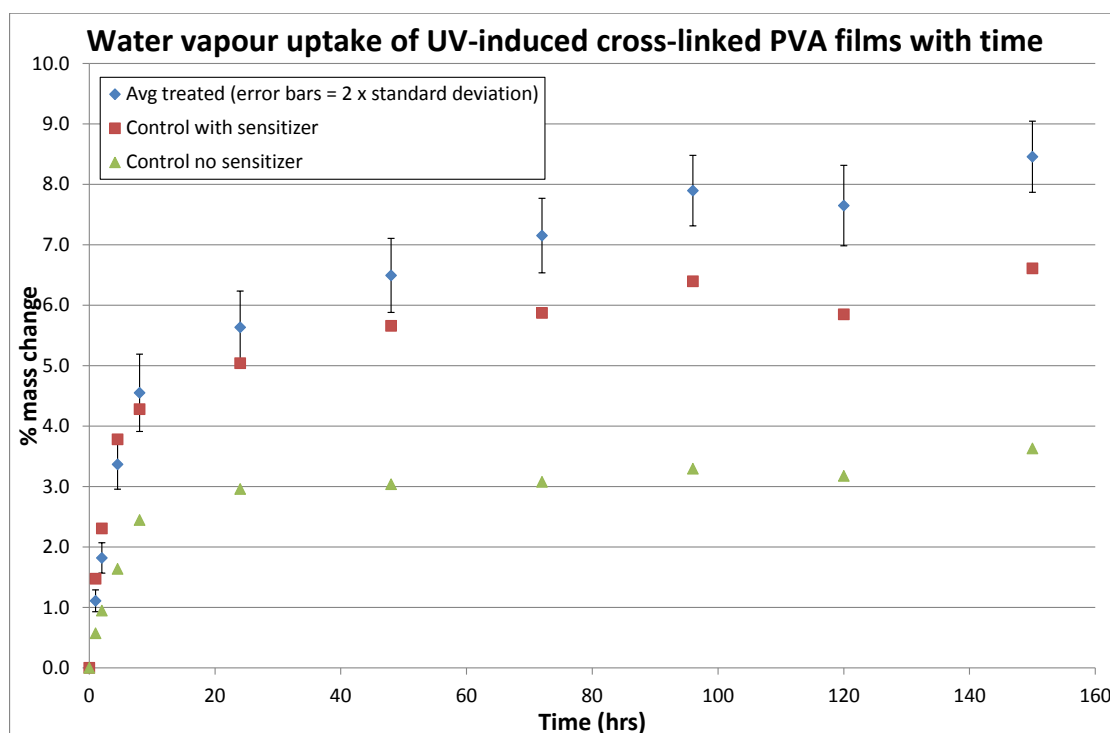


Figure 5.6: Water vapour uptake test for PVA films cross-linked (8hrs exposure to UV) on one surface.

5.2.3.4 Contact angle

After exposing a PVA film (containing sodium benzoate at 5wt%) to UV radiation for 4 hours on each side the contact angle of glycerol on the film was recorded (using dynamic contact angle analysis in the usual manner), as shown in figure 5.7.

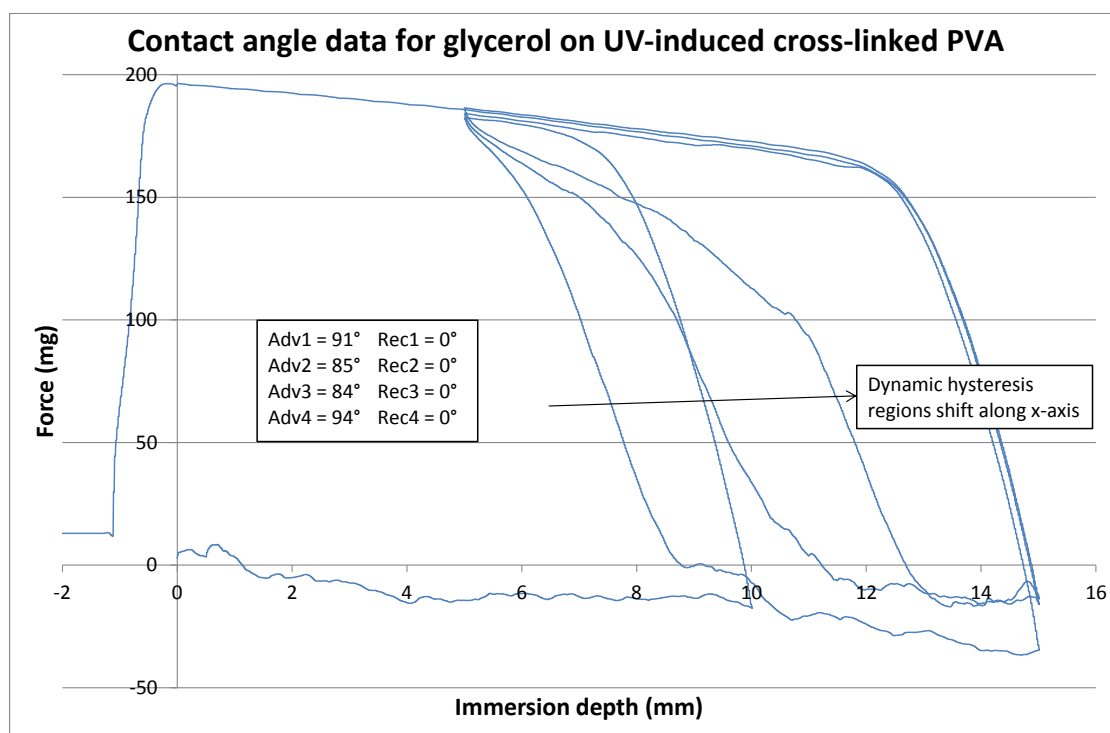


Figure 5.7: Dynamic contact angle analysis of PVA cross-linked using sodium benzoate and exposure to UV radiation for four hours.

The advancing ($\bar{x} = 89^\circ$) and receding (0°) angles are a negligible improvement on that recorded for plain PVA (75° advancing, 0° receding, see table 4.7) and the surface is not stable with time as the dynamic hysteresis portions of the graph are different for successive cycles, as expected, the cross-linking has not made a significant difference to the surface energy of the polymer.

5.2.3.5 IR results

Several sources report the disappearance of a peak associated with the photoinitiator in the infrared spectrum as a result of exposing sodium benzoate to UV radiation

[127, 129]. Takakura *et al.* also observed an intermediate peak [129]. Figure 5.8 shows infrared (ATR) spectra of the films treated in this work before and after exposure to UV radiation for eight hours.

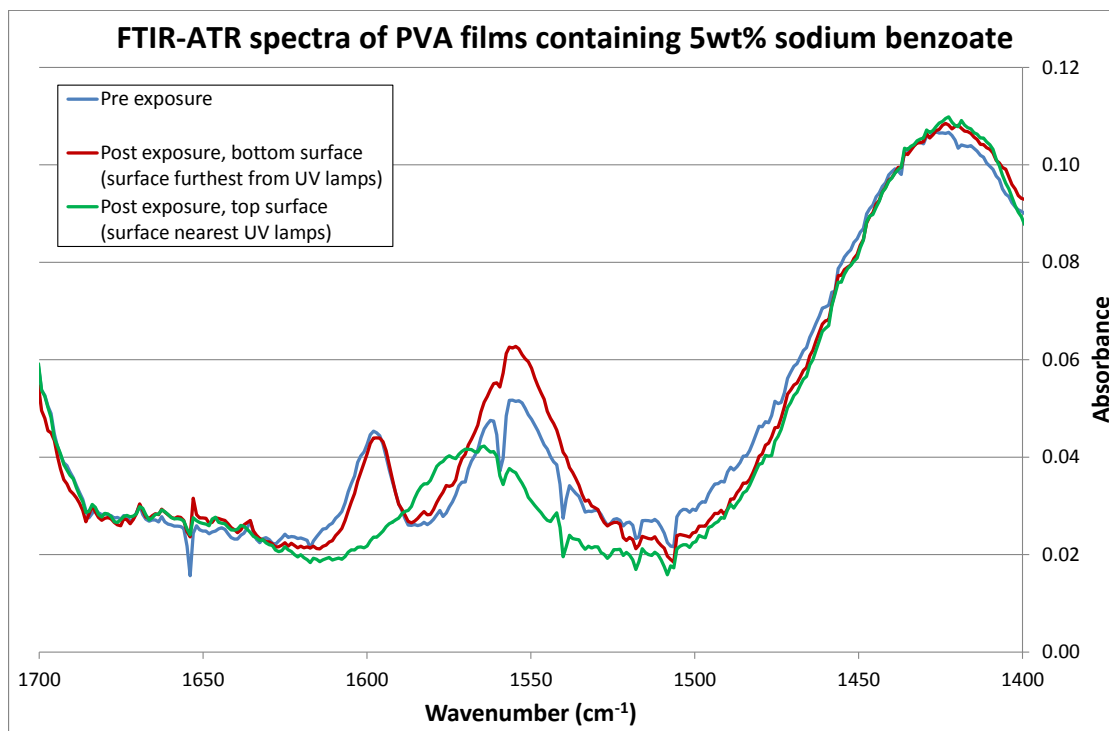


Figure 5.8: FTIR spectrum focussed on benzoate peak

The disappearance of the peak around 1600cm^{-1} from the treated surface suggests that the sodium benzoate molecules are breaking down (suggested mechanisms in figure 2.22).

It is also important to note that the bottom surface of the film (total thickness $\sim 100\mu\text{m}$) appeared chemically unchanged as a result of the exposure to UV, implying that the UV radiation did not penetrate through the film (which is consistent with figure 5.2). The remainder of the spectra (400 to 4000cm^{-1}) were identical to one another.

5.2.3.6 AFM

In order to investigate the surface morphology of the films AFM images were recorded. The system was set up such that a film of PVA and sodium benzoate and a plain PVA

film were treated side by side. In addition, each film was half covered with aluminium foil to prevent the UV from reaching half of each film. Typical micrographs obtained (using the Pacific Nanotechnology Nano-R AFM) are shown in figures 5.10 to 5.14.

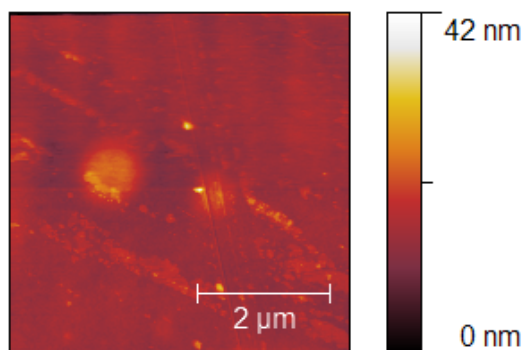


Figure 5.9: Topographical image of plain PVA, covered (hence not exposed to UV).

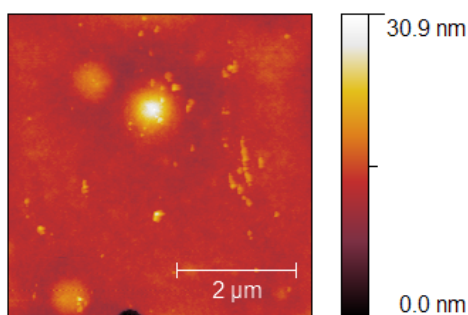


Figure 5.10: Topographical image of plain PVA, exposed to UV.

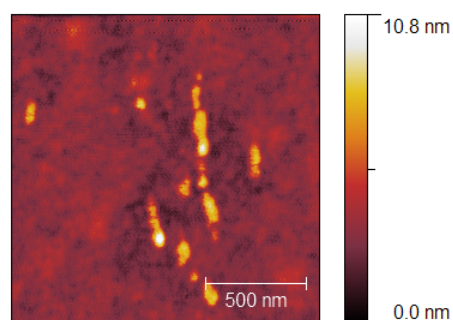


Figure 5.11: Figure 5.10 zoomed in.

There is some evidence of growth on the film surfaces of protruding structures (notably figures 5.10 and 5.12). These are possibly evidence of surface crystals (see chapter 6 for a detailed investigation of surface crystals). The temperature of the UV chamber was also recorded, and it was measured as 49°C (the heating due to residual heat from the UV lamps).

Otherwise the surface morphologies appear relatively unaltered. It is helpful to consider the root mean square (RMS) roughness values, and these are shown in table 5.1.

From this data it would seem that the introduction of 5wt% sensitizer to PVA in-

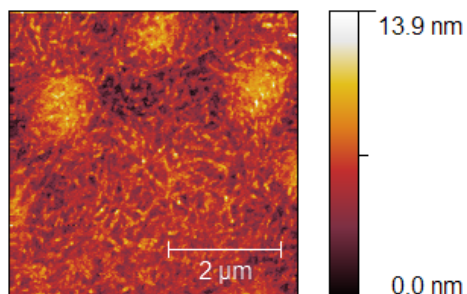


Figure 5.12: Topographical image of PVA containing sodium benzoate, covered (so not exposed to UV).

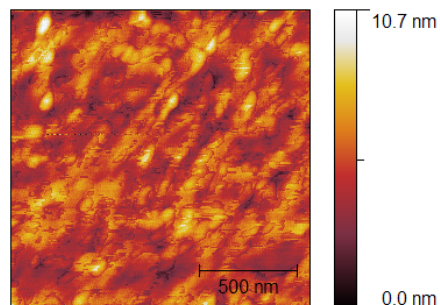


Figure 5.13: Figure 5.12 zoomed in.

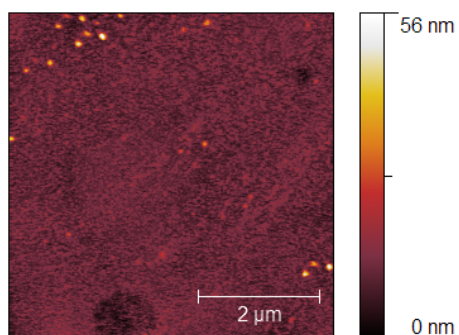


Figure 5.14: Topographical image of PVA containing sodium benzoate, exposed to UV.

Sample	R.M.S.
No sensitizer, no UV	2.1nm
No sensitizer, exposure to UV	1.7nm
Sensitizer, no UV	2.6nm
Sensitizer, exposure to UV	3.1nm

Table 5.1: RMS roughness values extracted from figures 5.9 to 5.14.

creases the surface roughness by the order of a nm or so. This could be if the benzoate molecules cannot fit into the PVA matrix without causing some distortion (the approximate width of a sodium benzoate molecule being 0.5nm).

5.2.3.7 DSC

Samples cross-linked on both sides have been assessed using DSC. The samples were heated at $100^{\circ}\text{Cmin}^{-1}$ from -20 to 220°C , then held for one minute at 220°C , quenched to -20°C at $200^{\circ}\text{Cmin}^{-1}$, held for one minute at -20°C and then heated again at $100^{\circ}\text{Cmin}^{-1}$ to 220°C . The recorded T_g s were as follows (table 5.2):

Sample	1st heat T_g ($^{\circ}\text{C}$)	2nd heat T_g ($^{\circ}\text{C}$)
Plain PVA	36	74
PVA & $\text{C}_6\text{H}_5\text{COONa}$	30	76
PVA & $\text{C}_6\text{H}_5\text{COONa}$ UV 2hrs each side	36	78
PVA & $\text{C}_6\text{H}_5\text{COONa}$ UV 4hrs each side	38	73
PVA & $\text{C}_6\text{H}_5\text{COONa}$ UV 6hrs each side	39	79
PVA & $\text{C}_6\text{H}_5\text{COONa}$ UV 8hrs each side	31	79

Table 5.2: T_g s as assessed by DSC.

The DSC traces (shifted vertically for clarity) are shown in figures 5.15 and 5.16. It can be seen that the presence of sodium benzoate and UV exposure appear to have no appreciable impact on the recorded T_g values.

DSC first heat traces for PVA treated with sodium benzoate

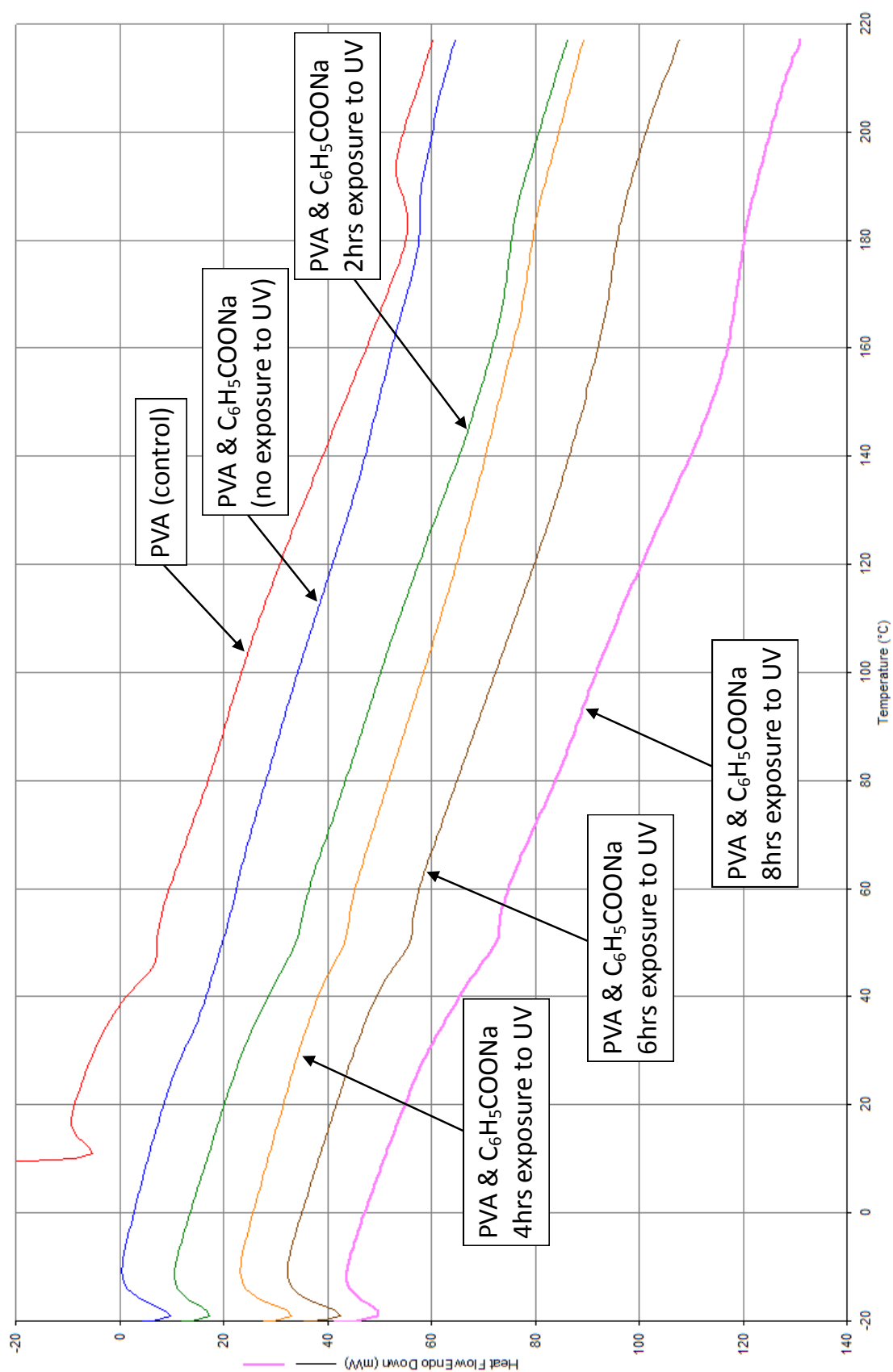


Figure 5.15: DSC traces used to determine first heat T_g s.

DSC second heat traces for PVA treated with sodium benzoate

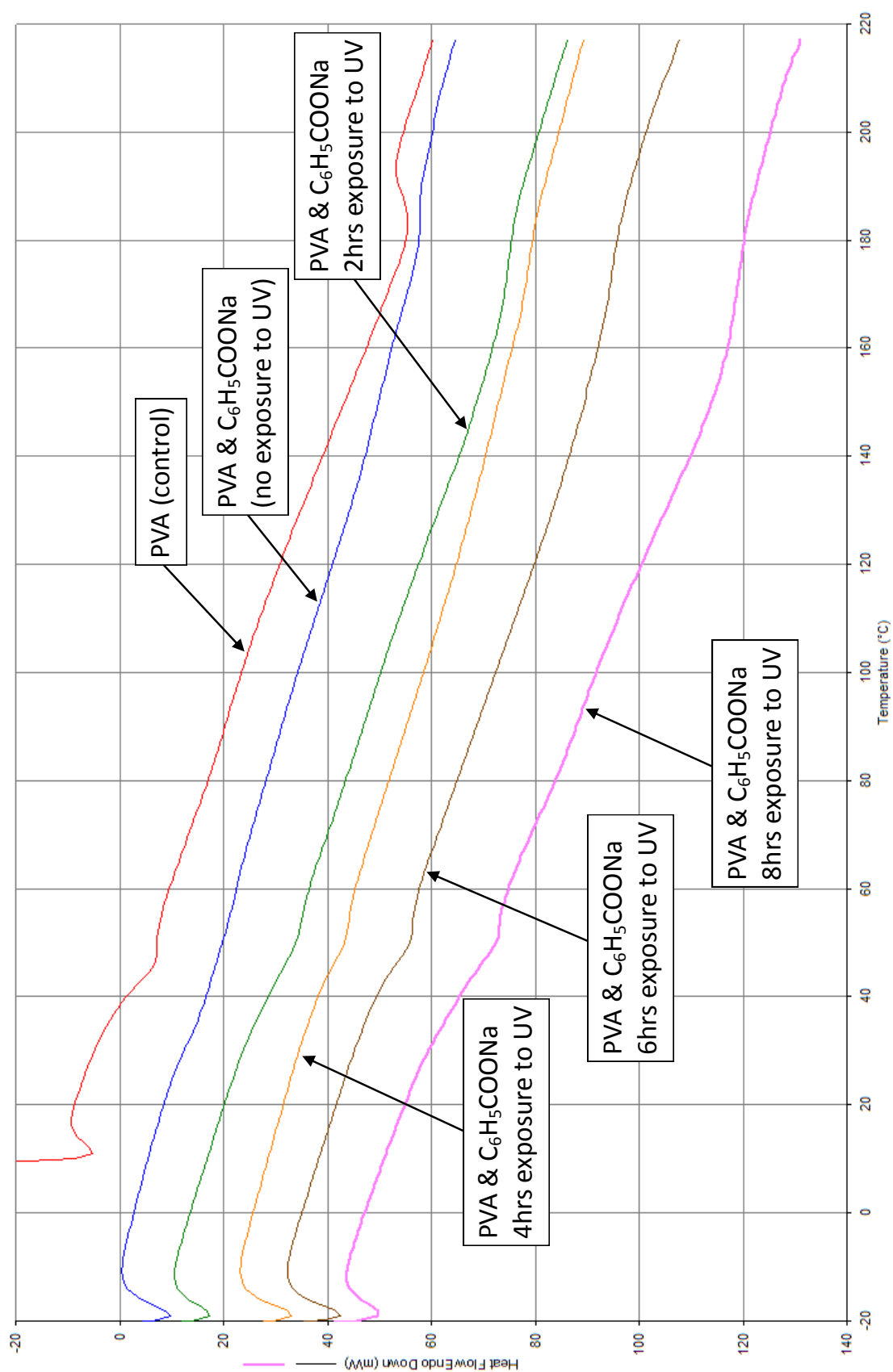


Figure 5.16: DSC traces used to determine second heat T_g s.

5.3 Maleic acid as a cross-linker

5.3.1 Hypothesis

As already discussed maleic acid has been successfully used to bulk cross-link PVA [120]. In that instance Gohil *et al.* used it to bulk cross-link a low molecular weight ($M_w = 14,000$) highly hydrolysed (98-99%) PVA. They formed 10wt% solutions by dissolving the PVA in water by stirring at 85-90°C. The maleic acid dose was varied between 10 and 60% by mass with respect to the mass of the PVA being dissolved. The solutions were then cast onto glass substrates, allowed to dry in air and subsequently annealed in an oven at various temperatures and for various lengths of time [120].

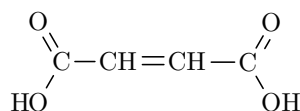


Figure 5.17: Structure of maleic acid.

The authors made use of the fact that each maleic acid molecule contains two carboxylic acid groups. When given enough thermal energy hydroxyl groups are removed from the carboxylic acid end groups, allowing attack of the hydroxyls on the PVA chains. Gohil *et al.* proposed the cross-linking structure as shown in figure 5.18.

5.3.2 Method

Based primarily on the work of Gohil *et al.* it was decided to use their findings to bulk cross-link 87-89% hyd. PVA, and then subsequently to attempt to surface cross-link said PVA films.

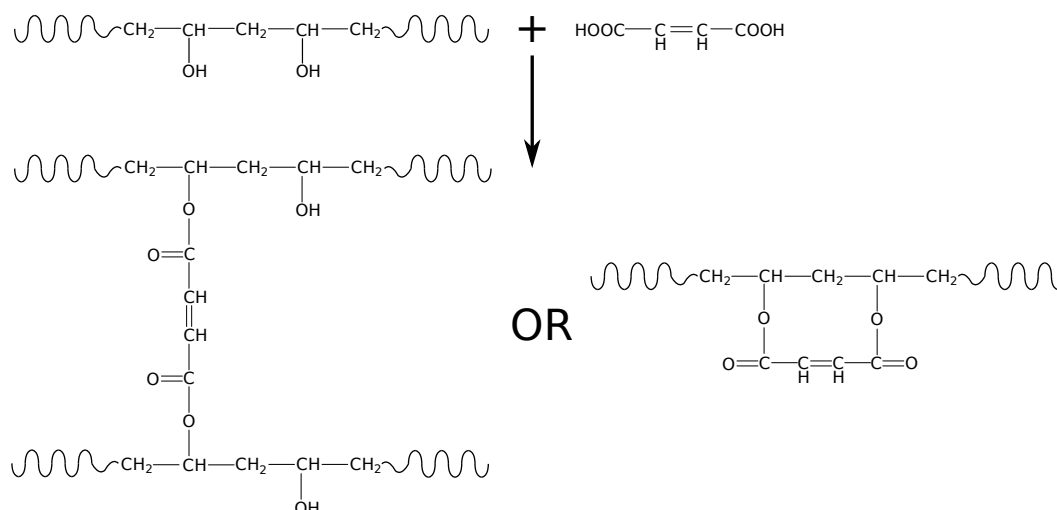


Figure 5.18: Proposed structure for PVA cross-linked with maleic acid, reproduced from [120].

5.3.2.1 Bulk treatment

Maleic acid (supplied by BDH) was dissolved at 30wt% (with respect to the mass of PVA) in a 5wt% solution of PVA in water at room temperature. These solutions were then cast and dried in the usual manner and shortly afterwards were annealed at 130°C for two hours in an oven.

The aforementioned experimental conditions were selected based on Gohil *et al.*'s findings. In order to get maximum benefit from the cross-linking agent they found that a curing time of at least 90 minutes and a curing temperature of at least 120°C were required (below which there was no cross-linking). They found that maximum interaction of the PVA with the maleic acid occurred at a concentration of 30w/w% or greater.

5.3.2.2 Surface treatment

After the success of bulk cross-linking 87-89% hydrolysed PVA a surface specific treatment was sought. The aim was to create a structure with only the surface layer of the PVA cross-linked, thus prior to the annealing step it was necessary to try and establish a film profile like that in figure 5.19.



Figure 5.19: Idealised PVA and maleic acid film cross-section prior to annealing.

Plain PVA films were produced in the usual manner, and subsequently solutions of PVA and maleic acid prepared. The aim was to coat the plain films with some of the solution. Dip coating was trialled first, though this proved problematic as the PVA film starting dissolving upon entering the solution. Even with immersion times of only a few seconds the films sustained significant damage. Smearing on of a concentrated solution of PVA & maleic acid was also attempted, although this proved tricky for a similar reason, along with the fact that it was very difficult to get a homogeneous coating using this manner. (Introducing bar coating would of course overcome the heterogeneous coating issue, but it would not overcome the film damage problem.)

Subsequently spin coating was trialled, and this initially proved to be a successful means of depositing the PVA and maleic acid solution onto the film surface. (The technique of spin coating is discussed in more detail in section 3.2). The experimental parameters settled on were a ten second ramp up to 2000rpm, followed by spinning at 2000rpm for one minute. The solution (5wt%) was added once 2000rpm had been reached; it was poured on quickly from a measuring cylinder but due to the viscosity of the solution took up to twenty seconds to be completely deposited.

The concentration of PVA and maleic acid in water was found to be important - and a lower concentration seemed to be more successful. The concentration can be said to be a compromise between the viscosity of the solution and the water content. A low viscosity is preferred for a thin and homogeneous coating, yet the water was found to damage the substrate - as such a higher viscosity (=lower water concentration) was required. A 5wt% solution was found to be a good compromise.

5.3.3 Results

5.3.3.1 Liquid water uptake

Liquid water uptake tests by the usual method were carried out as shown in figure 5.20.

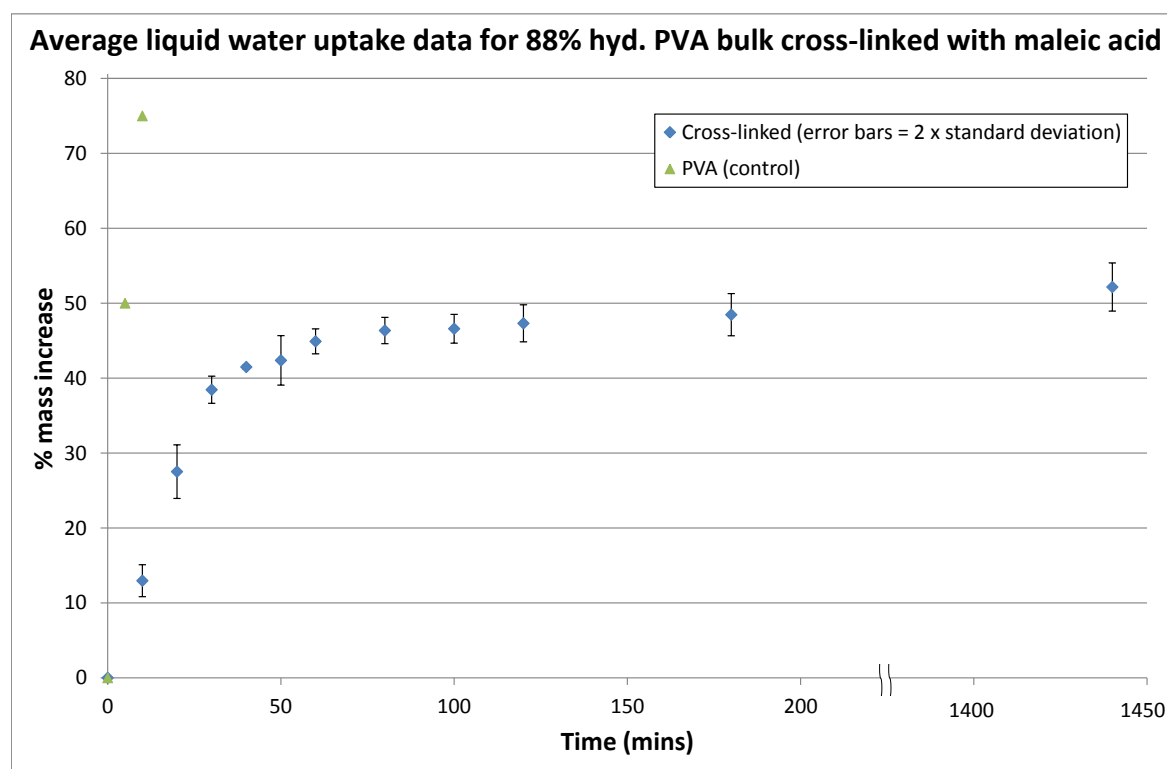


Figure 5.20: Liquid water uptake data for 88% hyd. PVA bulk cross-linked with maleic acid.

This was also carried out for 99% hydrolysed PVA (figure 5.21), comparing favourably with what Gohil *et al.* reported, as they recorded an equilibrium swelling % of around 40wt% [120].

5.3.3.2 Water vapour uptake

Samples were surface cross-linked by spin-coating a solution of PVA and maleic acid onto a plain solution cast PVA substrate (as discussed in section 5.3.2.2). A typical data set obtained is shown in figure 5.22. It can be seen that the treated samples took up more vapour than the untreated ones, with the amount absorbed being almost twice that of the control samples. Thus the cross-linking was obviously not

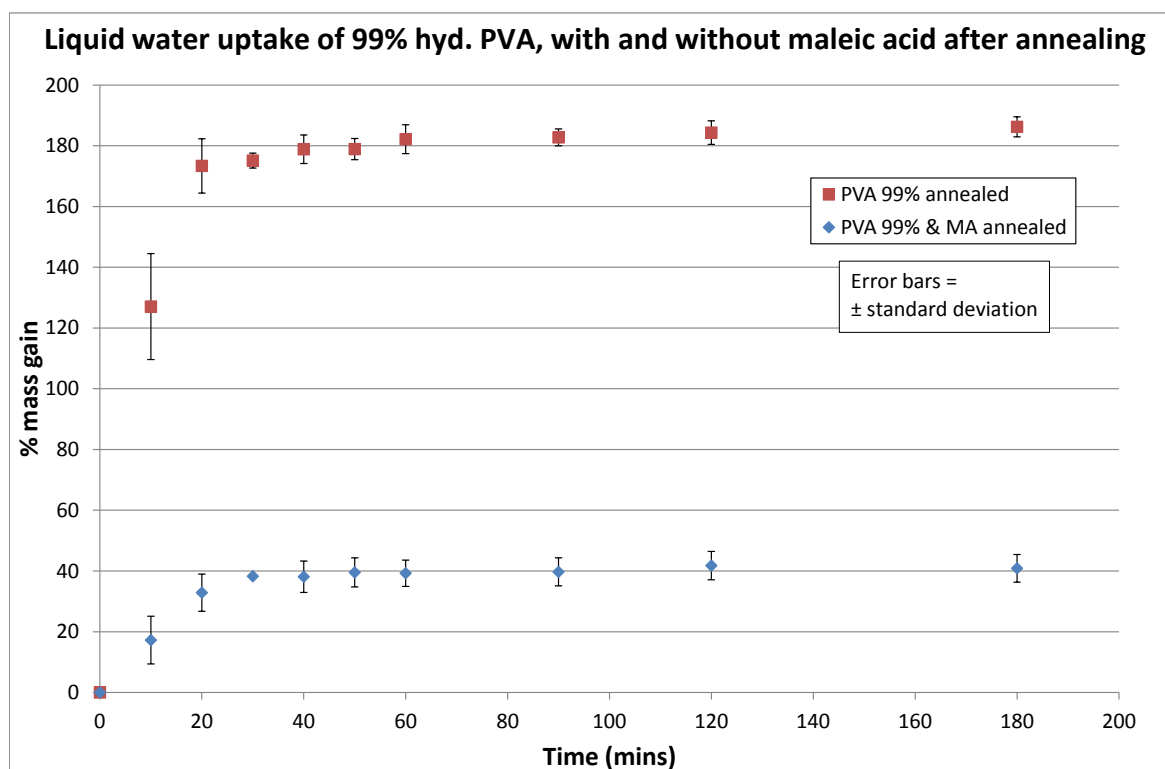


Figure 5.21: Liquid water uptake data for 99% hyd. PVA bulk cross-linked with maleic acid.

proceeding as hypothesised, and / or damage was being inflicted on the surface as a result of the spin-coating deposition procedure. As a result trials were carried out to assess the impact of using spin-coating to deposit onto PVA. 4ml of a 5wt% solution of PVA was spun onto several film samples. These were then dried and assessed by the water vapour uptake test and compared with plain solution cast PVA films. The results showed no difference in the moisture uptake and the coated and uncoated samples were within 0.3% of each other after 48 hours.

The next stage of the process to consider was the annealing. PVA films were annealed and the vapour uptake assessed and added to figure 5.22. The data recorded shows that there is no difference between the pre- and post- annealed PVA within experimental scatter. Further work is required to determine the unexpected performance decrease of the surface cross-linked film in figure 5.22.

The impact of a high water content (95wt%) solution being dropped onto the surface was also investigated. This was done by changing the substrate to 99% hydrolysed PVA (M_w 85k-124k). 99% hydrolysed PVA is insoluble in cold water and as such it is unlikely to be attacked by water in the same way as the 88% hydrolysed material.

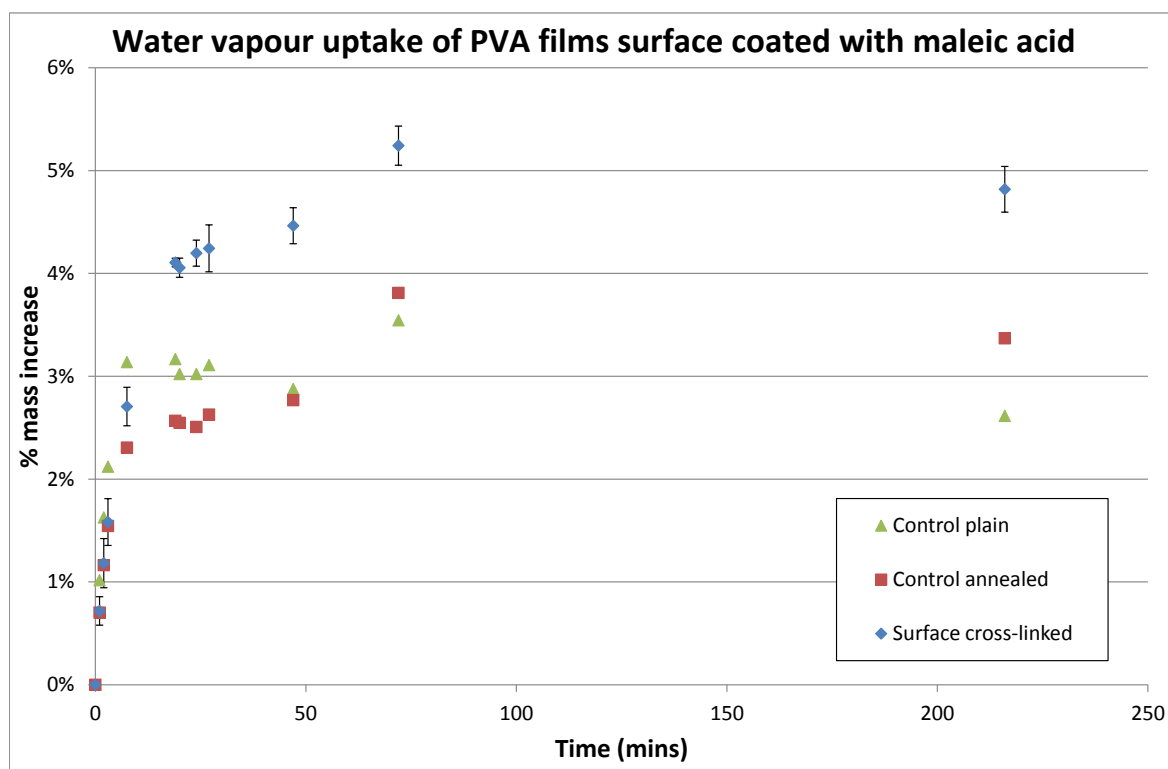


Figure 5.22: Water vapour uptake test for 88% PVA surface cross-linked with MA.

Figure 5.23 shows the impact of coating 99% PVA with maleic acid (via spin coating a solution of PVA and maleic acid) and in this instance the treated films have performed better.

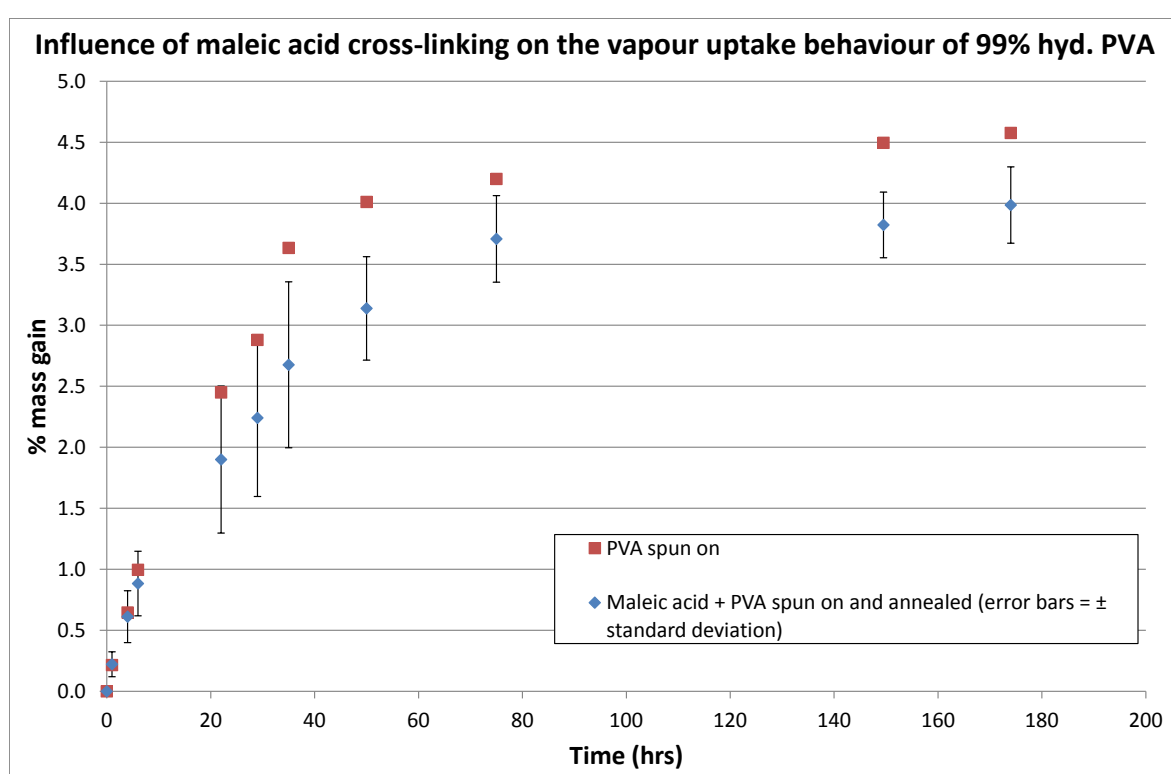


Figure 5.23: Influence of coating maleic acid onto a 99% hydrolysed film.

5.3.3.3 FTIR

FTIR is a useful technique to perform a quick chemical analysis of a given sample. In this work it has been used to monitor the cross-linking via maleic acid. First it is helpful to compare the FTIR spectra for 88% and 99% hydrolysed PVA films (figure 5.25) to aid with a subsequent comparison with published data.

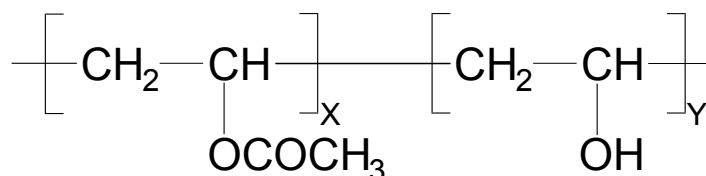


Figure 5.24: PVA repeat unit (for 88% hydrolysed $X=12\%$, for 99% hydrolysed $X=1\%$).

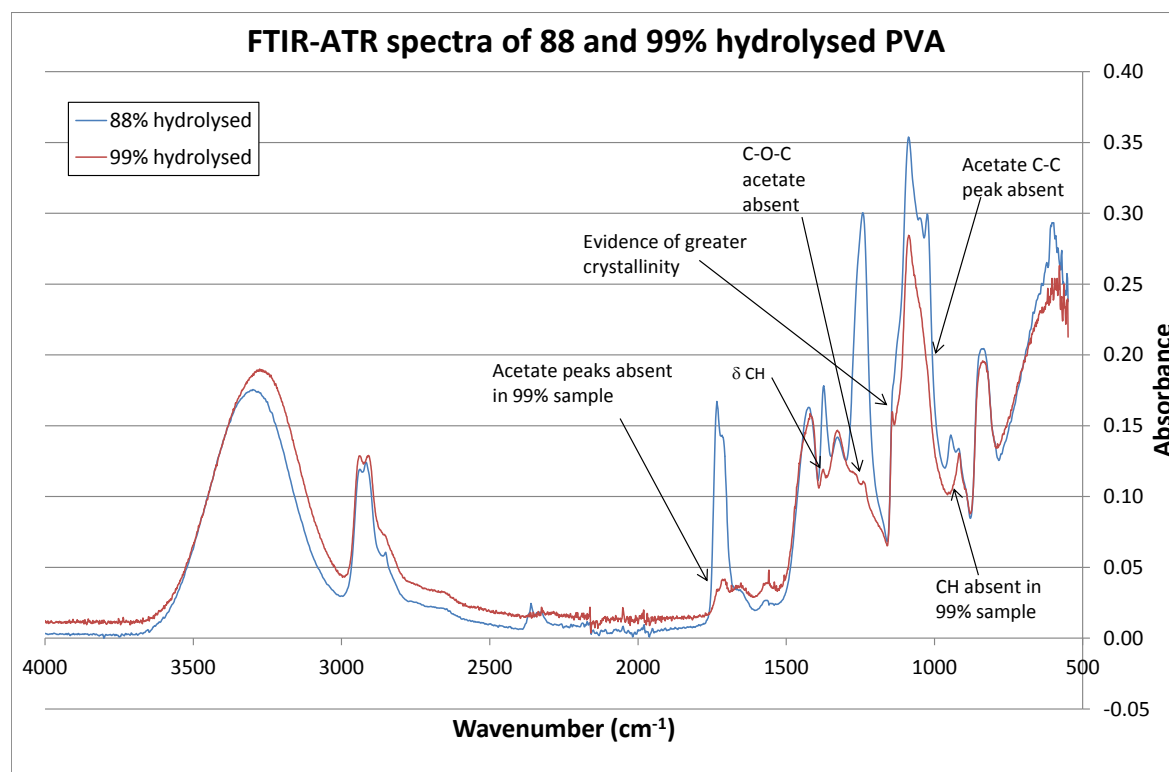


Figure 5.25: FTIR-ATR spectra of 88 and 99% hydrolysed PVA.

The 99% hydrolysed data compares favourably with that published by Gohil *et al.* [120]. There are two main differences between it and the 88% hydrolysed data, the peaks due to the acetate groups are absent or much weaker, namely those at 1733cm^{-1} , 1715cm^{-1} , 1243cm^{-1} and 1025cm^{-1} . Secondly two of the CH peaks are weaker or absent, that at 1374cm^{-1} (δCH) is much weaker and that at 947cm^{-1} is almost absent. The lack of the 1374cm^{-1} peak can possibly be attributed to the lack of

CH_3 groups in the 99% hydrolysed sample, likewise the 947cm^{-1} (although several sources state that the 947cm^{-1} band is due to the presence of a $\text{C}=\text{C}$ bond).

The stronger 1142cm^{-1} peak for the 99% hydrolysed sample implies that it has a greater crystallinity than the 88% hydrolysed material for the same sample preparation, as suggested by Marten [9].

Cross-linked samples

Samples of both 88 and 99% hydrolysed PVA were cross-linked with maleic acid and the resulting spectra are shown in figure 5.26. The weak absorption at 2853cm^{-1} in the 88% hydrolysed is only a shoulder in the 99% hyd. whilst the peaks at 1375cm^{-1} and 1250cm^{-1} are both noticeably lower for the 99% hydrolysed spectrum. The crystalline peak (1143cm^{-1}) is stronger in the 99% hydrolysed sample, though both materials show a slight strengthening of this peak (compared with the uncross-linked samples).

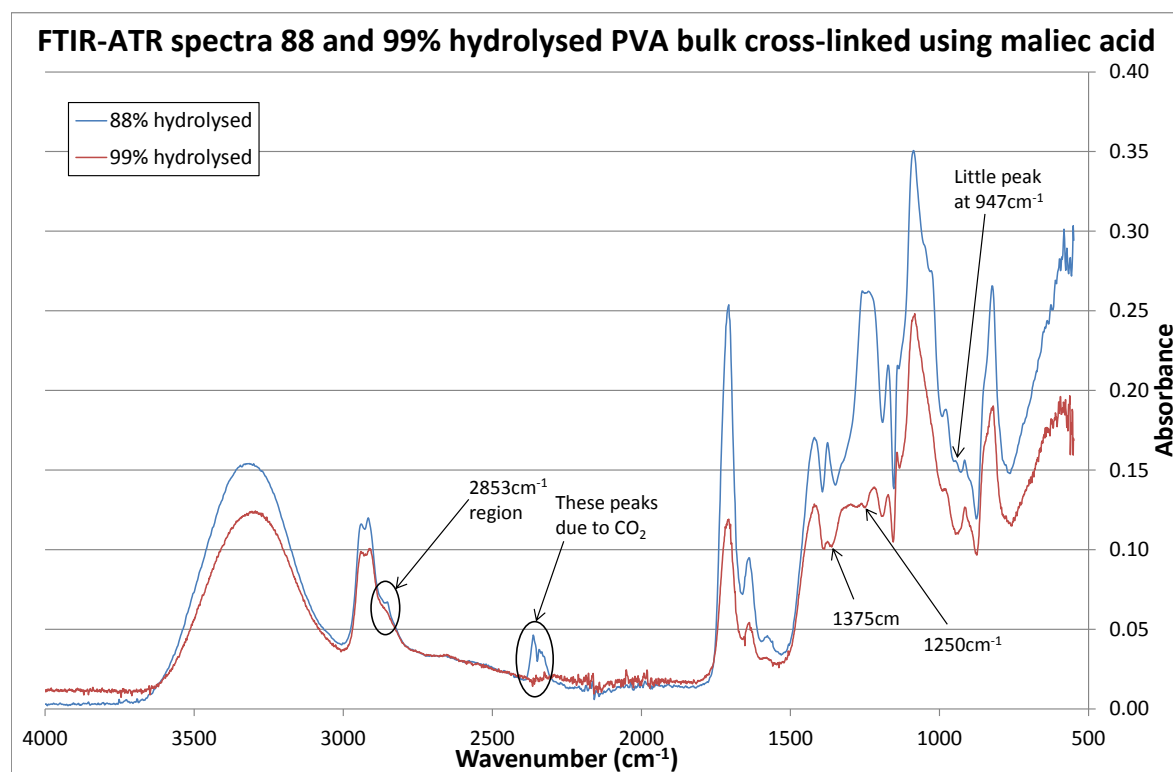


Figure 5.26: FTIR-ATR spectra of 88 and 99% hydrolysed PVA bulk cross-linked using maleic acid.

Before discussing the cause of these differences compared with untreated samples of

PVA it is helpful to consider further spectra which were taken at intermediate points during the cross-linking procedure (figures 5.27 and 5.28). The changes which occur are summed up in table 5.3.

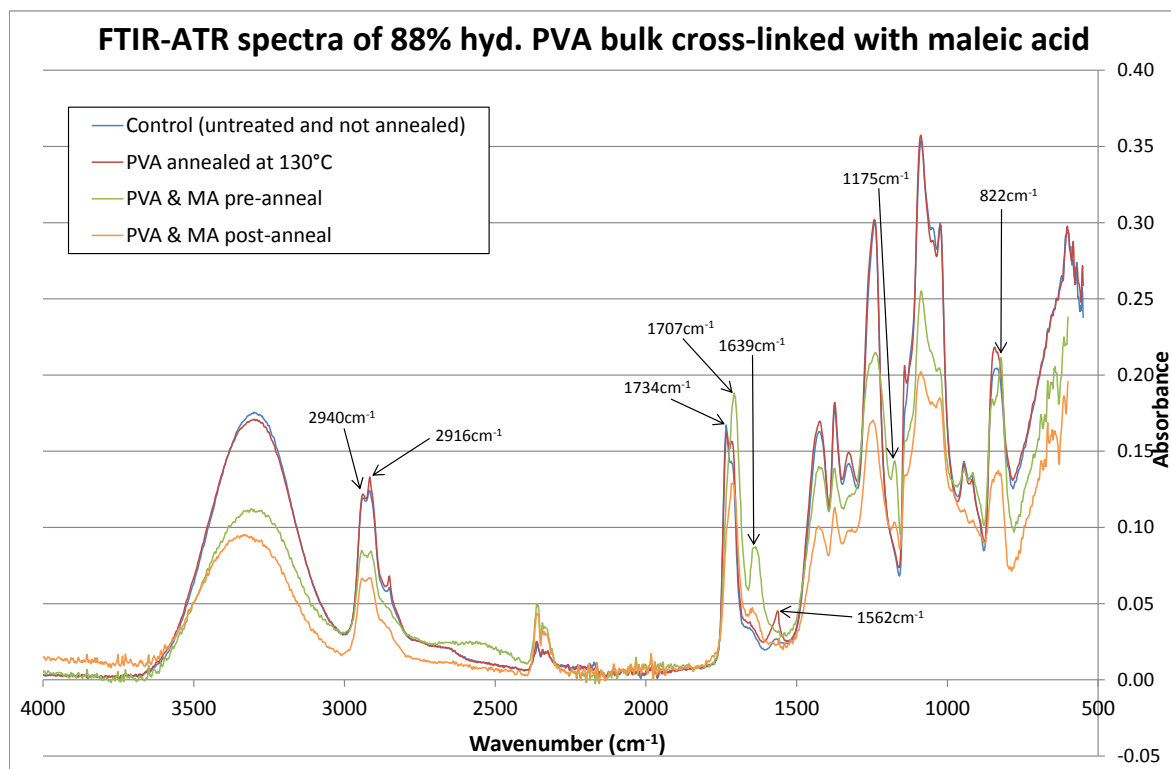


Figure 5.27: FTIR-ATR spectra of PVA (88% hydrolysed) pre- and post- annealing, with and without cross-linking molecules.

When Gohil *et al.* cross-linked 99% hydrolysed PVA in the same manner [120] they collected infrared spectra before and after cross-linking and they commented on several changes to the spectra as a result of the cross-linking. The hydroxyl band narrowed upon heating (due to water elimination), the C-H stretching band at 2928 cm^{-1} become sharper and stronger and new peaks were introduced at 1668 cm^{-1} and 2857 cm^{-1} , indicating the generation of a -C=C- structure and the elimination of the acetate groups during heating respectively [120].

A similar, but not identical change is seen for 88% hydrolysed material. Cross-linking the 88% hyd. material does cause the 2928 cm^{-1} (2916 cm^{-1}) band to sharpen a little upon heating. New peaks are also introduced as a result of the cross-linking, though not at exactly the same wavenumber. The principal peak due to the (residual) maleic acid is at 1639 cm^{-1} , though the peak at 1707 cm^{-1} has also be enhanced,

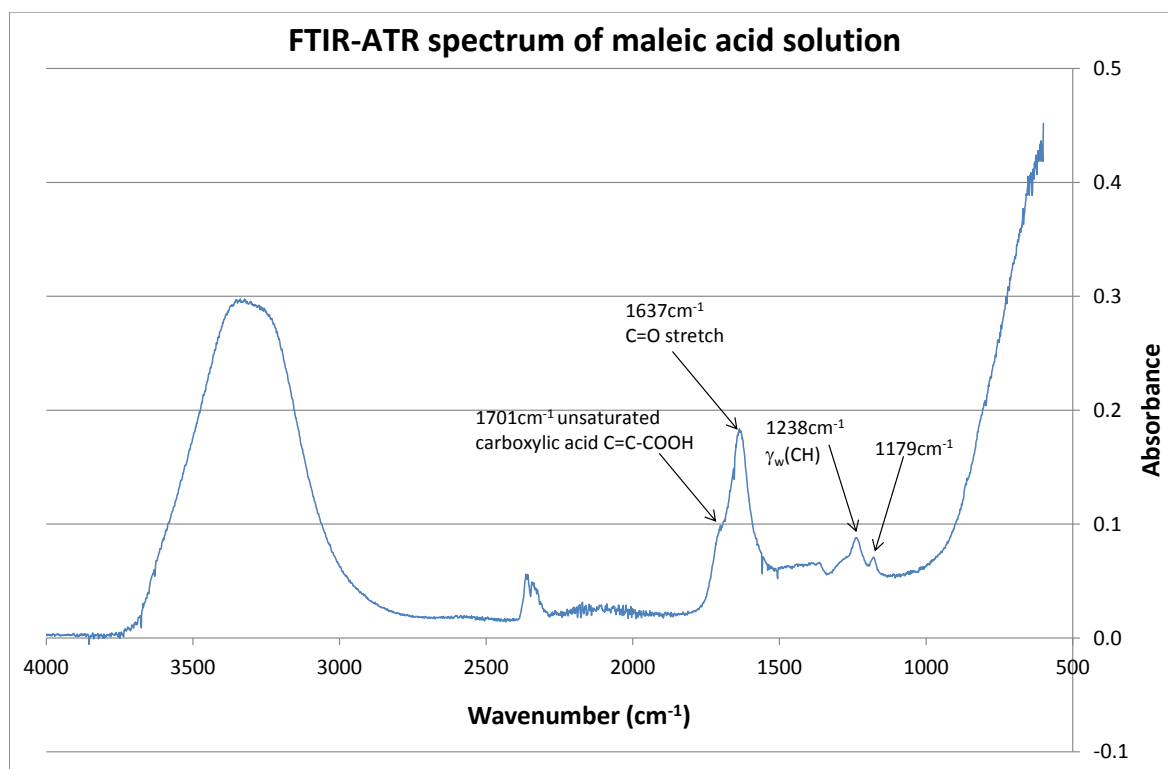


Figure 5.28: FTIR-ATR spectrum of a maleic acid solution.

Band (cm^{-1})	Group assignment	All relative to plain 88% hyd. PVA		
		88% annealed	88% & MA	88% & MA & annealed
2853	C-H	-	Weaker	Weaker
1734	C=O (acetate)	-	Much weaker	Much weaker
1707	unsaturated COOH	-	Much stronger	Slightly stronger
1639	C=O stretch (in MA)	-	Much stronger	Mildly stronger
1329	O-H & C-H	-	Weaker	Weaker
1175	C-O (MA peak)	-	Stronger	Only a little stronger
1142	C-O crystal peak	Much stronger	-	A little enhancement

Table 5.3: Summary of FTIR spectrum changes during the cross-linking procedure.

thus a peak at 1639cm^{-1} can be taken as illustrating the presence of maleic acid, and its intensity as to whether the maleic acid has reacted with the PVA or not.

Surface cross-linked samples.

Since FTIR is able to convincingly detect the presence of maleic acid it has also been used to study the surface treated samples. The ATR mode of operation is particularly suited to this task (as it samples only the first $1\mu\text{m}$ or so of a sample's surface). By depositing according to the spin coating procedure (as described in section 5.2.2) and then annealing, the treated surface was compared with that of a bulk treated sample (as shown in figure 5.29).

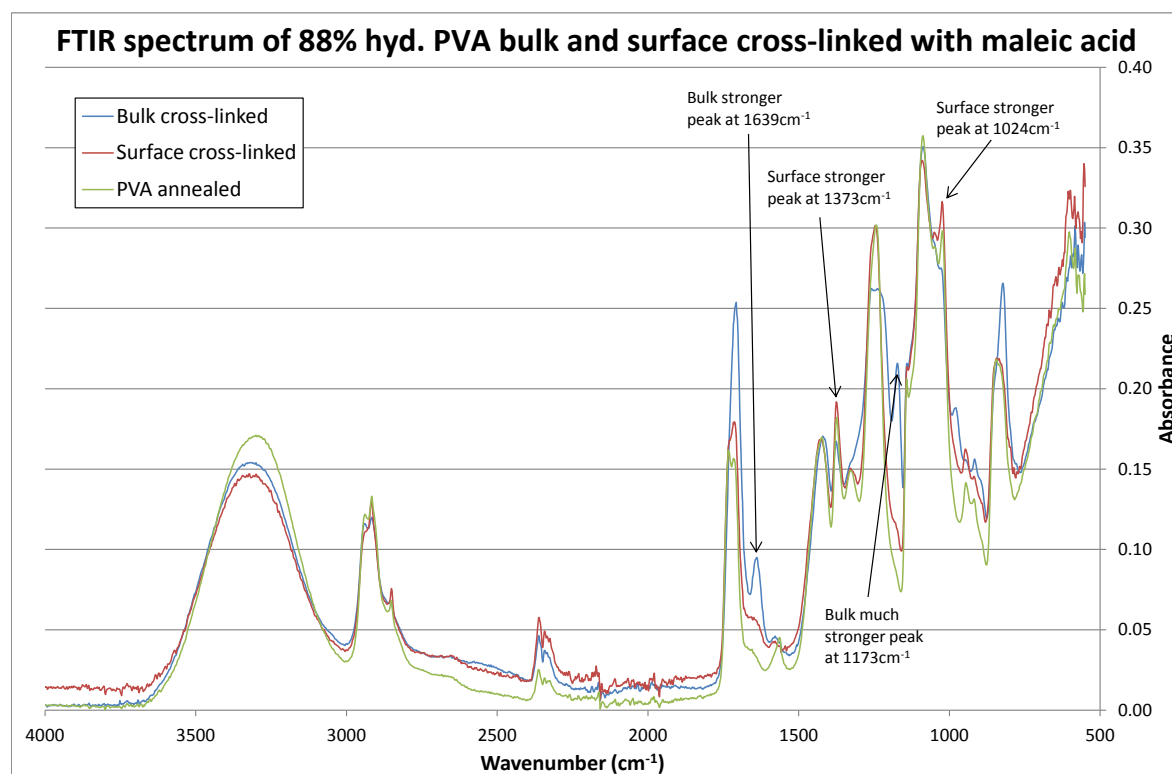


Figure 5.29: FTIR-ATR spectra of bulk and surface cross-linked PVA.

From this data it appears that spin coating is not depositing as much maleic acid per unit volume as in bulk cross-linking, given that 1639cm^{-1} and 1173cm^{-1} peaks (characteristic of maleic acid) are much stronger for the bulk cross-linked sample. However these peaks are marginally stronger than plain annealed PVA for the surface cross-linked case, implying that a small amount of maleic acid has been deposited.

5.3.3.4 Contact angle

The contact angles of the cross-linked samples were assessed to help produce a further quantitative comparison with untreated PVA. This was carried out using dynamic contact angle analysis in the usual manner (repeat loops into glycerol) as documented previously. The results are shown in figures 5.30 and 5.31.

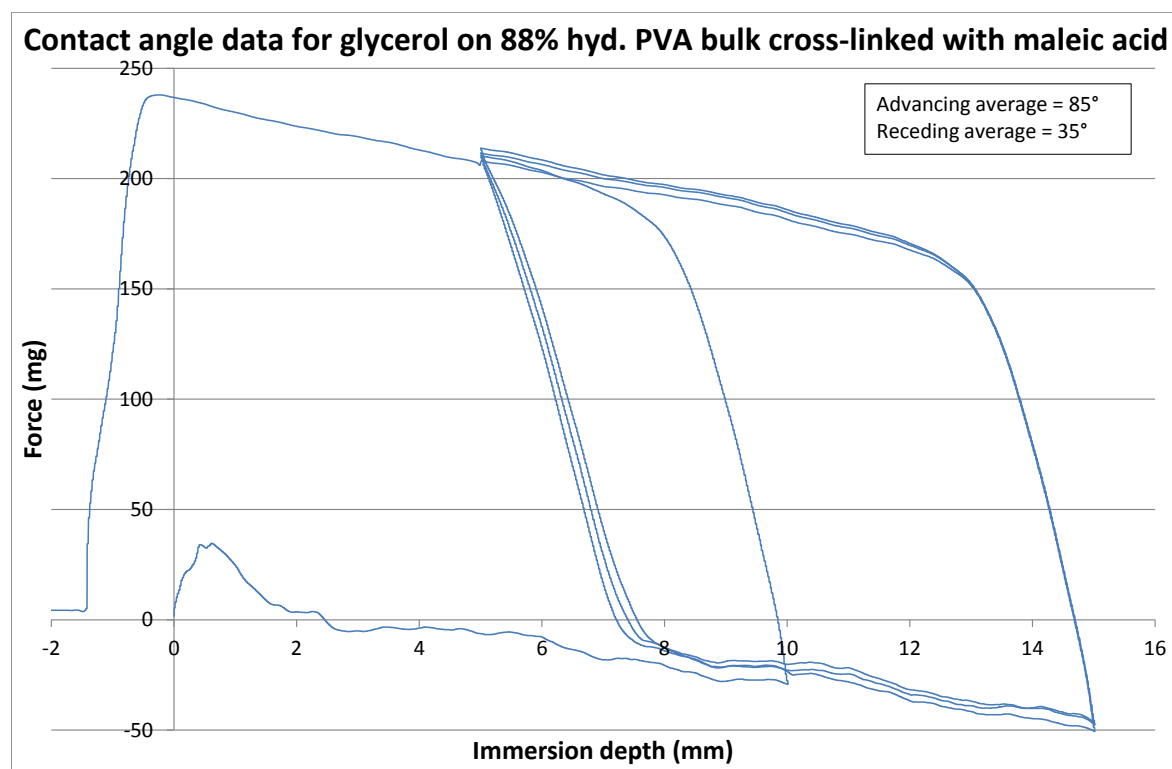


Figure 5.30: DCA analysis of bulk cross-linked 88% hydrolysed PVA (using maleic acid).

Average angles obtained:

Sample	Average advancing angle	Average receding angle
88% bulk cross-linked	85°	35°
99% bulk cross-linked	74°	31°
Untreated 88% PVA	75°	0°
Untreated 99% PVA	67°	12°

Table 5.4: Average contact angles obtained for bulk cross-linked PVA.

In all instances it can be seen that the cross-linking has effected an improvement in the solvent resistance of the films. The 88% hydrolysed film seems to have improved

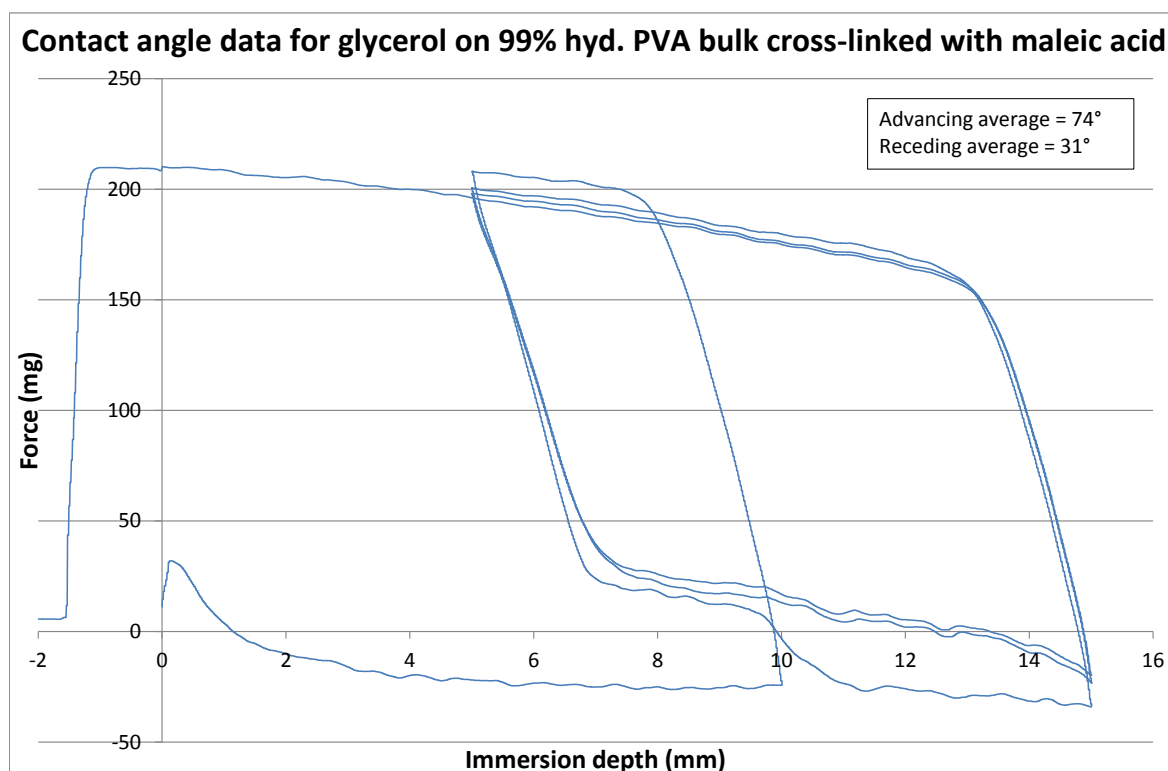


Figure 5.31: DCA analysis of bulk cross-linked 99% hydrolysed PVA (using maleic acid).

the most. (Interestingly it is the 99% hyd. untreated sample which initially seems the most hydrophilic [it has the lowest advancing angle], however the receding angle suggests otherwise). Successive cycling of a sample suggests some evidence of intrinsic hysteresis for the case of 99% hydrolysed, thus surface change is taking place here (perhaps a preferential ordering of the small number of acetate groups to the surface).

The fact that the 88% hyd. cross-linked sample seems to have been made more hydrophobic than the 99% hyd. sample is in disagreement with the liquid water vapour data (figures 5.20 and 5.21) whereby the 99% sample performed slightly better. This is perhaps because whilst liquid water uptake and contact angle are related (interaction between the polymer and the water) they are different as swelling requires conformational changes. The ease with which this will occur is dependent on other factors (such as the cross-link density) which the contact angle is not dependent on.

5.3.3.5 AFM

AFM images were taken to analyse the surface microstructure of bulk cross-linked 88% hyd. PVA. Both topographical and phase images show some change in microstructure as a result of the cross-linking, notably due to the presence of maleic acid (see figure 5.36 in particular).

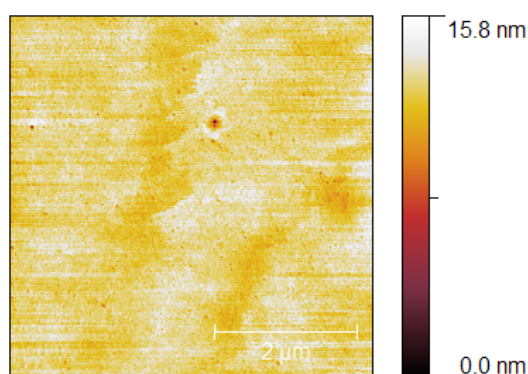


Figure 5.32: Topographical AFM image of untreated PVA.

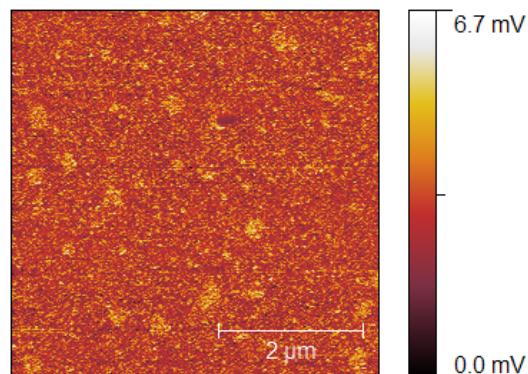


Figure 5.33: Corresponding AFM phase image of untreated PVA.

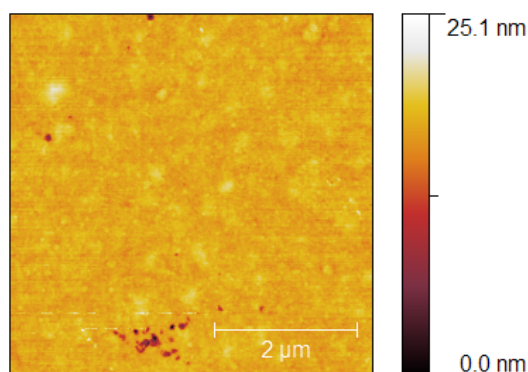


Figure 5.34: Topographical AFM image of annealed PVA.

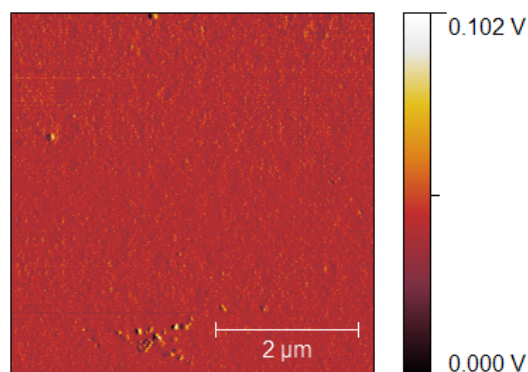


Figure 5.35: Corresponding phase AFM image of annealed PVA.

The images show very little change as a result of annealing the plain PVA, however for the maleic acid containing films they hint at a two phase structure (as illustrated in figure 5.40) and the corresponding phase image (figure 5.37) hints at the same structure too. It is conceivable that there might be some segregation of the maleic acid (given it is mixed at 33wt% w.r.t. PVA). Also the two-phase type structure is retained after annealing, implying that it is thermodynamically favoured at high temperatures too.

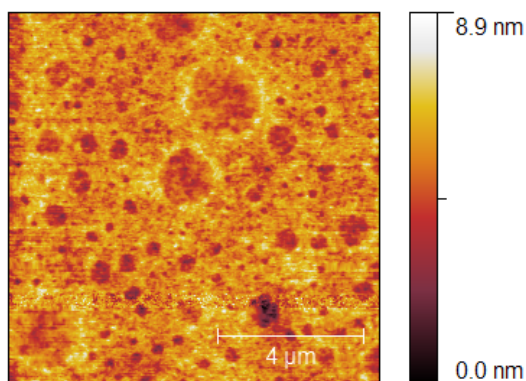


Figure 5.36: Topographical AFM image of PVA & MA mixed prior to annealing.

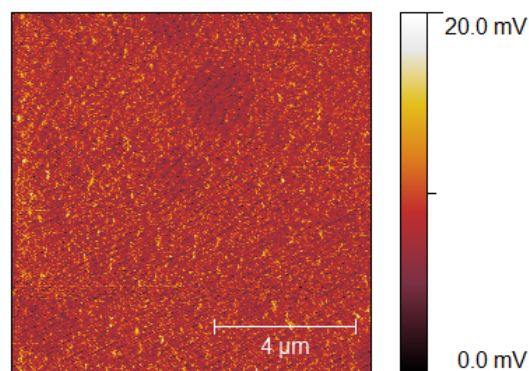


Figure 5.37: Corresponding phase AFM image of PVA & MA mixed prior to annealing.

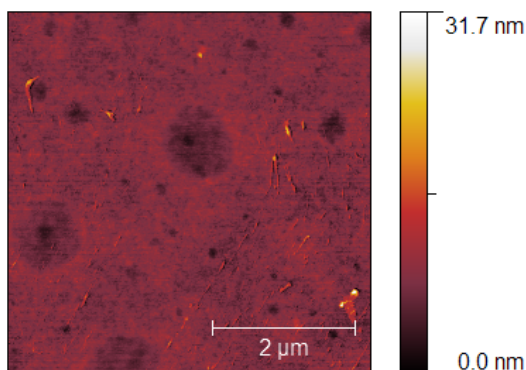


Figure 5.38: Topographical AFM image of PVA & MA after annealing.

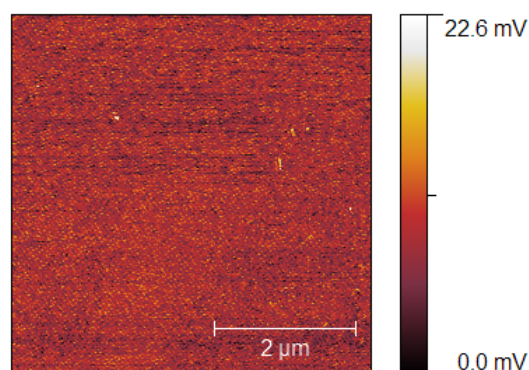


Figure 5.39: Corresponding phase AFM image of PVA & MA after annealing.

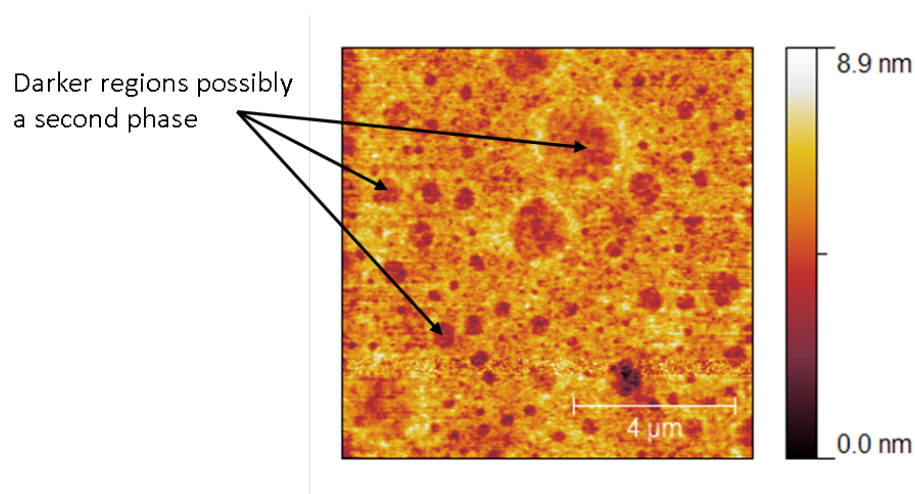


Figure 5.40: Topographical AFM image of PVA & MA mixed prior to annealing.

It is not clear what the two phases might be, though an MA-rich PVA and MA-poor PVA is one possibility. This could be established by imaging PVA films containing varying amounts of maleic acid.

5.3.3.6 DSC

DSC scans were taken (by heating at $100^{\circ}\text{Cmin}^{-1}$ from -20°C to 150°C) to further assess the miscibility of the PVA and maleic acid. For the case of mixing the two components the traces revealed two potential glass transition temperatures (24 and 76°C) as shown in figure 5.41. The T_g on the second heating cycle was recorded as 47°C (figure 5.42). There is only a slight chance of cross-linking occurring as a result of the first heating cycle because the time spent at elevated temperature (130°C to 150°C) is small (12 seconds). For the case of the cross-linked films the first and second heat T_g s were 53 and 86°C , both of which were higher than plain PVA (36 and 74°C).

Several conclusions can be drawn. Firstly the maleic acid is likely acting as a plasticizer for PVA, as evidenced by the lower second heating cycle T_g (47°C) when compared with that of plain PVA (74°C) (this also agreed with the physical properties of the mixed films when they were handled between experiments). Secondly upon cross-linking the T_g has been raised which is to be anticipated in a cross-linked system. A further point of note is that in the first heating cycle for PVA and maleic acid mixed the possibility of two T_g s hints at a two phase system. However first heat cycle DSC measurements must be treated with some caution as 'apparent' transitions may in fact be as a result of poor initial sample-pan contact.

DSC first heat traces for PVA mixed with maleic acid

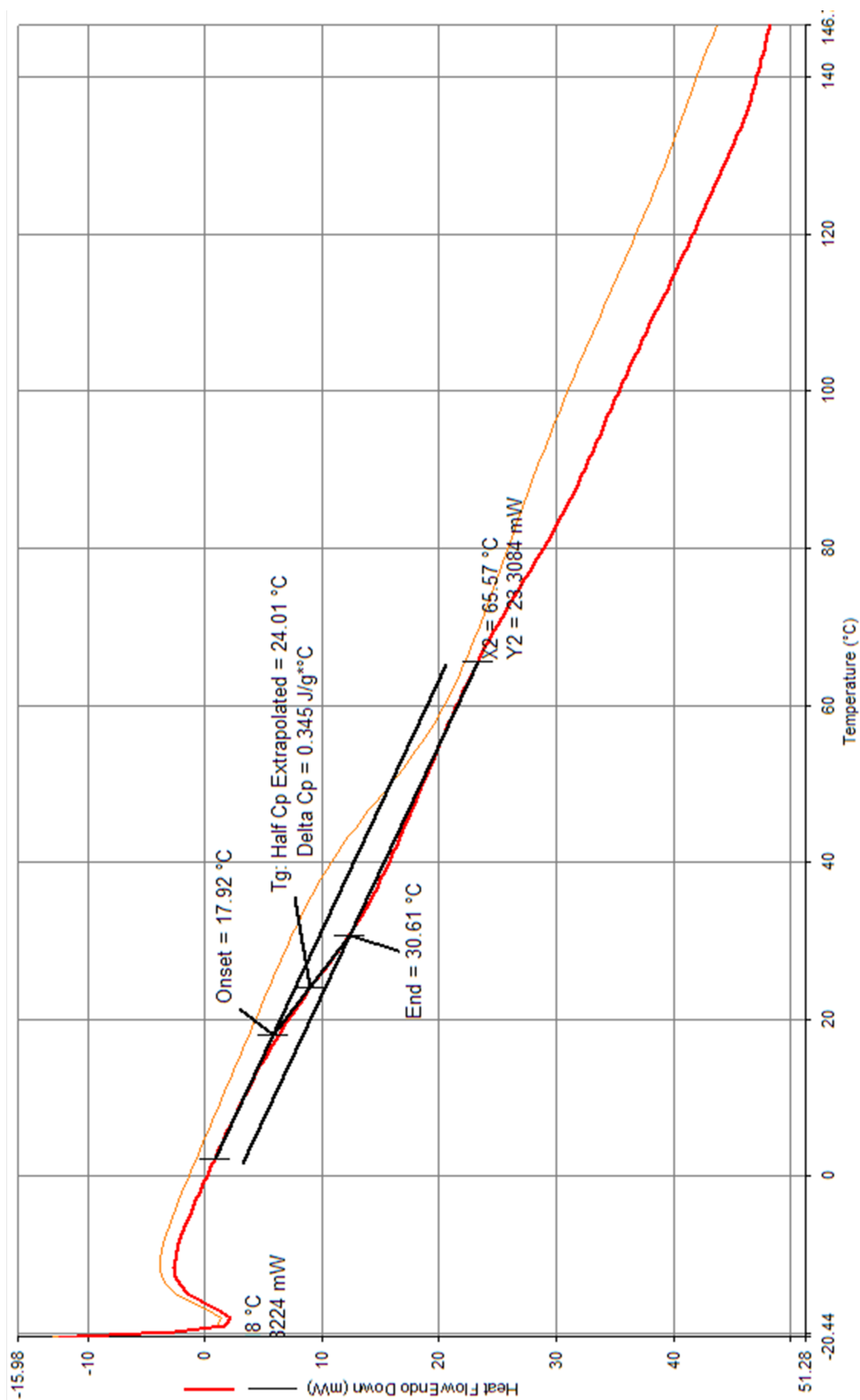


Figure 5.41: DSC scan for PVA and maleic acid mixed (by solution casting together) but not cross-linked.

DSC second heat traces for PVA mixed with maleic acid

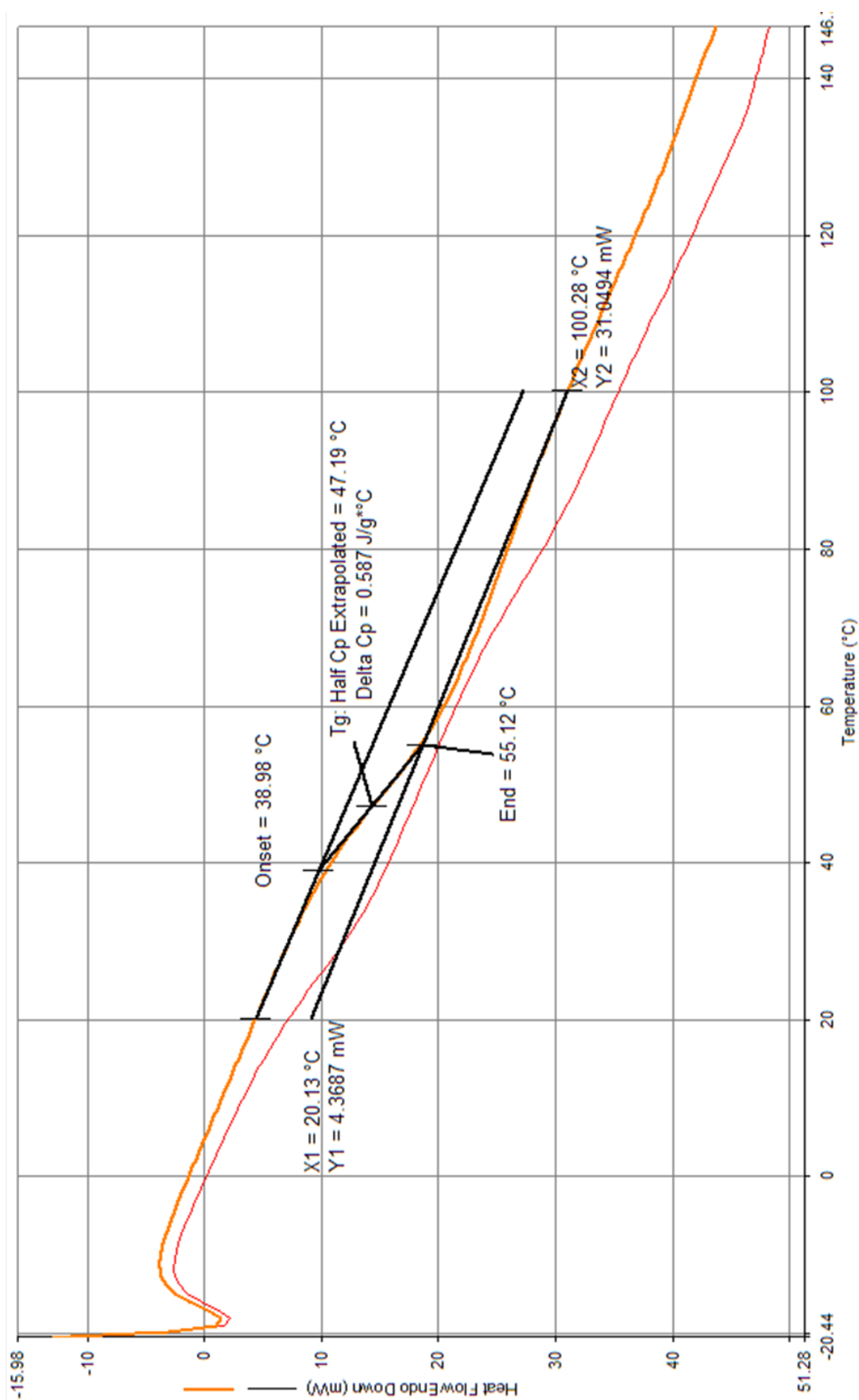


Figure 5.42: DSC scan (second heat) for PVA and maleic acid mixed (by solution casting together).

5.3.4 Maleic anhydride

Method & results for maleic anhydride

To try and overcome the problem posed by dissolving the substrate whilst depositing maleic acid, maleic anhydride was considered as a possible alternative cross-linker. Maleic anhydride is similar to maleic acid in structure however it is soluble in a different variety of solvents. Maleic anhydride can be converted to maleic acid simply by the addition of water, as shown in figure 5.43.

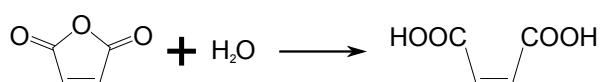


Figure 5.43: Hydrolysis of maleic anhydride (based on [191])

Previously published work suggests that cross-linking of PVA (88% hydrolysed) using maleic anhydride is possible, Yang *et al.* [2] having done so by electrospinning a solution of the two. No additional thermal or other energy input was required (though the solution was set to a pH of between 2 and 3). The authors also suggest that the same cross-linked structure was formed to that proposed by Gohil *et al.* [120], as in figure 5.18.

Interestingly Yang *et al.* also commented, “The results indicate that rapid evaporation of water ... during electrospinning process can promote esterification reaction.” [2]. This can also be considered in terms of Le Chatelier’s Principle, whereby removing the water we are driving the equilibrium of the esterification to the right, thus accelerating the cross-linking.

Trials began by using maleic anhydride in place of maleic acid for bulk cross-linking of PVA. Solutions were mixed (5wt% PVA in water, and 33wt% maleic anhydride w.r.t. PVA) and cast into films. They were then annealed at 130°C as before to induce cross-linking. Liquid water uptake tests were then performed and the films behaved similarly to PVA cross-linked with maleic acid (see figure 5.44) as of course the maleic anhydride would have been hydrolysed during the solution casting.

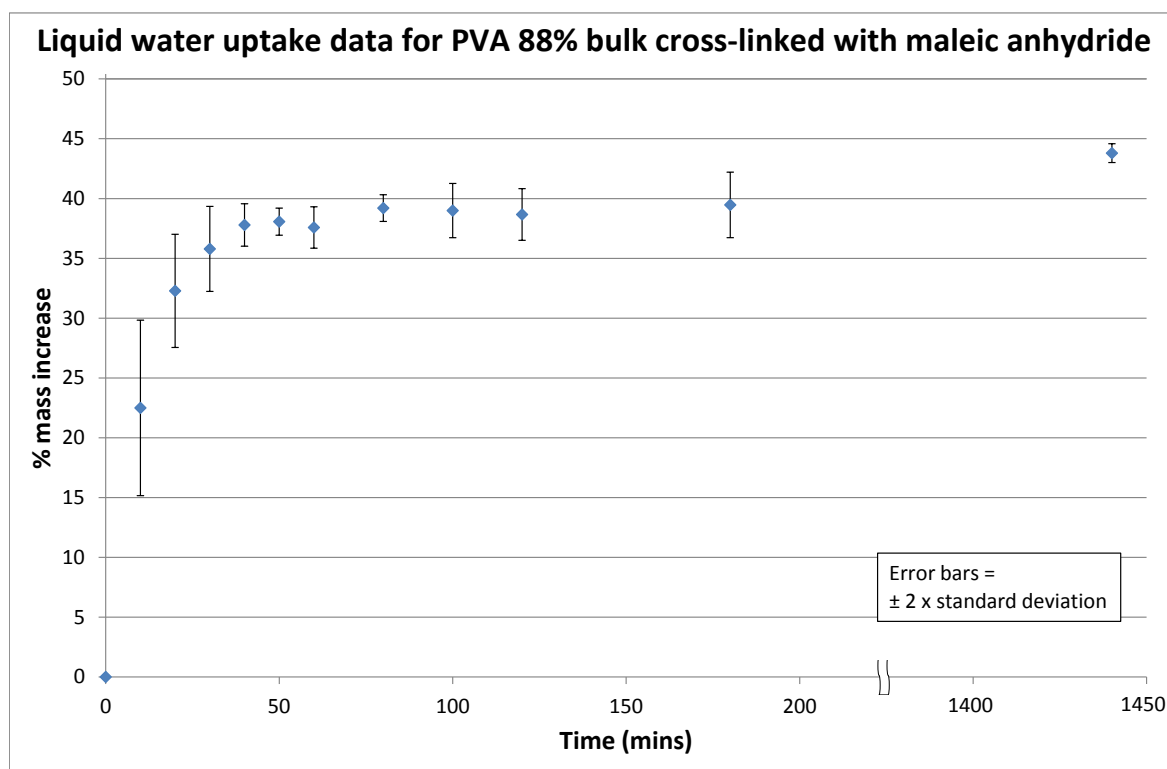


Figure 5.44: Liquid water uptake data (in water) for PVA bulk cross-linked with maleic anhydride.

Comparing this data with that for maleic acid cross-linked (figure 5.20) it can be seen that the saturated swelling values are similar, with that for maleic anhydride being 44% after 24hrs, and that of maleic acid being 52%, thus implying that the mechanism of cross-linking is the same in both cases.

Bulk cross-linked films have also undergone the surface water vapour uptake test, and the results of that are shown in figure 5.45.

Although repeat runs were not performed the near identical water vapour uptake profile for the maleic acid and anhydride systems supports the conclusion that the maleic anhydride is completely transformed to maleic acid before cross-linking.

To examine a case in which maleic anhydride would not be converted to maleic acid before the cross-linking reaction it was successfully dissolved in toluene at 5wt%. The solution was then spin-coated onto the surface of solution cast PVA films (88% hyd.). The films were dried and annealed for 2hrs at 130°C before undergoing the water vapour uptake test, the results of which are shown in figure 5.46.

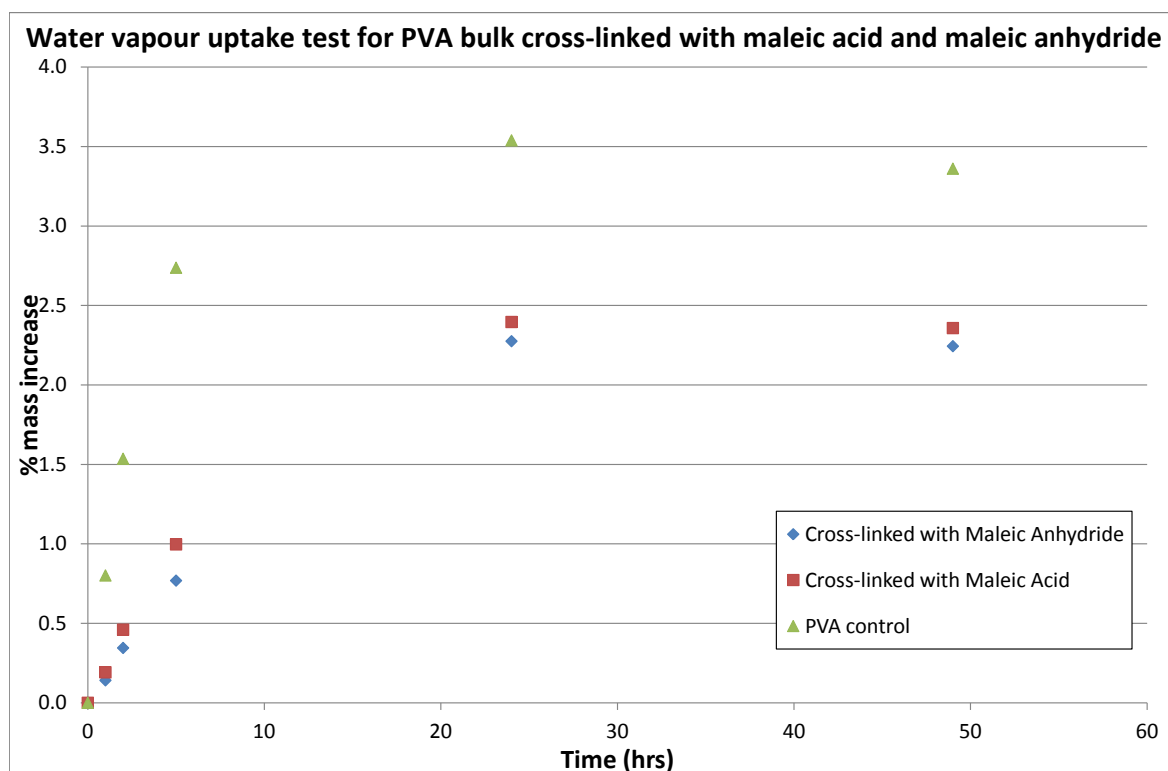


Figure 5.45: Water vapour uptake test for PVA bulk cross-linked with maleic acid and maleic anhydride.

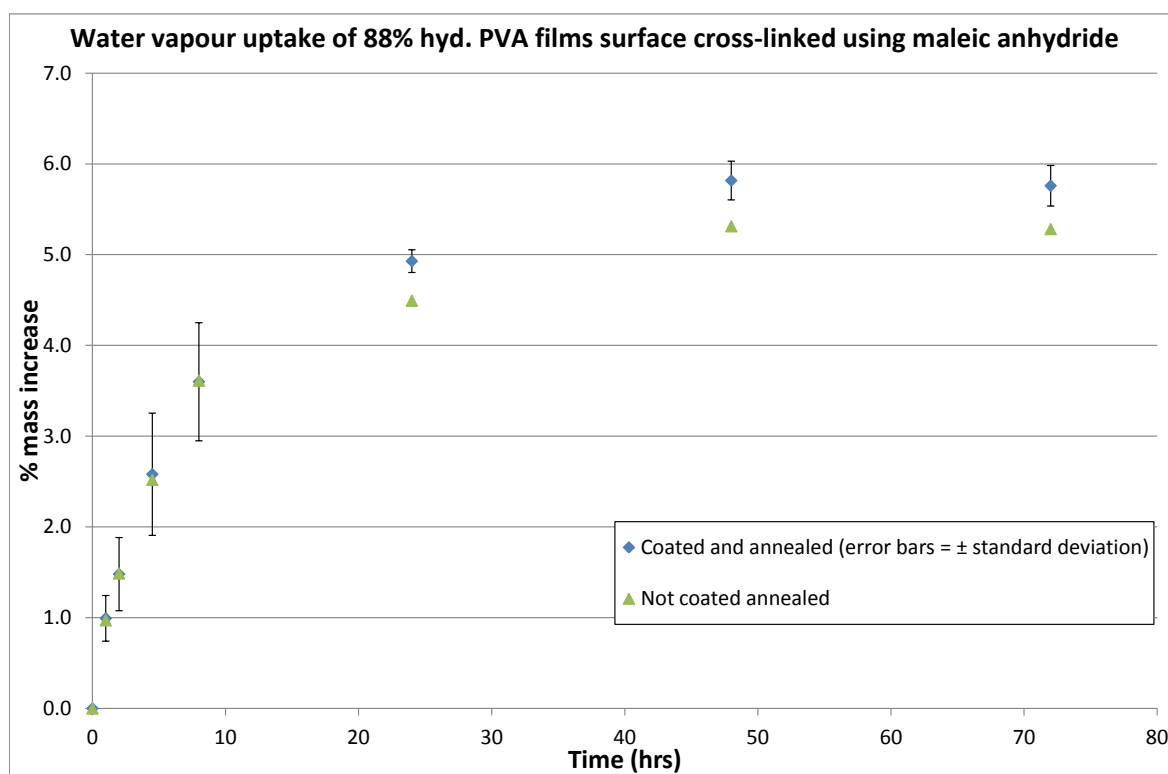


Figure 5.46: Water vapour uptake test data for samples surface cross-linked with maleic anhydride.

During the spin coating process no perceivable damage to the film surface took place (which is in contrast to the case of spin coating on maleic acid in water). The surfaces seemed unperturbed and they dried quickly.

Considering the water uptake data in figure 5.46 there is no evidence of an improvement. This may be because the cross-linking is not as efficient when using maleic anhydride in toluene (based on the fact that less of the solution seems to have been deposited).

To shed further light on the swelling data FTIR spectra of various samples have been recorded. Spectra of samples bulk cross-linked with maleic anhydride and maleic acid are shown in figure 5.47. The same peaks are present in both cases, thus implying that the anhydride has been hydrolysed and that the chemistry of the cross-linking is the same (as expected).

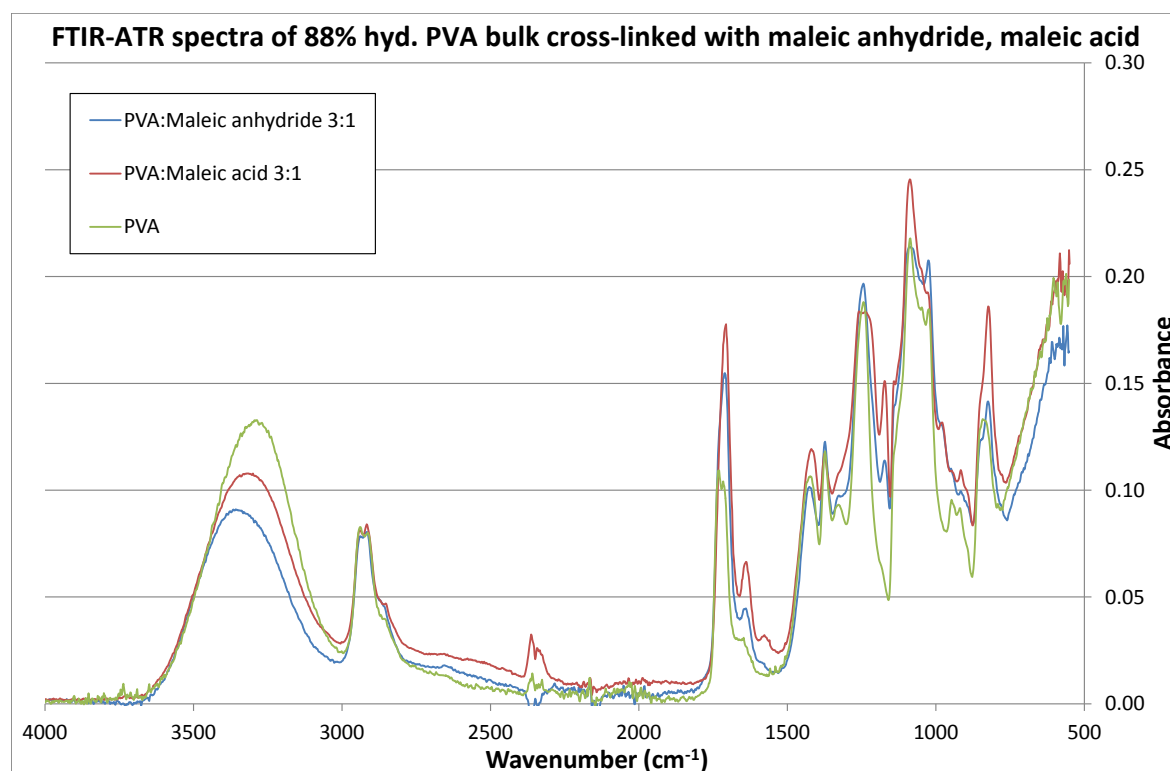


Figure 5.47: FTIR spectrum of PVA (88% hyd.) bulk cross-linked with maleic anhydride & maleic acid.

The surface coated films (with maleic anhydride in toluene) were also examined and they produced the spectra shown in figure 5.48. There are very few differences be-

tween the spectra. The treated samples have a stronger crystalline peak (1142cm^{-1}), but this can be attributed to the annealing step during the processing. The other difference is that the 2906cm^{-1} peaks are slightly different in strength, with it being strongest for the non-coated surface, followed by the coated surface and then the untreated control sample. This peak can be attributed to a C-H stretch. It is possible that some minor chain realignment takes place as a result of the annealing, (but nothing further can be concluded than this). Thus from the FTIR there is no evidence of a significant reaction between the maleic anhydride and the underlying PVA.

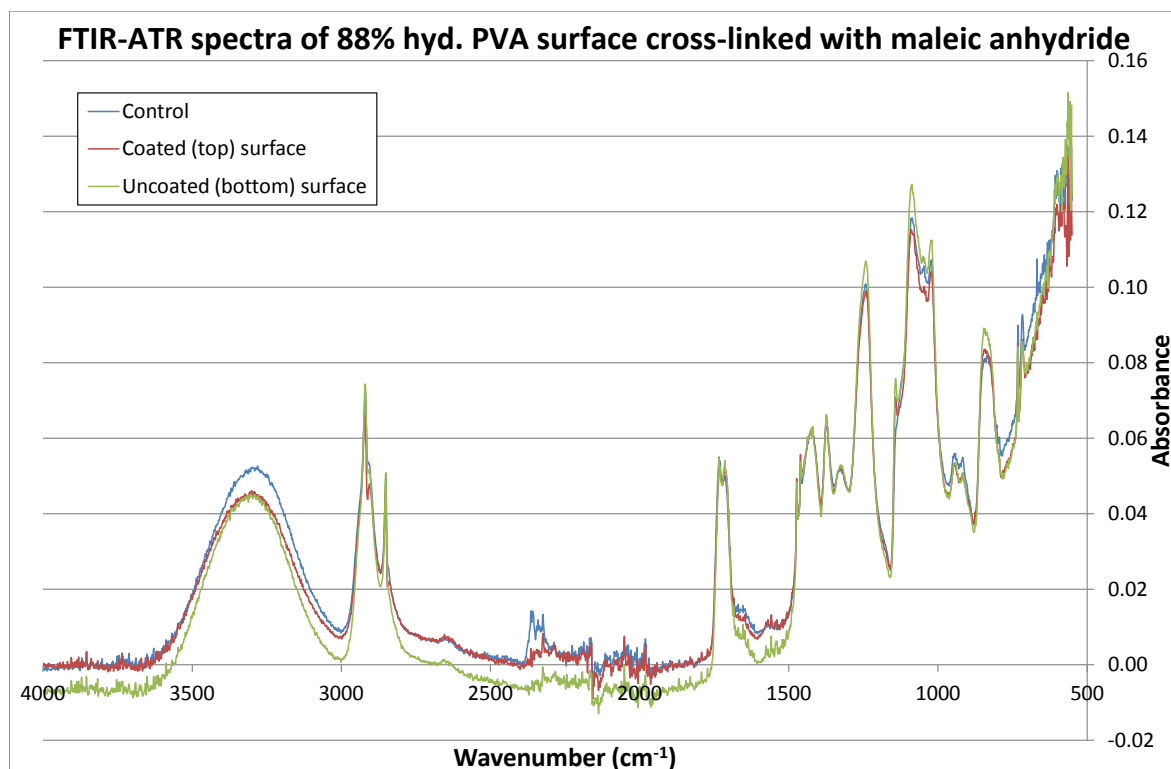


Figure 5.48: FTIR spectrum of PVA (88% hyd.) surface cross-linked with maleic anhydride.

5.4 Discussion

5.4.1 UV-induced cross-linking

From the data shown it can be concluded that UV-induced cross-linking has the potential to produce surface specific cross-linked PVA. Whilst the experimental conditions in this work have not resulted in a total insolubilisation of the film surfaces they have nonetheless been a small step in the right direction as evidenced by the insoluble fraction of material left after treatment, along with improved contact angles.

Several questions remain however as to the mechanism by which cross-linking proceeds, indeed Miranda *et al.* [127] commented (in 2001) that the exact mechanism of cross-linking of PVA by sodium benzoate was not yet clear (according to their survey of the literature). They referred back to Takakura *et al.* [129], who claimed that a peak in the UV spectrum at 225nm decreased during irradiation and that this was proof of the sensitizer photolysis. They also commented on a peak at 270nm, showing that a peak here increased within the first hour of treatment, but then decreased again by the fourth hour. However what is strange in their data (figure 2 in [129]) is that the optical density is not particularly high (0.15 at 254nm), whilst for the samples examined in this work it was (> 95% after one hour of treatment).

Nonetheless it is widely accepted that photolysis of sodium benzoate takes place upon exposure to UV radiation at 254nm (see figure 2.22 and section 2.5.1.2). This has been confirmed by FTIR spectroscopy, whereby the sodium benzoate absorption peak is absent upon exposure to radiation at 254nm (figure 5.8). However if we consider again the sensitizer photolysis mechanisms then if they are correct it would be anticipated that we would observe some residual benzoic acid, benzene or benzaldehyde in the sample (based on figure 2.22).

Major absorbencies anticipated would be at:

- Benzoic acid: 1689cm^{-1} , 1327cm^{-1} and 1294cm^{-1} (and also 1464cm^{-1} and 1426cm^{-1} to a lesser degree).
- Benzaldehyde: 1703cm^{-1} and 1204cm^{-1} (and also 1597cm^{-1} , 1584cm^{-1} , 1456cm^{-1} , 1311cm^{-1} , 1168cm^{-1} to a lesser degree).
- Benzene: 3036cm^{-1} and 1479cm^{-1} (and 1038cm^{-1} to a lesser degree).

An examination of the post- exposed PVA film (containing sodium benzoate at 5wt%) reveals the presence of none of these peaks, and the 1599cm^{-1} peak has been lost (C=C stretching vibrations of the benzoate ring [127]). The volatility of the products must be taken into account, benzoic acid is solid at room temperature whilst benzaldehyde and benzene are liquid at room temperature (benzene in particular being highly volatile). Therefore it can be concluded that one of the residual products suggested by Delville *et al.* [130] is incorrect, as since benzoic acid is solid at room temperature it would show on the FTIR spectrum. Benzaldehyde and benzene are thus more likely as it is reasonable to suppose they can diffuse out of PVA and hence evade detection.

Cross-linking progression mechanism

It is helpful to consider a conclusive finding as a result of figure 5.8, that the UV radiation ($\lambda = 254\text{nm}$) does not penetrate through from one surface of the film to the other. Thus whilst the exposed surface is cross-linked, the opposite one is not - and it is this effect (albeit controllably) which has been sought in this chapter of work.

The question which must be addressed is what happens after the initial cross-linking of the top surface layer? The radiation either continues to be blocked by whatever post-sensitizer species remain in the film (recalling that PVA itself is transparent to UV radiation - figure 5.1). Or alternatively the beam gradually penetrates deeper and deeper into the film as successive 'layers' are cross-linked.

In support of the former there is the fact that whilst a fraction of the films has al-

ways been made insoluble, increasing the cross-linking time seems to have effected little change on the amount of cross-linked material (see figure 5.4). This suggests a limit to the depth cross-linked, regardless of the cross-linking time. Takakura *et al.* reported a limiting value to the gel fraction of 90% for cross-linking 99% hyd. PVA in a similar manner, whereby beyond 2hrs exposure to UV radiation no increase in gel fraction was seen [129].

Of course another possibility is that all of the sensitizer has been used up in the whole sample, however testing of the transmission of thin films ($20\text{-}30\mu\text{m}$) at 254nm (which has $\sim 80\%$ transparency without sensitiser) during UV exposure showed that UV radiation was still absorbed after a period of 12 hours (figure 5.3) when the reaction could be said to be complete.

Whilst in support of the latter it is possible that cross-linking proceeds through the system via a 'front'. Such a mechanism has been commented on by Decker, for the case of sensitizer polymerization of a monomer [125]. Such a mechanism relies on the photoinitiator being destroyed and thus incident radiation subsequently being able to reach to deeper layers. The time scale involved is different - in that for polymerization the reaction proceeds in a matter of seconds through the sample. However the principle should hold for cross-linking, although there is very little evidence in the literature of authors commenting on a frontal cross-linking system.

In conclusion, this work supports the former mechanism - in that there is an apparent limit to the depth of material cross-linked. It is likely that other variables (for example the bulb power) might have an impact on this depth, though such other factors were not investigated in this work.

It is also necessary to consider why this method seems not to have given the water-resistance hoped for. Whilst cross-linking has occurred it is likely that the cross-link density is extremely low. Thus swelling of the film is still possible, and hence permeation of water. In order to improve the system it would be useful to have an estimate of the cross-link density followed by suitable attempts at increasing it

such that swelling becomes much more difficult. Also it should be noted that the as-cast films contain pre-existing crystals and it is not certain whether the crystalline regions will be more or less able to cross-link by using this treatment.

5.4.2 Maleic acid cross-linking

From the data presented in this thesis it can be concluded that maleic acid can be successfully used to cross-link 88% hydrolysed PVA. The mechanism proposed by Gohil *et al.* is valid for 88% PVA owing to the high fraction of hydroxyl groups available for cross-linking (via the esterification reaction as shown in figure 5.18). However it is unclear what proportion of inter- and intra- molecular cross-linking takes place, and also whether or not the $\sim 12\%$ acetate groups are affected by the cross-linking reaction. It is reasonable to suppose that they are not, as the proposed cross-linking mechanism is an esterification reaction, requiring an alcohol group on the polymer. Brazel *et al.* [192] produced a similar conclusion when using glutaraldehyde to cross-link PVA.

A comparison of the performance of 88% and 99% hydrolysed PVA yields favourable results, with the 88% hydrolysed performing almost as well in the liquid water uptake test (figures 5.20 and 5.21) and performing better in the contact angle tests (table 5.4).

The objective of this section of work was ultimately to surface cross-link PVA and ideally the cross-linking molecules would be deposited onto the surface without disturbing the underlying bulk. This was initially attempted by depositing a thin layer of PVA and maleic acid onto a bulk PVA substrate. However for the case of using water (which is a good solvent for PVA) the underlying bulk material seems to have been attacked by spin coating with a good solvent. As such a non-solvent for PVA for used, but then it was impossible to deposit a solution of cross-linker and PVA, thus only maleic anhydride was deposited from toluene (non-solvent for PVA). This has shown no evidence of inducing cross-links on the surface (water vapour

uptake fig. 5.46 and FTIR data fig. 5.48), hence it can be concluded that there has not been enough interaction (if any) between the cross-linker and the underlying PVA. Ideally a poor solvent for PVA would be sought - such that it would dissolve the cross-linker and slightly swell the substrate allowing PVA-cross-linker interaction.

A prime advantage of pursuing this kind of method is that it eliminates the adhesion problems of a conventional coating method, as the cross-linker molecules imbibe into the substrate.

A further point to note is that the presence of a non-trivial fraction of acetate groups ($\sim 12\%$) seems to disrupt the cross-linking mechanism a little (comparing 88% and 99% hyd. cross-linked material), and to a first approximation this can be attributed to the cross-linking mechanism requiring an alcohol group to work.

5.5 Further work

Given the methodology developed in this work it would be good to attempt an increase in performance of the spin-coating deposition method. This could likely be achieved by seeking a solvent which readily dissolves the cross-linking molecule, but which only sparingly dissolves PVA. By this the substrate should not be unduly damaged and yet will be able to swell slightly to absorb cross-linking molecules into the surface layer to allow the cross-linking reaction in this region. Alternatively another method could be trialled in order to overcome some of the limits of spin-coating. Spraying on of a solution of the cross-linker (in a non-solvent for PVA) is one possibility as this removes the problem of loss of cross-linking molecules as a result of centrifugal forces during spin-coating.

As stated previously it appears that as a cross-linker of 88% hydrolysed PVA maleic acid is limited, in that it is likely that it only cross-links via the alcohol groups. As such alternative cross-linkers could be sought which would act on both the acetate and hydroxyl moieties - hopefully raising the insolubility to that of cross-linked 99%

hyd. PVA.

It would be helpful to establish the depth to which samples are cross-linked by the various methods trialled in this work. Secondary Ion Mass Spectroscopy (SIMS) is one way of doing this (with the deposited species containing deuterated hydrogen or ^{13}C). Performing a scan would then reveal the depth to which the surface treatment procedure has penetrated. NanoSIMS would allow the mapping of the species in the plane of the surface to measure the uniformity of the treatment. Alternatively a cross-linker with a fluorescent marker could be used and then a cross-section imaged using X-ray fluorescence spectroscopy. However neither of these techniques would be able to determine whether a chemical bond had actually formed between the cross-linker and the PVA.

An alternative means to deposit maleic acid onto the surface of PVA would be to first melt the solid maleic acid and then deposit it in liquid form (to give an even coating, via dip-coating or otherwise). The melting point of maleic acid is 139°C , and PVA is stable for short periods at this temperature. (It should be noted that the T_m of maleic anhydride is around 54°C , hence from a processing point of view this might be even more favourable.) However this might also suffer from the same problem of the need for the PVA to absorb the cross-linker a little to ensure enough material is cross-linked to noticeably impact on the solubility.

It would also be interesting to perform annealing experiments on 88% hydrolysed PVA and then assess the resulting impact on bulk solubility in cold water. This is because most existing work considers 99% hydrolysed PVA, which only swells in cold water. 88% hydrolysed however is fully soluble, however it is reasonable to suggest that the extra crystallinity induced by annealing would decrease the dissolution rate and this would be useful information to have for further analysis of the cross-linking procedure used in this work.

Chapter 6

Surface crystallization

6.1 Literature recap

Semi-crystalline polymers were discussed in section 2.2. There it was noted that crystalline and amorphous phases have different properties, with the property of solubility being of particular interest in this work. It is considered by many authors that crystalline regions are insoluble, or at the very least that the kinetics of dissolution is such that they take an added time-scale to dissolve (as a result of the chain unfolding processes required) when compared with amorphous regions [105].

Numerous authors have also reported a decrease in the T_g at a polymer's surface, and a resulting increase in crystallization at the surface for the case of some semi-crystalline polymers (see section 2.2.3).

To date very little data has been reported on the surface behaviour of PVA. Zhang *et al.* induced surface alignment of polymer chains by rubbing [193] and they then trialled the technique on PVA [194]. They produced alignment of the chains, and the aligned material was subsequently found to partially relax as the T_g was approached upon sample annealing; although no comment was made as to the surface crystallinity of the sample. Similar rubbing experiments were performed by Damman *et al.* on PET and PEKK [57].

6.2 Hypothesis

Although there is no clear evidence of it being documented in the literature to date it is reasonable to suggest that PVA will have a lower surface T_g compared with the bulk T_g . This is because the effect is a fundamental phenomenon associated with long macromolecules and it has been observed in other polymers. Given also that PVA is semi-crystalline it is possible that we will be able to produce crystals on the surface prior to producing them in the bulk (if annealing conditions are correct). The size of this ‘window’ (wherein surface crystals grow and bulk crystals do not) also has to be established and of course it needs to have a range at least the size of the temperature resolution of the experimental setup in order for surface crystals to be independently observed.

Thus it can be hypothesised that upon annealing for long enough at a temperature below the bulk T_c of a sample we might be able to induce the formation of surface crystals.

6.3 Method

Thin films of PVA were produced, principally by spin coating from a solution onto silicon and glass substrates. Only PVA of degree of hydrolysis 88% and molecular weight 85k-124k was used in this chapter.

6.3.1 Thin film production

Solutions of PVA in water were prepared in the usual manner by dissolving PVA powder at a concentration of 5wt%. Silicon and glass substrates were then prepared by first cutting them to shape and secondly cleaning the surfaces by use of an air-duster. 200 μ l of the PVA solution was then deposited onto each substrate piece

before they were spun at 3000rpm for a period of 30 seconds (with an acceleration of 1000rpm/s). The spin coater used was a Laurell WS-650SZ-6NPP and it was operated with a nitrogen purge gas.

Films produced in this manner were measured for thickness using a Veeco Dektak 6M Stylus Profiler and were recorded as being 300nm thick (to 1 s.f.).

6.3.2 Ex-situ annealing

Spun cast films were then processed via two routes, the first being *ex-situ* annealing. Samples were placed in a thermostatically controlled oven or on a hotplate for a set period of time (between 20 minutes and 4 hours) at temperatures ranging from 40 to 180°C. These samples were then cooled rapidly to room temperature by placing them on a cold metal block. By this it was possible to assess the impact of both annealing time and temperature on any resulting surface structure.

6.3.3 In-situ annealing

The second processing route was to take a spin-cast film of PVA and simultaneously anneal it and image it using the AFM. This relied on the construction of a heating stage, the schematic of which is shown in figure 6.1. The films were placed on the heating stage (in contact with the carbon sticky pads) and then a power supply was connected to the heating element to provide a voltage across it. The supplied voltage was correlated with a temperature by annealing low melting point metals and using their melting points as reference points.

The benefit in using such a stage is that in principle it allows the repeated imaging of the same area of a given sample as a function of temperature.

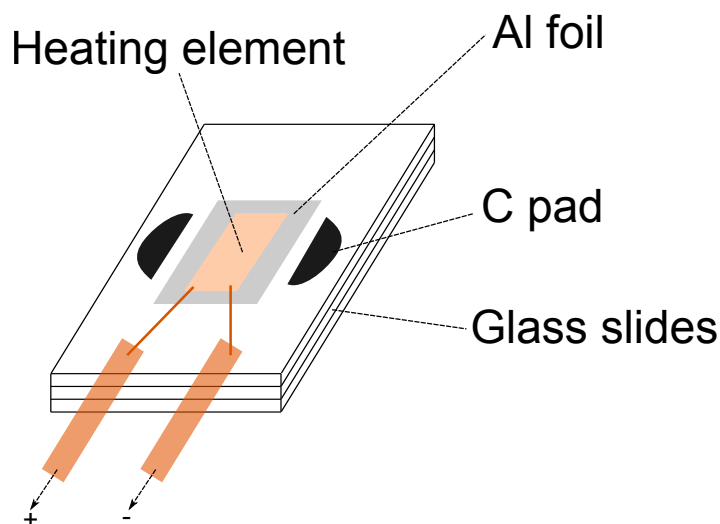


Figure 6.1: Diagram of custom made AFM heating stage

6.3.4 Force-distance AFM

The AFM was also operated in force-distance mode. In this mode the cantilever is not scanned across the surface but is instead probed into and retracted from the surface at a single point [48]. By this the mechanical properties of the surface can be measured. In addition the T_g can be determined by observing changes in the viscoelastic response which occur as a result of passing from the glassy to rubbery state.

To obtain the force-distance measurements the AFM was operated with a force constant of 30nN, and cantilevers with a stiffness of around 4.5Nm^{-1} (minimum 3.5Nm^{-1} maximum 8.5Nm^{-1} according to the manufacturers' specification) were used. The cantilever was oscillated at a frequency of 1Hz. For each sample examined an area was probed repeatedly until the force-distance data produced was stable, a single indent and retract was then recorded. At least four more representative areas on each sample were recorded so that average gradients produced were of at least five runs.

6.4 Results

The majority of the sample analysis was performed using an AFM since it is an excellent tool to map the topography of a polymer surface, and its resolution is ideally suited to the features of interest. Complimentary techniques in this work include XRD, DSC & FTIR .

6.4.1 AFM

The AFM was operated in non-contact tapping mode. This enabled imaging with negligible damage to both the samples and tips used. The topography feed proved the most useful, as it illustrated most clearly the differences between crystalline and amorphous regions. The phase and error feeds were also collected though these did not usually yield any extra information.

The AFM images were processed using both WSxM and Gwyddion (as mentioned in section 3.6). Typically images were treated by removing a polynomial background (of degree four) to account for the non-planarity of the surface and then by removing surface scratches (typically arising from artefacts causing a whole line on the image to be damaged).

6.4.1.1 Topography

Topographical images were recorded of samples annealed at various temperatures and comments on the resulting surface structures observed (with regards any surface crystallization) are shown in table 6.1. It can be seen that both the annealing temperature and time have an impact on the resulting surface structure with the temperature being the more significant variable of the two.

Table 6.1 suggests that there is a range of temperatures (roughly between 60 and 140°C) in which surface crystallization takes place. Beyond this temperature the

Annealing temperature (°C)	Annealing duration		
	20mins	2hrs	4hrs
40°C	n/a	Poor images	n/a
60°C	Nucleation	Nucleation	Nucleation
80°C	Growth (sparse)	Growth (sparse)	'Needle' growth (prolific)
100°C	Growth (frequent)	Growth (prolific) & nucleation	'Needle' & normal growth (prolific)
120°C	Growth (prolific)	Growth (prolific)	Growth & fragmentation (prolific)
140°C	Some crystals	Some crystals	No surface crystals
160°C	Deformed crystals	No surface crystals	No surface crystals
180°C	n/a	No surface crystals	n/a

Table 6.1: Summary table of surface observations upon annealing. (n/a = not available)

surface crystals appear to break down (in a similar way as reported for PET [7]) and they are absent at the higher temperatures of 160 and 180°C.

The Root Mean Square (RMS) roughness values have been used as an indication of the presence of bulk crystals. This was found to vary with temperature (for annealing for 2hrs which had the most obvious crystalline morphology) as shown in table 6.2. The RMS peaks with the sample at 120°C. This is in contrast to that reported by Shinotsuka, who found that that RMS roughness increased significantly (almost an order of magnitude) as the surface crystalline morphology was thought to be replaced by bulk crystallization [7].

Annealing temp (°C)	RMS
60	0.63nm
80	0.82nm
100	1.52nm
120	2.37nm
140	1.26nm
160	0.70nm
180	0.32nm

Table 6.2: RMS as a function of temperature for annealing at 2hrs

Typical AFM images recorded for 2 hours annealing across the temperature range are shown following in figures 6.3 to 6.10.

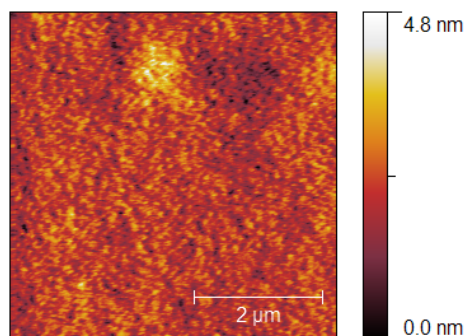


Figure 6.2: AFM image of PVA spun cast and kept at room temperature (topography image, tapping mode).

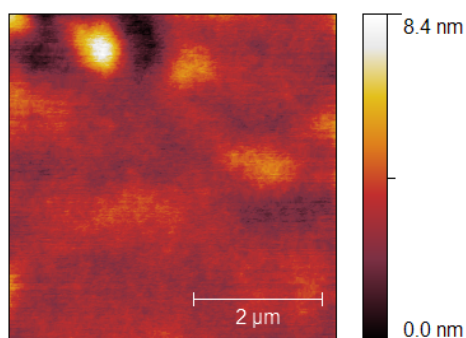


Figure 6.3: AFM image of PVA annealed for 2hrs at 40°C (on glass) (topography image, tapping mode).

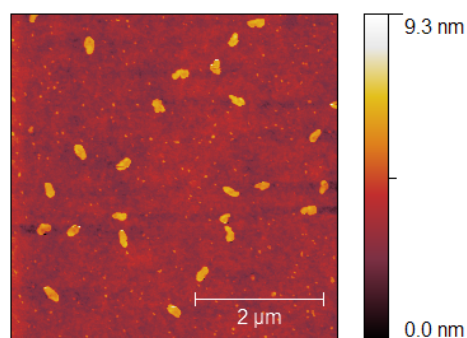


Figure 6.4: AFM image of PVA annealed for 2hrs at 60°C (topography image, tapping mode).

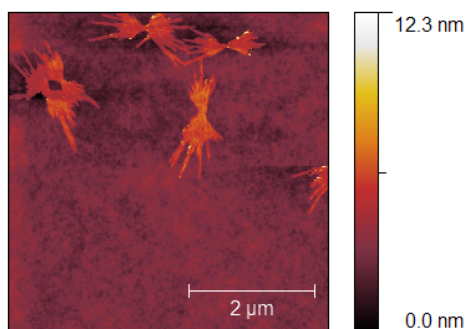


Figure 6.5: AFM image of PVA annealed for 2hrs at 80°C (topography image, tapping mode).

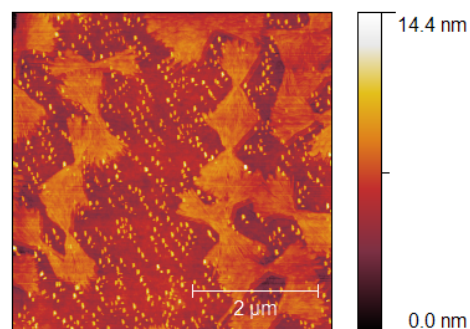


Figure 6.6: AFM image of PVA annealed for 2hrs at 100°C (topography image, tapping mode).

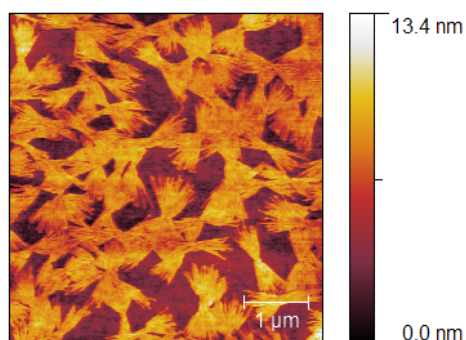


Figure 6.7: AFM image of PVA annealed for 2hrs at 120°C (topography image, tapping mode).

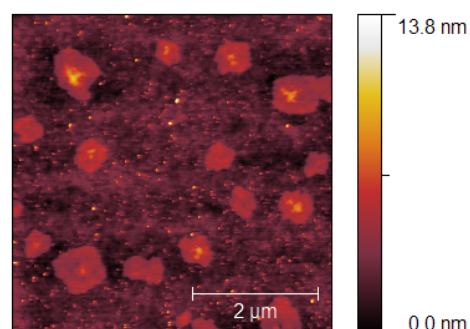


Figure 6.8: AFM image of PVA annealed for 2hrs at 140°C (topography image, tapping mode).

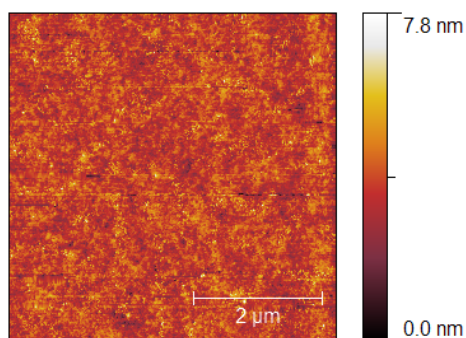


Figure 6.9: AFM image of PVA annealed for 2hrs at 160°C (topography image, tapping mode).

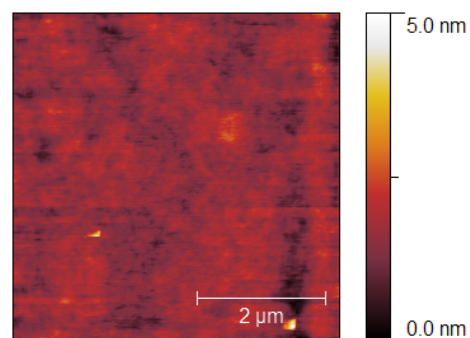


Figure 6.10: AFM image of PVA annealed for 2hrs at 180°C (topography image, tapping mode).

Other images of note include those taken after an extended period of annealing. Figure 6.11 gives an indication as to how the growth of surface crystals proceeds with time.

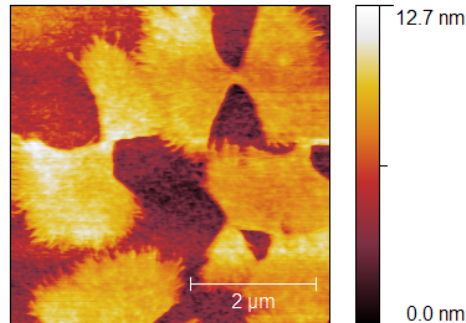


Figure 6.11: AFM image showing growth of surface crystals after annealing for 48hrs at 80°C (topography image, tapping mode).

In addition, figure 6.12 helps elucidate how crystals break down at higher temperatures, as whilst the ‘wheat-sheaf’ crystal shapes can be seen, there is also clear evidence of fragmentation of the crystals.

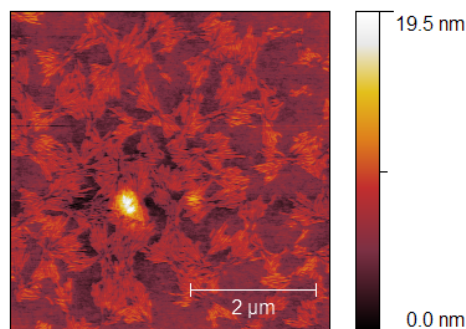


Figure 6.12: AFM image showing fragmentation of crystals after annealing for 4hrs at 120°C (topography image, tapping mode).

Surface features

Figure 6.6 is reproduced here but the surface features have been labelled (figure 6.13). Such labelling is consistent with that seen elsewhere for the surface crystals [58].

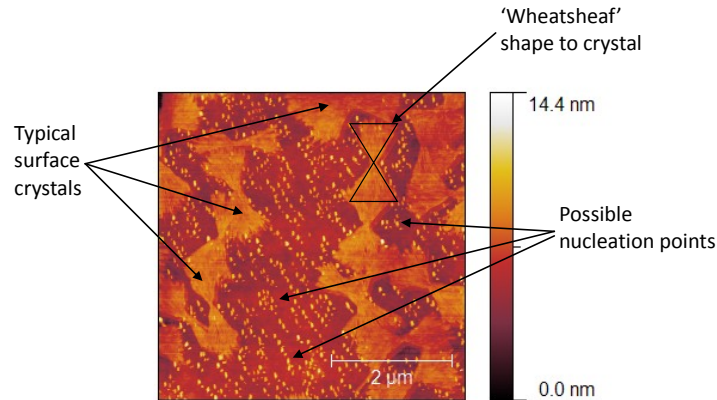


Figure 6.13: Topographical AFM image of PVA annealed for 2hrs at 100°C with surface features labelled.

Line profiles

Using the Gwyddion analytical software it was also possible to extract line profiles from the images to give an indication of typical surface cross-sections. A typical line-profile extract used to determine the example crystal volume protruding from the bulk surface is shown in figures 6.14 and 6.15.

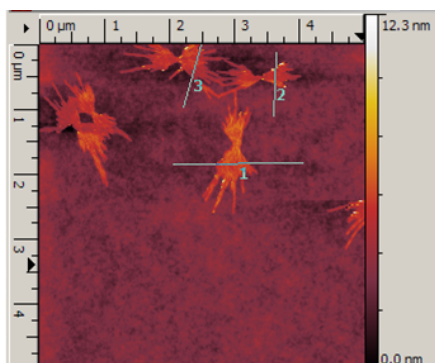


Figure 6.14: Line profiles extracted from figure 6.5.

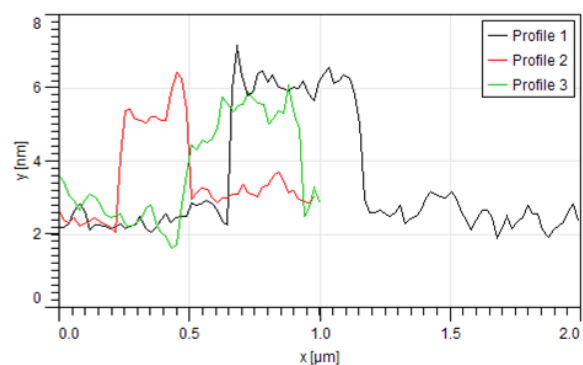


Figure 6.15: Line profile plot for figure 6.14.

For figures 6.5 to 6.7 three surface crystals have been considered and their protruding dimensions recorded in a similar way to produce table 6.3.

	Sample crystals					
	Crystal 1		Crystal 2		Crystal 3	
Annealing temp.	Width	Height	Width	Height	Width	Height
80°C	550nm	4nm	300nm	3nm	500nm	3nm
100°C	400nm	3nm	750nm	3nm	500nm	4nm
120°C	500nm	6nm	500nm	5nm	400nm	4nm

Table 6.3: Typical surface crystal dimensions observed upon annealing.

Thus from this brief analysis it can be concluded that typical surface crystal protruding dimensions are 500nm wide and 4nm high (both to 1.s.f). It can also be concluded that the the size and height vary little with temperature, with perhaps a slight increase in height for the higher anneal temperature samples.

Heating stage

As detailed in section 6.3.3 samples of PVA were simultaneously imaged and annealed in the AFM. However this technique proved difficult to work in practice, and as such the results are of a somewhat disputable quality. The main barrier to imaging was image stability, namely it was often very difficult to obtain any meaningful image due possibly to several factors.

Firstly there is the issue of thermal expansions, as displacements of the sample due to thermal expansion can be large compared with the tip-sample distance. Thus tip 'drift' away from the sample surface was often observed upon increasing the sample temperature. This necessitated a re-approach and as such it was impossible to maintain the same imaging area across a temperature range.

Secondly interference was often more prevalent at higher voltage readings, leading to the belief that electromagnetic interference was also taking place. This was minimized by improving the power supply quality and also by more thoroughly shielding the supply cables to the stage; however it still proved difficult to image anything beyond 90°C.

Typical images obtained at various temperatures are shown in figures 6.16 to 6.19.

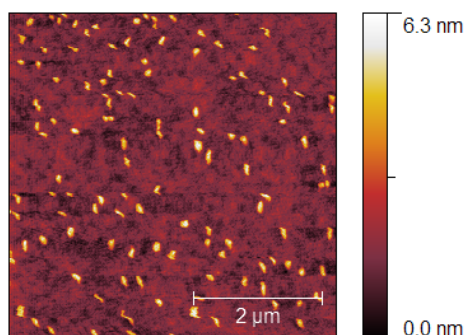


Figure 6.16: AFM image of PVA annealed at 60°C for 30 minutes using the *in situ* heating stage (topography image, tapping mode).

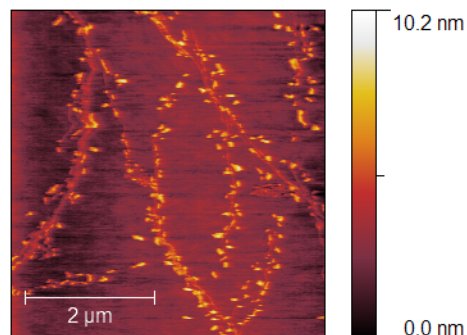


Figure 6.17: AFM image of PVA annealed at 70°C for 30 minutes using the *in situ* heating stage (topography image, tapping mode).

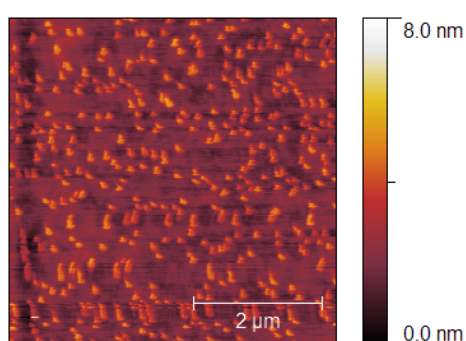


Figure 6.18: AFM image of PVA annealed at 80°C for 30 minutes using the *in situ* heating stage (topography image, tapping mode).

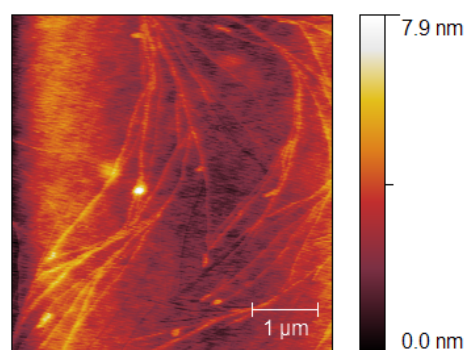


Figure 6.19: AFM image of PVA annealed at 90°C for 30 minutes using the *in situ* heating stage (topography image, tapping mode).

Figures 6.16 thru 6.19 have been processed to remove polynomial backgrounds and individual lines which were previously scratched have been fixed by converting them to the average topography of the neighbouring two lines. From these images it can be seen that there is some evidence of nucleation occurring on the heating stage, in a manner similar to that seen in ex-situ annealing at 60°C. However there is a lack of any evidence of crystal growth at the higher temperatures, as would be expected based on the ex-situ images.

The time of annealing can be eliminated as a possibility as ex-situ annealing for short periods of time (20mins) has yielded clear evidence of surface crystals, and this is a shorter annealing time than the attempts with the in-situ heating.

The samples were regularly imaged during the in-situ annealing in an attempt to monitor any surface changes as a function of time. It is a possibility that tip-surface interactions could have disrupted crystal growth.

6.4.1.2 Force-distance curves

Force-distance curves were taken on samples annealed using the in-situ heating stage. The following interactions take place as the tip approaches and retracts from the surface (shown schematically in figure 6.20):

1. Probe approaches the surface.
2. Attraction felt as probe ‘feels’ outer orbitals from top atomic layer.
3. Repulsion as electrons repel.
4. Material deforms elastically and / or plastically.
5. Probe reverses and moves away from the surface.
6. Probe separates / leaves the surface.

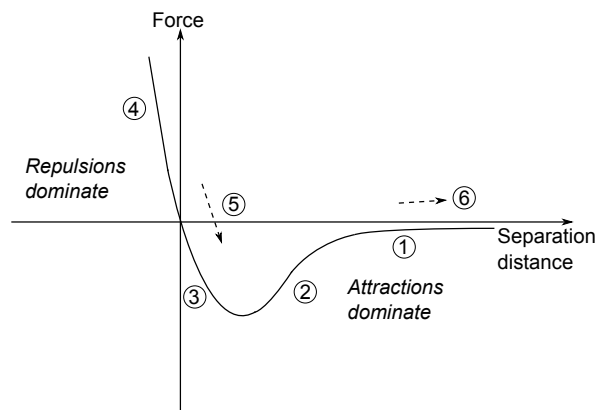


Figure 6.20: Force-distance curve for an AFM tip interacting with a sample.

If the surface has deformed in a purely elastic manner then the sample will recover to its original shape after the tip has left the surface. As such the approach and retract force-distance curves will be identical (excepting perhaps the pull-off point). The gradient of the force-distance plot can be used as a measure of surface stiffness. If however the sample has deformed viscoelastically at all then the two curves will differ depending on the time required for complete recovery. Of course the frequency at which the surface is probed can also have an impact, and in this work

all tests have been carried out at 1Hz. This means that viscoelastic effects occurring over a greater time could be hidden. Bliznyuk *et al.* produced the following useful diagram (figure 6.21) [48].

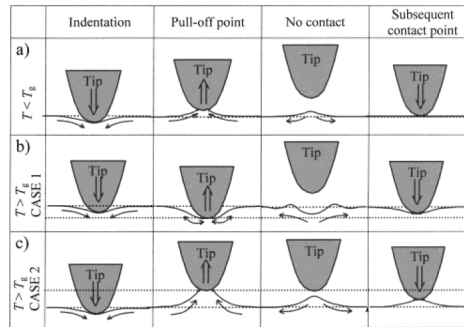


Figure 6.21: Diagram showing possible tip-surface interactions for both elastic and viscoelastic deformation, reproduced from [48].

By referring to cases b) and c) in figure 6.21 it is possible to appreciate how it is possible to leave the surface higher or lower in height after an initial indentation and retraction. Any resulting difference in height at which the probe makes / loses contact with the surface for its approach / retract can be a useful measure of the occurrence of any plastic deformation.

Three ways of assessing whether there is any viscoelastic deformation or not (hence indicating that the sample is around / above T_g) have been helpfully summed up by Bliznyuk *et al.* in figure 6.22.

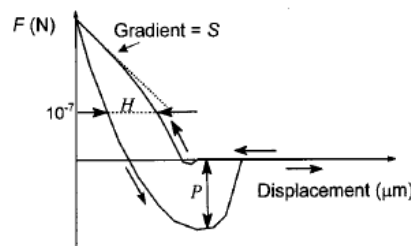


Figure 6.22: Three methods which can be used to determine surface plasticity, reproduced from [48].

Where H is the hysteresis width, S is the gradient and P the pull off distance (also defined by Tsui *et al.* [173] as $F_a d$).

Force-distance as a function of temperature

Force-distance data has been recorded at least five times for each temperature of interest. A typical data set obtained is shown in figure 6.23 for that obtained at 60°C.

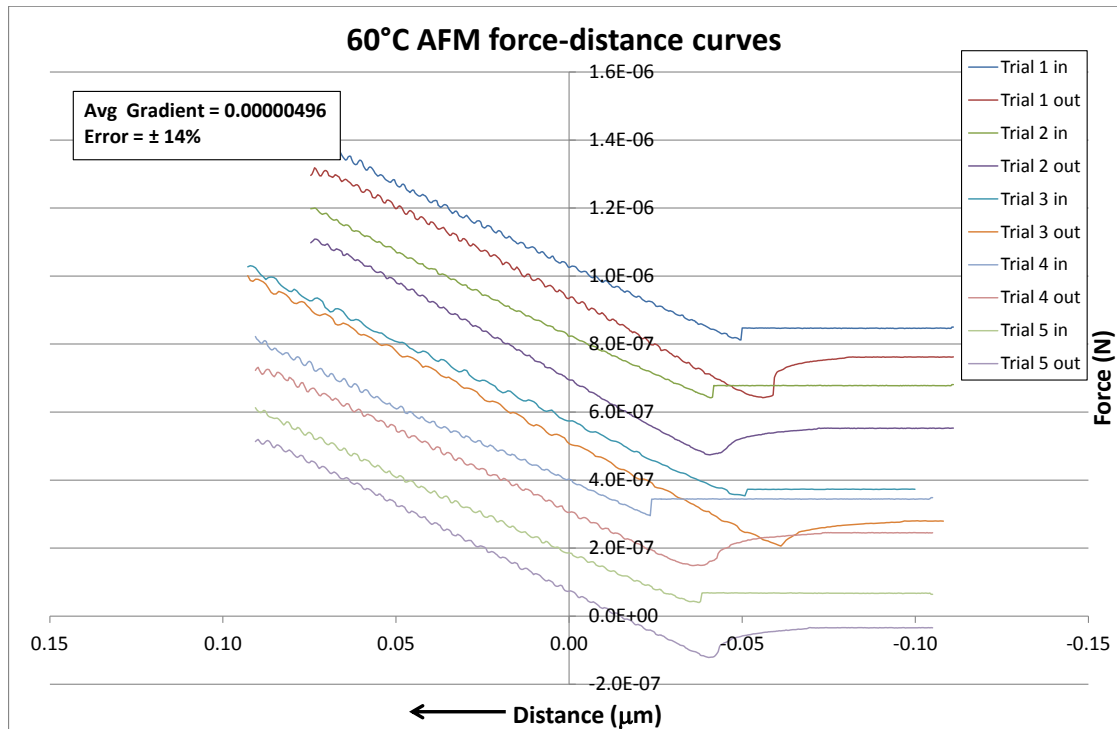


Figure 6.23: Force-distance data obtained at 60°C (curves shifted vertically for clarity, and x-axis plotted in reverse to correlate with figure 6.22).

The approach and retract curves take on characteristic shapes at the point of initial / last interaction with the surface respectively (figures 6.24 & 6.25).

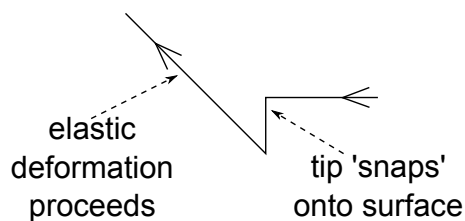


Figure 6.24: Approach curve schematic

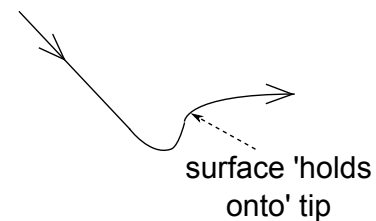


Figure 6.25: Retract curve schematic

The main difference between the two curves is that the retract profile shows a more gradual separation from the surface, whilst the approach one shows a more instantaneous 'snap' onto the surface. A change in the retract profile reveals a change in

the surface deformation mechanism, and this has been examined for the temperatures 20 to 100°C. For all cases it was found that the approach curve exhibited a sharp ‘snap-on’ whilst the retract profiles all showed a smooth retract profile. It is unlikely however that this is indicative of viscoelasticity, as expected other tell tale signs are not present.

Using 6.22 the pull off height and gradients have been examined for all the data collected. The pull-off heights were found to be roughly the same between samples at all temperatures (though these have not been accurately measured). This implies we have not gone through the T_g of the polymer, as an increase in pull-off height represents an increase in viscoelastic behaviour.

Figure 6.26 shows the average gradient (‘S’ in figure 6.22) for all of the data obtained. The error bars are twice the standard deviation for each data set of ten readings (five approach and five retract) and in each case the indentation force was 30nN.

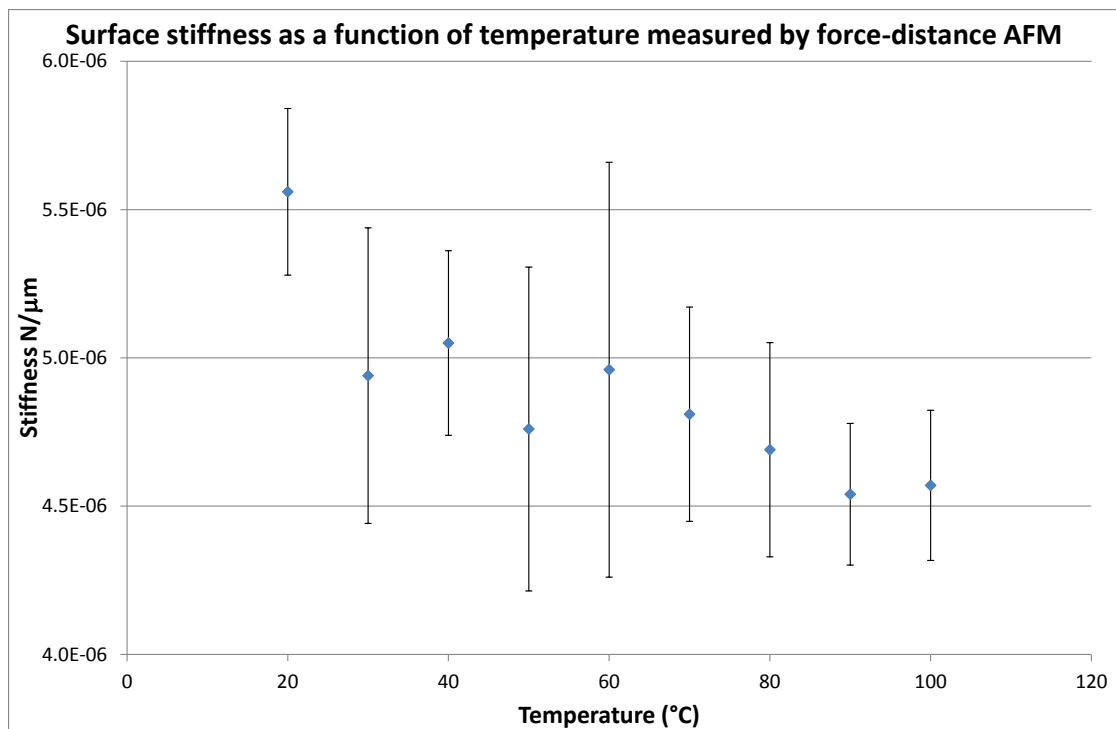


Figure 6.26: Summary of force-distance data obtained

The horizontal ‘snap-off’ displacement (as defined by Shinotsuka [7]) has been looked at for my samples, it was found to vary little with temperature, giving typical snap

off distances of $0.036\mu\text{m}$, $0.038\mu\text{m}$ & $0.022\mu\text{m}$ at 30, 60 and 100°C respectively. This is less than that which Shinotsuka recorded, whereby typical snap-off displacements were of the order of $0.5\text{-}1.0\mu\text{m}$ for PET [7].

6.4.2 Water vapour uptake

Based on the previously obtained AFM data free-standing PVA films were cast and subsequently annealed at 120°C for 2 hours (with the intention of producing a surface microstructure like that in figure 6.6, since this microstructure has the highest surface coverage and no crystal fragmentation). It was not possible to image these cast films with AFM as they proved too rough for analysis. The treated films then underwent the water vapour uptake test, the results of which are shown in figure 6.27. It can be seen that there was no overall improvement in the saturated vapour level, however the kinetics of vapour uptake have been improved (see figure 6.28 in particular) - with the readings up to and including 8 hours suggesting a slower water vapour uptake for the treated samples.

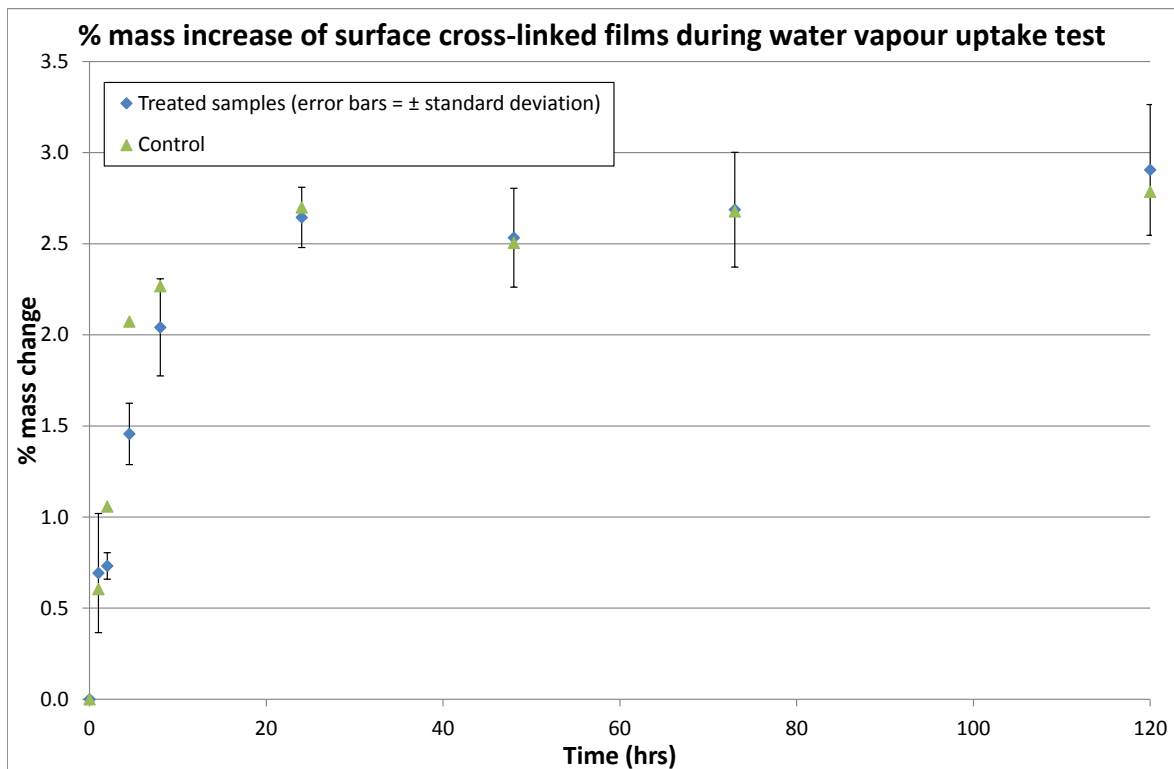


Figure 6.27: Water vapour uptake test for surface crystallized PVA films.

Diffusion exponents were calculated (as per section 3.4.2) and gave $n = 0.6$ for the surface crystallized sample and $n = 0.7$ for the control sample (as shown in figure 6.29). This tentatively suggests that the diffusion mechanism of the treated samples

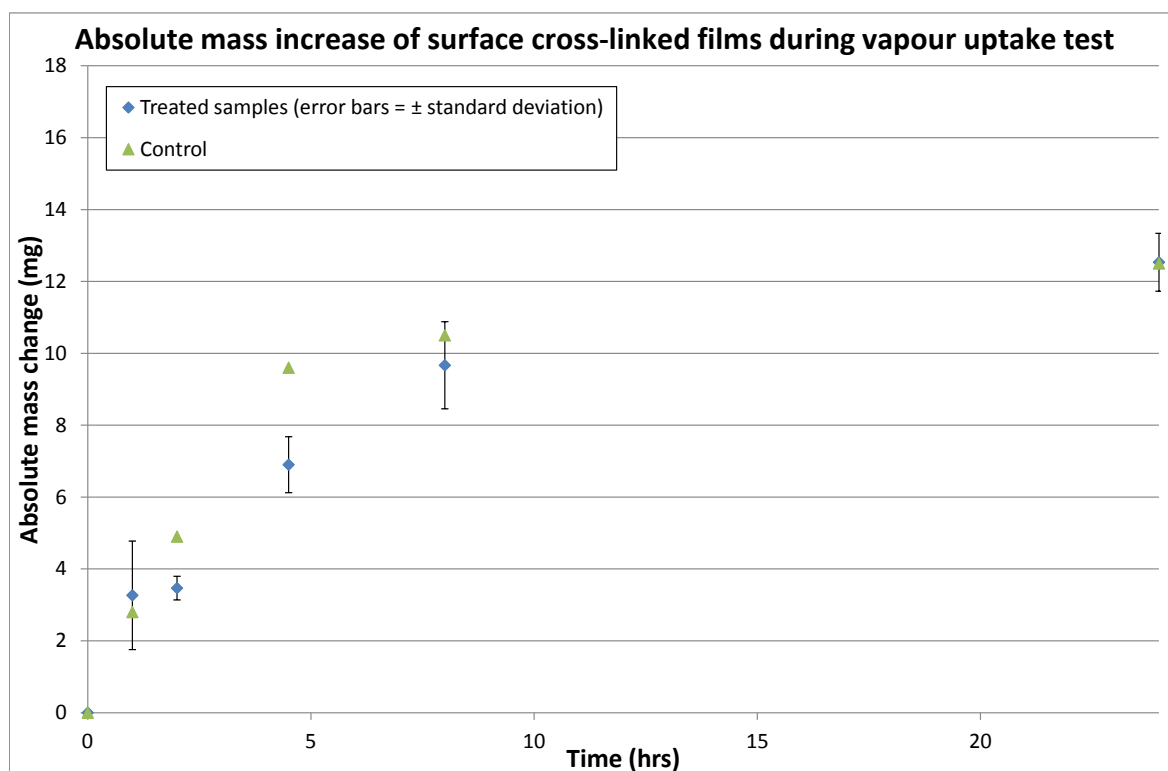


Figure 6.28: Water vapour uptake test for surface crystallized PVA films.

has been altered such that there is a greater resistance to solvent molecule diffusion.

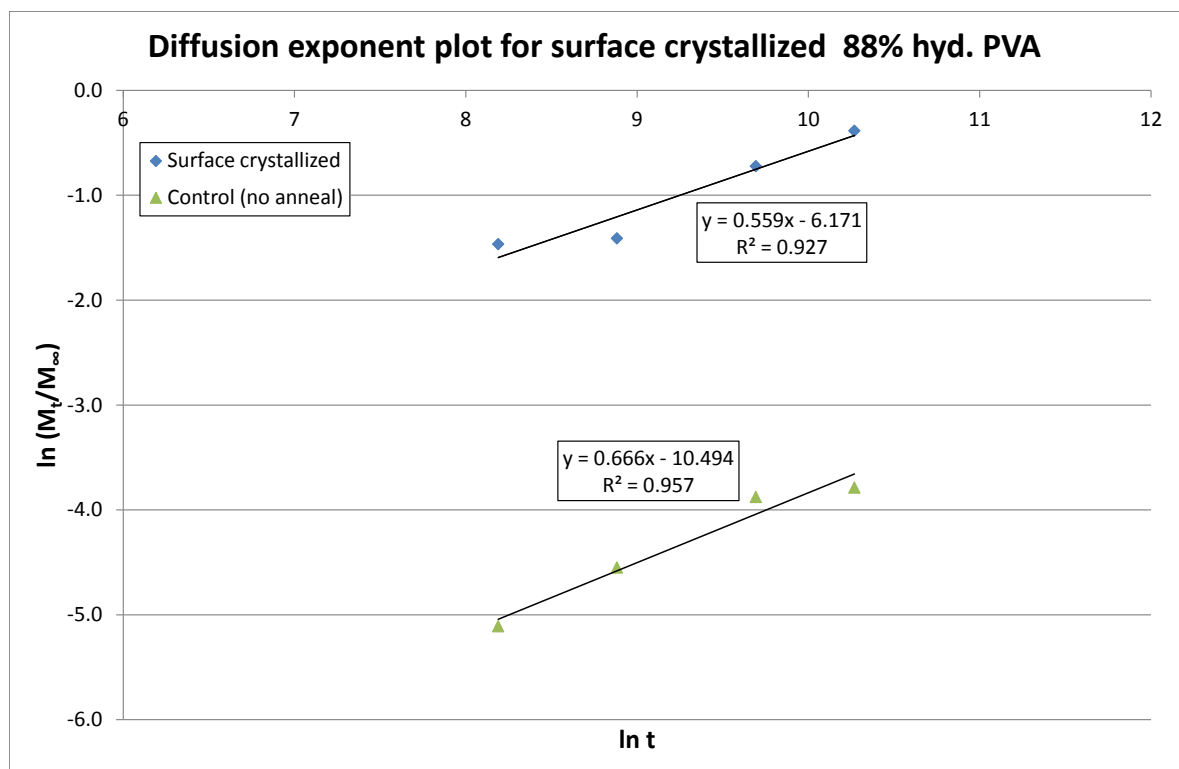


Figure 6.29: Diffusion exponent calculation plot for surface crystallized PVA.

6.4.3 XRD

XRD data has been obtained in order to assess the bulk crystallinity as a result of annealing, this will help distinguish the presence of surface from bulk crystals.

Initially the spun-cast films were run through the XRD, however they proved too thin to yield a signal. As such thicker ($\sim 100\mu\text{m}$ films) were solution cast, annealed at various temperatures for two hours and then successfully run through the XRD. A typical XRD data plot is shown in figure 6.30. Some plots showed a few very sharp peaks - these were ignored as they were a result of the blu-tack supporting the film or the aluminium sample holder producing a count.

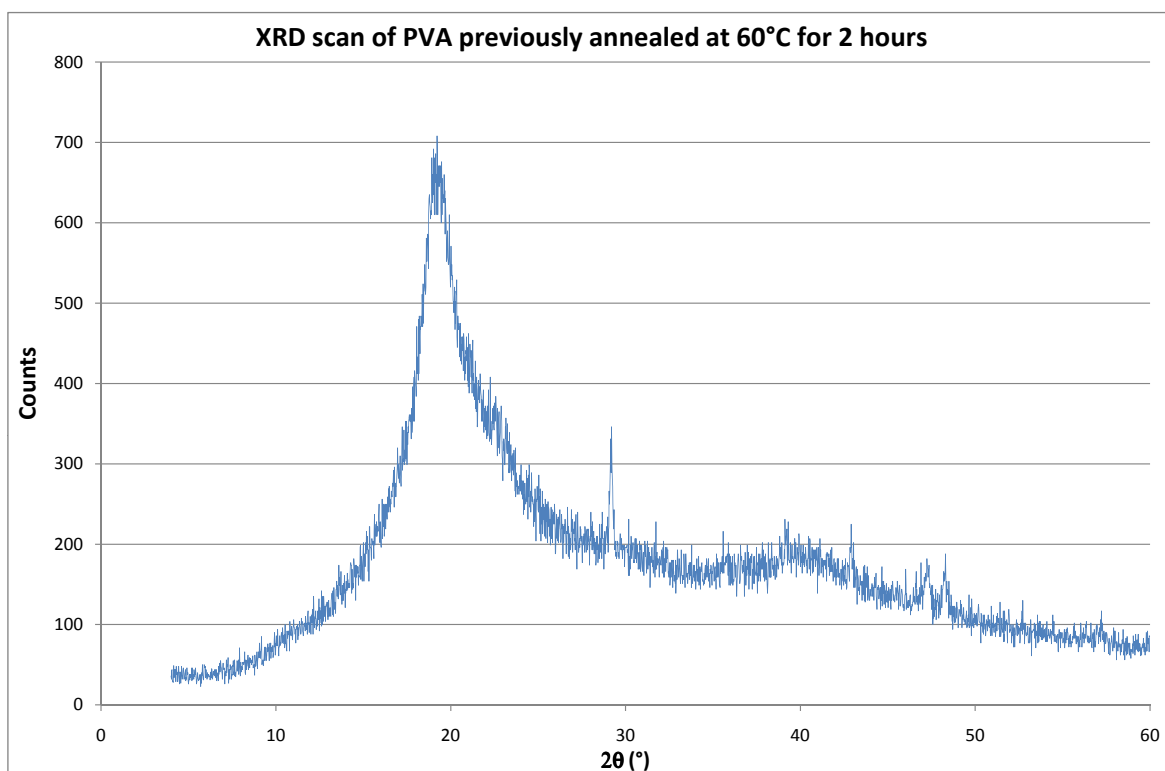


Figure 6.30: XRD spectrum of PVA annealed at 60°C for 2hrs.

Samples were also run at other temperatures up to and including 180°C. In each case the samples were scanned with a step size of 0.02° per second from 4 to 60°. Analysis of the data focussed on separating the crystalline and amorphous contributions to the spectrum count to give a percentage crystallinity value. There are two common

techniques for this, Gaussian and Lorentzian curve fitting; though no published work gives a physical justification for one method over the other.

Assender *et al.* [29] opted for a Gaussian curve-fit to assess the crystallinity, which they found to vary between 38 and 50%. In particular they examined the crystallinity in PVA ($\geq 99\%$ hydrolysed) as a function of annealing temperature. They observed four principal diffraction peaks in the data and attributed them to Bunn's assigned crystallographic planes [195] as follows: $2\theta \approx 16.1^\circ$ as 001; $2\theta \approx 19.4^\circ$ as $10\bar{1}$; $2\theta \approx 20.0^\circ$ as 101; $2\theta \approx 22.7^\circ$ as 200 [29].

Hodge *et al.* recorded XRD spectra of PVA swollen by varying levels of water. They showed a considerable error fraction in the crystalline fraction of their readings ($\pm 4\%$ - see fig. 2 in ref. [196]) and as such crystallinity readings determined from XRD must undergo sufficient repeat runs and / or be treated at such a confidence level of around $\pm 4\%$. Hodge *et al.* also used a simple equation, performing $X_C = I_C / I_T$ simply from the integrated crystalline and total intensities [196].

Factor *et al.* commented that it is sometimes possible to fit a Gaussian curve when the noise associated with the data would prevent fitting by any other method [197].

Therefore taking the previously published work into account a Gaussian curve-fitting procedure was subsequently selected. Ricciardi *et al.* [198] performed work which involved a highly crystallized sample of PVA, yielding peaks at 2θ values of around 11,16,19,20,23,32,40,42,47 & 50° . An amorphous halo was also fitted as a curve (albeit a much wider curve) by fitting it as best as possible to the region between 25 and 30° (where it is assumed that no crystalline peaks are present). The peak angle of the amorphous curve was allowed to vary to best fit the data; though it was typically best around 23° . These values for 2θ were then used to perform the curve fitting (an example fit being shown in figure 6.31). The calculated crystallinity values from this method are shown in table 6.4.

This compares favourably with the AFM data, as table 6.4 suggests that bulk crystallization begins around 160°C , and in the corresponding AFM images this was the

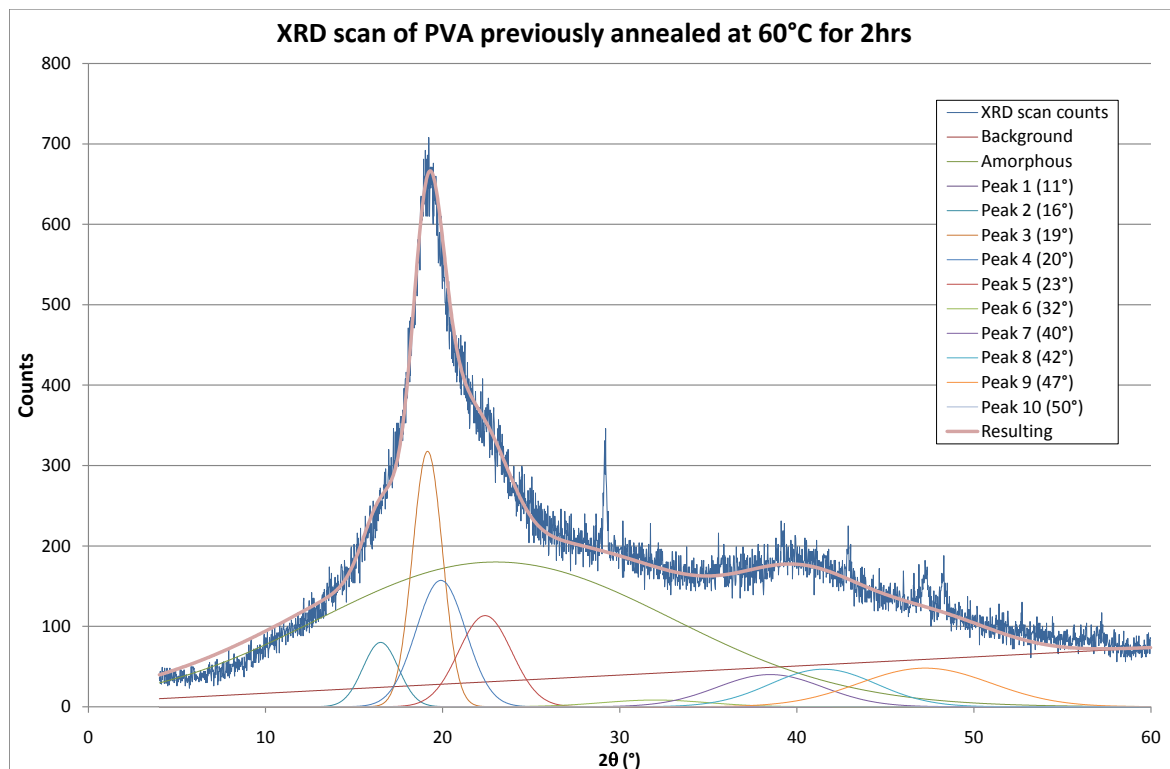


Figure 6.31: XRD spectrum of PVA after annealing at 60°C for 2hrs; Gaussian curve fitting.

Temp. (°C)	% crystallinity by Gaussian
Room temp	43
60	41
80	43
100	46
120	44
140	44
160	50
180	52

Table 6.4: Summary of crystallinity as determined by XRD and a Gaussian fit

temperature at which surface crystals were first no longer observed (possibly as a result of destruction by bulk crystals growing from within the film matrix). The DSC results are shown in section 6.4.4 and there it is reported that the onset temperature of bulk crystallization was 178°C. (The value being higher likely because the rate of crystallization is dependent on the temperature, and using DSC means the sample only remains at a given temperature for a brief time period - thus resulting in an apparently higher bulk T_c .)

6.4.4 DSC

DSC has been used as another means of determining the temperature for the onset of bulk crystallization for the samples used in this work (as there is minimal published data on 88% hydrolysed high molecular weight PVA). One previous paper of note is that by Galya *et al.* [175], where they found the T_g to be 69°C as measured by DSC (for 88% hydrolysed material with an M_w of 67k).

Samples were heated in an aluminium pan from 10°C to 220°C at 100°Cmin⁻¹, held for 1 minute at 220°C, quenched back to 10°C at 200°Cmin⁻¹, held for 1 minute at 10°C and then heated again to 220°C at 100°Cmin⁻¹. Typical data obtained is shown in figure 6.32.

The data was processed using PerkinElmer™ Pyris Software software and the internal 'peak search' function was used to detect the crystal peaks. This process was repeated on a further sample to yield an average crystallization temperature of 178 ± 2°C.

DSC can also be used to calculate the crystalline fraction of a sample, by integrating the area under the crystallization peak. However this is believed to be less accurate than calculating it via XRD [12]. Also the thermal energy required to melt 100% crystalline PVA is needed for this calculation [64] which was not available for partially hydrolysed PVA.

DSC scans showing the first (red) and second (orange) T_g and T_c for 88% hyd. PVA

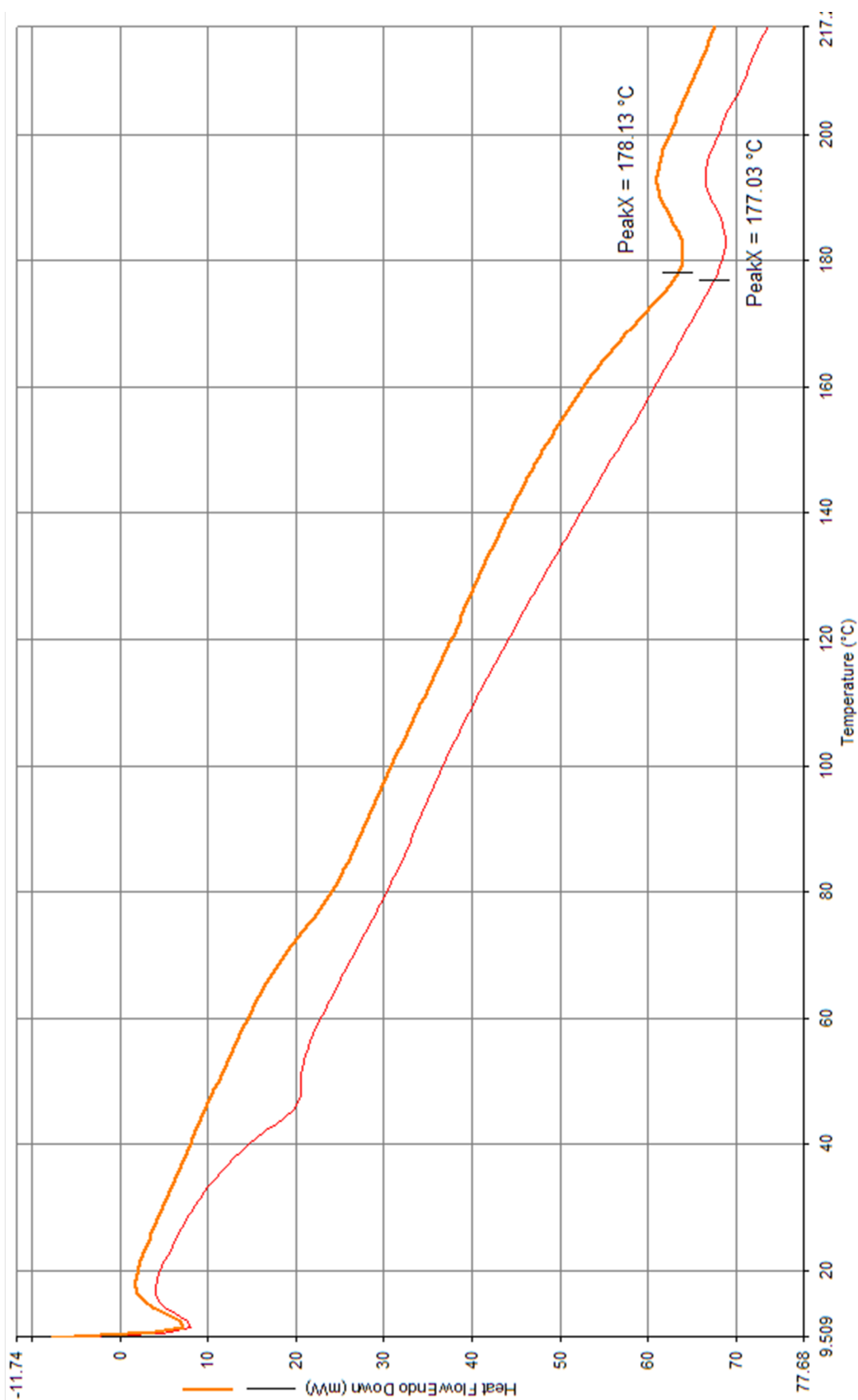


Figure 6.32: DSC scan showing the bulk T_g s and the bulk crystallization temperatures (both appear as 'dips' on the graph), the T_g being around 45 and 75°C for the first and second runs, and the T_c being near 180°C.

6.4.5 FTIR

It is also possible to determine crystallinity by using FTIR. This has been performed by several authors and is done by comparing the relative strength of two absorption bands, 1096 ± 5 and $1144\pm5\text{cm}^{-1}$, which are due to C-O bonds being in amorphous and crystalline phases respectively [8]. Several groups have all successfully used FTIR to study the crystallinity of PVA or a PVA -containing blended polymer [28, 32, 62, 63, 199].

Mallapragada *et al.* [64] gave more details on the use of the 1144cm^{-1} (1141cm^{-1} according to [64]) band to determine the crystalline fraction. They suggested that the 1141cm^{-1} band is due either to the C-C symmetric stretching mode or to a $\nu(\text{CO})$ mode of a portion of the chain. The method of crystallinity determination has been described in more detail by Peppas [168].

$$X(\%) = A \left(\frac{a}{b} \right) - B \quad (6.1)$$

Whereby A and B are coefficients calculated by calibration (obtained using known values of the degrees of crystallinity [64]); a is the height of the 1141cm^{-1} band; b is the height of the 854cm^{-1} peak (which was found to be constant up to an including an annealing temperature of 120°C by Mallapragada *et al.* [64]). This method works for data obtained in transmission mode.

Samples of PVA have been annealed for two hours at various temperatures, as for the XRD analysis. ATR mode spectra of the samples were then recorded and the results are shown in figure 6.33. A comparison of the absorption of the crystalline (1142cm^{-1}) and amorphous (1088cm^{-1}) peaks is made in table 6.5.

It can be seen that the 1142:1088 ratio increases up to and including 160°C , thus implying that the crystalline fraction is increasing up to this annealing temperature. To determine the fraction explicitly it is necessary to use the formula as stated by

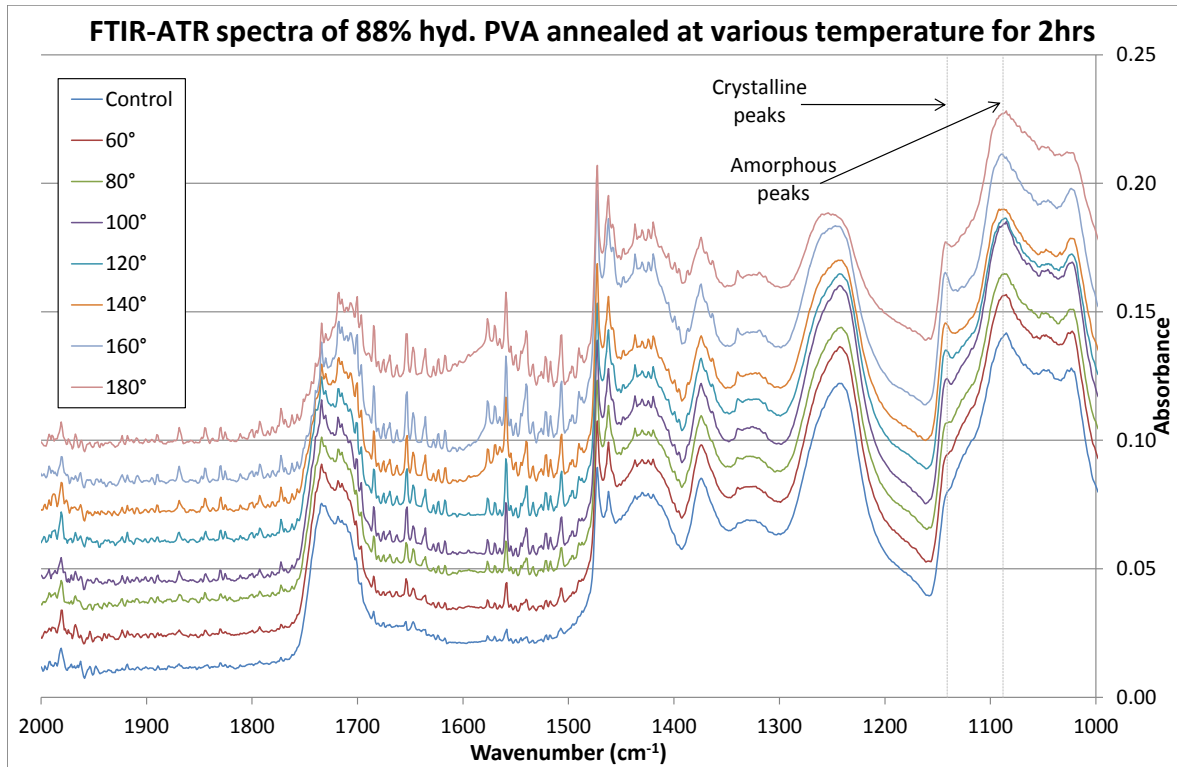


Figure 6.33: FTIR-ATR spectra of solution cast PVA annealed at various temperatures.

Annealing temp.	1142	1088	Ratio 1142/1088
room temp	0.0705	0.1318	0.535
60°C	0.0745	0.1367	0.544
80°C	0.0717	0.1298	0.552
100°C	0.0839	0.1451	0.578
120°C	0.0776	0.1289	0.602
140°C	0.0757	0.1199	0.631
160°C	0.0853	0.1313	0.650
180°C	0.0821	0.1321	0.621

Table 6.5: Comparison of crystalline and amorphous peaks

Peppas [168]. However this necessitates conversion from absorption to transmission (which can be done using equation 6.2). This method is not particularly useful for ATR data though as not only is it necessary to convert the individual peaks from absorption to transmission, but also the entire spectrum (to allow the necessary extrapolation to give the correct values of a and b [168]).

$$A = \log_{10} \left(\frac{1}{T} \right) \quad (6.2)$$

Another point to note is that the C-O crystalline peak might be influenced by the tacticity of the sample [200], though in this work it is not a concern as the tacticity of all the samples was the same.

The simplistic method of comparing relative peak intensities yields a different result to that of the XRD, in that the ATR data suggests an increase of crystallization up to and including 160°C, whilst the XRD suggests a steady level of crystallinity in the film until the annealing temperature reaches 160°C. It is possible that the ATR is being influenced by the growth of surface crystals (recalling the fact that it only samples the top μm or so of the film).

6.5 Discussion

The results obtained allow several conclusions to be drawn related to surface crystallization in PVA.

6.5.1 Surface crystals

Through the ex-situ annealing of thin films of PVA surface crystals have been successfully induced as evidenced by figures 6.2 to 6.12. The temperature of annealing appears paramount to the formation of crystals, whilst the length of annealing time impacts on the frequency and size of the observed crystals. Surface crystals were first observed at a temperature of 80°C and were absent at 160°C and above.

Annealing temperature (°C)	Annealing duration		
	20mins	2hrs	4hrs
40°C	n/a	0.92%	n/a
60°C	5.09%	3.33%	1.45%
80°C	10.59%	7.14%	28.39%
100°C	13.44%	40.01%	55.57%
120°C	59.64%	65.27%	39.78%
140°C	16.30%	14.66%	3.10%

Table 6.6: Surface crystal fraction given by AFM & Image J image processing software.

The shape of the surface crystals was that of a ‘wheat-sheaf’ seemingly growing outwards from a central nucleation point (as shown in figure 6.34).

This compares favourably with published data on the shape of PET surface crystals, as both De Cupere *et al.* (figure 6.35) [58] and Shinotsuka (figure 6.36) [7] report reasonably similar structures.

As mentioned previously (section 2.2) bulk crystal growth is often analysed by an

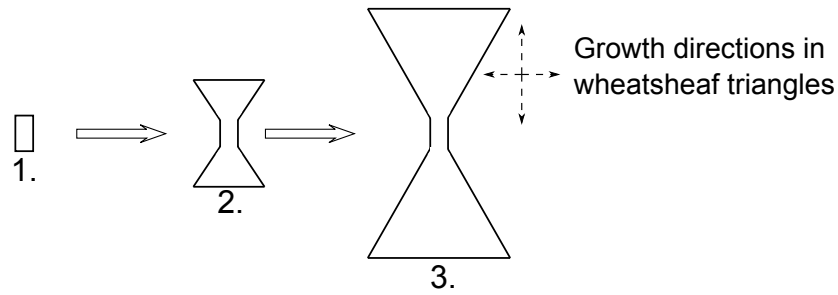


Figure 6.34: Schematics of surface growth into wheatsheaf shaped structures.

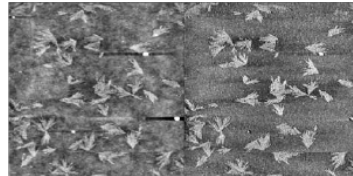


Figure 6.35: Figure 8a taken from reference [58].

Avrami analysis. Instances of surface-crystals being analysed in this way are fairly rare, nonetheless such an effort has been made to perform such an analysis here.

Cowie helpfully lists the Avrami exponent as a function of the morphology of a growing crystal [24] (see table 6.7).

Growth unit	Avrami exponent n
Fibril	2
Disc	3
Spherulite	4
Sheaf (3D)	6

Table 6.7: Avrami exponent as a function of crystal morphology (reproduced from [24]).

Referring back to table 6.6 the Avrami constants for PVA can be calculated using the Avrami equation (given by Hamley [25] and others):

$$1 - X_r = \exp(-kt^n) \quad (6.3)$$

(X_r = fraction crystallized, k = rate constant), which then rearranges thus:

$$\ln[-\ln(1 - X_r)] = \ln k + n \ln t \quad (6.4)$$

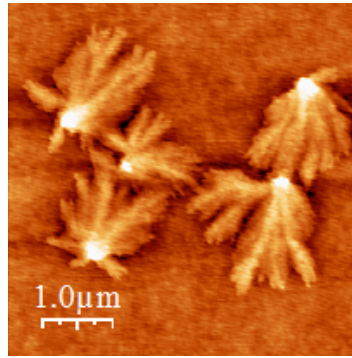


Figure 6.36: AFM topographical image of 680nm thick PET annealed for 2hrs at 75°C taken from [7]. Reprinted with permission from K. Shinotsuka.

Thus plotting $\ln[-\ln(1 - X_r)]$ vs $\ln t$ yields the exponent ' n ' and the constant ' k '. This has been done for annealing at 60,80,100,120 & 140°C. (In using this equation it should be noted that according to Maffezzoli *et al.* [201] X_r is the degree of crystallinity as a fraction of the maximum possible value, which has been set to 100% for the purpose of simplicity.)

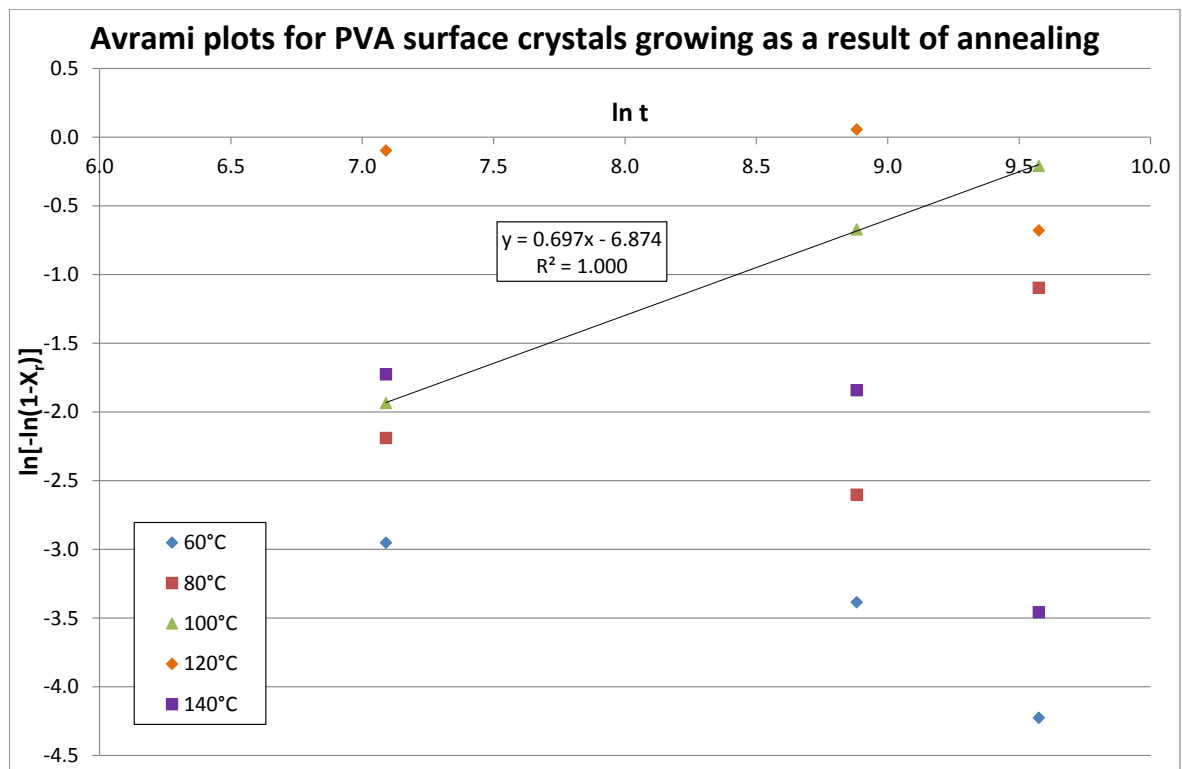


Figure 6.37: Graph showing Avrami growth exponent data for PVA annealed at various temperatures.

Unfortunately the data is not robust enough to produce good values of n and k ; the lack of multiple areas analysed and a certain amount of human subjectivity in the ImageJ image analysis being the primary cause of the discrepancies. The only

temperature at which a good fit was produced was for 100°C, whereby n is 0.70 and k is 1.04. At 60°C and at 80°C (for short times) the X_r is dominated by nuclei, whilst at temperatures above 100°C (for long times) X_r drops, possibly as a result of the onset of bulk crystallization. Thus for the case of surface crystallization the Avrami analysis seems to hold only for crystal growth in a relatively narrow temperature window.

We would anticipate a low value of n (as tentatively recorded) as the growth is in one dimension, but as mentioned further repeat runs and more automated analysis will help improve the reliability of the recorded values of n and k but the question must also be asked as to whether or not the Avrami analysis is suited to surface-specific crystal growth.

Surface and bulk crystals

It is interesting to compare the recorded values of surface and bulk crystallinity as a function of temperature as shown in table 6.8. Significant crystal growth is seen approximately 60°C lower for the case of surface crystals cf. bulk.

Annealing temp.	Bulk crystallinity (by XRD)	Surface crystallinity (by AFM)
60°C	41%	3%
80°C	43%	7%
100°C	46%	40%
120°C	44%	65%
140°C	44%	15%

Table 6.8: Comparison of surface and bulk crystallinity as a function of annealing temperature.

It should be noted that pre-existing crystals are present in the solution cast films as a result of the casting process, whereby the solvent is evaporated slowly enough such that crystal formation is possible. However it can be deduced that growth of surface crystals does not occur during solution casting - else they would be visible in the room temperature AFM images. This could be because for the bulk case crystallization is possible in any direction, whilst for the surface case it is restricted to growth within the plane (along with the constraint that the bulk material must be below its T_g).

In addition for a drying film the surface is not stable; hence any crystals forming on the 'surface' would most likely end up in the bulk (except of course those forming right at the end of casting; though the rate of crystallization likely slows as the amount of solvent remaining falls).

Given that bulk crystals appear to grow from 160°C and that surface crystals are absent at 160°C it is likely that bulk crystallization is occurring and that as bulk crystals grow they absorb / amalgamate with the surface crystals. Shinotsuka reported such an effect for the case of surface crystals on PET [7]. However the RMS values and trend do not agree with that reported by Shinotsuka, PVA films are smoother, with RMS values all <5nm (table 6.2). Comparing the morphologies in both cases

it appears that in the case of PET the surface crystals grow into / merge with bulk crystals. Whilst for PVA the surface crystals do not seem stable and appear to break up as bulk crystals grow.

Crystal dimensions

The morphology of the observed crystals has now been discussed but what is also noteworthy is the fact that the crystals only protrude a few nms from the surface of the bulk film. Typical crystal protrusion dimensions have been determined by extracting AFM line profiles (as demonstrated in figures 6.14 & 6.15) leading to an average protrusion height of just 4nm to 1.s.f.

The regions adjacent to the crystals have also been analysed and have shown little evidence of any depletion region. This is in contrast to other authors. Reiter *et al.* mention the existence of a depletion region ahead of a growing crystal interface [202], whilst Ivanov *et al.* hint at a reason for this - in that due to the different densities between amorphous and crystalline material local depletion of material will occur [203]. On an AFM line profile the depletion zones should be apparent as being vertically lower than the surrounding material (Pearce *et al.* [204] reported this for PEO).

Crystal growth

It is possible to consider the crystal growth mechanisms at work for the growth of the surface crystals shown in this work. The most common theory for crystal is that proposed by Lauritzen and Hoffman. Hamley loosely defined the three crystal growth regimes of the theory which can be summarised as follows [25]:

- Regime I: Lateral crystal growth dominates, very little linear growth and very little new nucleation.
- Regime II: Further crystals form by the activation of new nucleation sites. Growth of existing crystals are no longer confined to a single monolayer. However growth in this regime is slower than nucleation.

- Regime III: Prolific nucleation, growth of crystals both laterally and linearly.

Further details on the Lauritzen Hoffman growth mechanism are given by Hoffman *et al.* [19] and Cheng *et al.* [21] (including a helpful diagram of the three regimes in figure 3 of [21]).

Considering figures 6.2 to 6.10 it can be concluded that different growth regimes operate at different temperatures. The first evidence of crystal formation is at 60°C and there nucleation is evident whilst growth appears slow - suggesting regime II is at work. At 80°C however regime I is more likely - as the crystals present seem well developed yet they are few and far between. At 100 and 120°C the data suggests regime III is at work - as the crystals are well developed and nucleation appears to be taking place across the surface.

6.5.2 Surface T_g

The AFM force-distance data is presented in section 6.4.1.2. The aim was to determine a surface T_g , however the data is unclear as to even roughly where the surface T_g is. It is possible that the surface T_g lies to the edge of the temperature range trialled, with a possible candidate being the change between 20 and 30°C (according to figure 6.26 which shows the biggest change between these temperatures).

However were this correct the samples above this temperature should appear to have rubbery properties but the AFM tip force-distance results do not show this. A possible cause is if the film substrate (silicon) is impacting on the PVA film by making it appear stiffer than it actually is (the PVA film being several hundred nms thick on top of the silicon). It is also conceivable that the surface crystallization processes could be affecting the force-distance curves.

In summary without further work it is difficult to conclusively state even an approximation for the surface T_g of PVA.

6.5.3 Surface and bulk T_c gap

Despite the lack of a firm conclusion on surface T_g a strong piece of evidence suggesting it is in fact a fairly low temperature is the presence of surface crystals. DSC & XRD show that for 88% hydrolysed (M_w 85k-124k) PVA bulk crystallization does not occur until 160°C or over, thus around 60°C hotter than for the onset of surface crystallization as observed in this work. This ‘window’ is large, though it is difficult to compare it with anything as there are very few instances in the literature of a similar investigation, the best example being that reported by De Cupere *et al.* for the case of PET, where they found the surface T_g to be 85°C and the bulk around 150°C [58].

A possible experimental cause of such a large T_c gap is to do with the moisture levels of the spin cast films (which were not measured). The spin cast films were all kept in ambient conditions during storage and analysis and as such it is quite possible that there would have been some retained moisture in the film. Water molecules act as a plasticizer in PVA [103, 205] and thus lower the T_g , thus being a possible cause for the colder crystallization.

6.5.4 Influence of spin-coating

As previously detailed spin-coating has been used to produce thin film samples. It is worth considering the effect that this process has on the resulting microstructure of the deposited material. Reiter *et al.* [206] sought to answer the question as to whether sample preparation plays a part in leading to the anomalous properties often observed in a thin polymer film (such as a lower T_g or an M_w independent dewetting process) [206]. In particular they discussed spin-coating and the fact that it results in polymer conformations far from equilibrium. They argue that in solution polymer chains are likely to be independent of each other, and that due to the rapid solvent removal in spin-coating the chains are not given time to interpenetrate fully with one another.

Electrospinning has some parallels with spin coating, and on electrospinning it has been commented by Yang *et al.* that most of the water evaporates rapidly during the deposition [2]. Whilst spin coating involves slower evaporation than electrospinning it is still reasonably quick. As such since Yang *et al.* [2] commented that electrospinning means there is no time for re-alignment / formation of crystals it is reasonable to suspect a similar situation for spin coating.

Qian discusses the influence of undercooling on crystallization. He comments that for the case of quenching from the melt to a glass and then subsequently annealing, crystallization begins at a larger undercooling compared with cooling directly from the melt [15]. We can apply the same reasoning to spin-cast samples, in that by driving off the solvent so quickly we are essentially quenching to the glassy state (though of course we are beginning from a dilute environment as opposed to a 100% polymer melt environment).

Considering this and Reiter's argument it is logical to deduce that the stored energy (as a result of quenching to a non-equilibrium microstructure) could provide a driving force to polymer motion at a lower temperature than the usual T_g and thus permit colder crystallization.

6.5.5 Influence of molecular weight

The molecular weight of a polymer impacts on the T_g (and hence the ease with which molecular motion may occur). As such reducing the molecular weight will probably make surface crystallization more likely. However according to Cowie [24] above a repeat unit number of ~ 300 the impact on T_g for most polymers becomes negligible, and given that the PVA used in this work has a degree of polymerization of over 1700 the M_w impact is of no concern.

6.5.6 Influence on solubility

Given the promising microstructure shown in figure 6.7 solution cast free standing films were annealed for two hours at 120°C and then assessed using the water vapour uptake test. As seen in figure 6.27 the saturated water vapour uptake level did not show any improvement (see figure 6.28), however the kinetics showed a slight improvement. It is likely that vapour is able to cross any non-crystallized area of the surface just as easily as in the non-annealed samples, however the crystallized areas likely hinder or block vapour transport, causing the net possible flux of the surface to fall. In this scenario, the saturated water content at long times would be very similar to the non-surface crystallized films as the underlying polymer is unaffected, and indeed this is observed.

6.6 Further work

Given the work presented in this chapter there are lots of opportunities for further work. One of the limits of studying surface crystallization with AFM is that the depth of crystallization from the surface and into the bulk is not determined. A means of overcoming this would be to study the treated films by using grazing incident x-ray scattering. Such measurements allows the incident angle of the X-ray beam to be varied - thus altering the penetration depth of the beam (between 10nm and 10 μ m [54]). Of course this would only produce the average crystal fraction as a function of sample depth (and would not reveal the size of individuals crystals). Nonetheless the typical individual size can be estimated as the surface 'wheat-sheaf' dimensions are stable (as shown by the AFM data in this chapter).

It has been concluded in this chapter that crystals have successfully been grown on the surface of a PVA film without affecting the bulk properties. However it is frustrating not to have yielded a confident value of the supposed reduced surface T_g . Thus a more rigorous analysis using force-distance AFM should be attempted

(principally by varying the indentation force and frequency).

The experiments detailed in this chapter could easily be extended to 99+% hydrolysed PVA. This would be an interesting avenue to pursue as it could yield data which would contribute to understanding on the impact of the acetate group on crystallization of PVA.

Chapter 7

Conclusions and Further Work

In this work a variety of modification routes have been investigated in order to help further research into the surface manipulation of poly(vinyl alcohol). Experiments centred mainly around 87-89% hydrolysed PVA which is the most soluble form (indeed it is readily water soluble) at room temperature [9]. This thesis examined a number of options and considered their level of success and the applicability of the various options for surface modification.

Chemical grafting

The first method trialled was that of grafting various species onto the surface of a PVA substrate. Phenylpyridyl diazomethane was successfully attached onto the surface of PVA utilising the relatively recent 'carbene insertion method' [181]. This method has the potential to allow for the introduction of other groups onto the surface of PVA, although it is slightly limited in that due to the onset of thermal degradation of PVA around 150°C the temperature of the reaction must be kept lower than what is optimum.

Further grafting was carried out using -trichlorosilane capped molecules. This mechanism of attachment is relatively well understood as a result of a substantial body of prior work by grafting onto silicon substrates. The attachment reaction occurs between the Si-Cl bonds and the hydroxyl groups on the surface of PVA to form

permanent covalent bonds. In this work it has been shown that the -trichlorosilane capped molecules have been deposited, however it should be pointed out that it is not certain whether the covalent reaction has taken place and there has also been a significant mass of excess material which has been deposited. The increased solvent resistance (through the degree of swelling and the contact angle data) suggest that the hydroxyl groups have been removed by the reaction as the surface has been made significantly more hydrophobic. Comparing the fluorinated and non-fluorinated attached groups strongly suggests that it is the presence of an attached group (rather than what specific group it is that is attached) which is key to reducing the surface solubility. AFM images of the treated surfaces also revealed an interesting morphology which is believed to result from the excess deposition (and likely agglomeration) of the graft species onto the surface.

Overall, grafting onto the surface of PVA shows good potential, with the data presented herein showing that it is a viable method for modification on the lab bench scale. The scope of potential graft species is encouraging giving the opportunity for subsequent investigations in several directions.

The natural next step following this work is to establish greater control over the deposited microstructure. As discussed earlier (see section 4.4.2) it is possible that a disordered configuration of the deposited graft species is in place, thus perhaps hindering the best possible solvent resistance for a given graft species. Repeating the procedure at a lower temperature would be the first step (section 4.5.2).

Given the findings that a non-fluorinated molecule gave almost the same solvent resistance as a fluorinated one it would be natural to attempt much shorter -trichlorosilane capped molecules to confirm that the hypothesis of hydroxyl removal being key to good solvent resistance still holds.

In addition it would be helpful to attempt to quantify the level of graft species on the surface, perhaps using XPS.

Surface cross-linking

The trials undertaken to induce surface-specific cross-linking have been partly successful. Bringing across an established bulk treatment for surface-specific use has not been without difficulty. For the case of using maleic acid to bulk cross-link PVA the experimental setup is straightforward; the cross-linker is mixed with the bulk polymer upon casting and is subsequently activated by annealing the film. The experimental difficulties arose when attempting to deposit the cross-linker molecules into the surface region of the film only (whilst simultaneously avoiding damaging the bulk PVA substrate).

It has been shown in this work that one possibility is via the use of spin coating. Two extremes have been presented, whereby in the first a good solvent for PVA was used, and a good level of cross-linker (concurrently with PVA) was deposited (although some substrate damage occurred) whilst in the second a non-solvent for PVA was used and no damage occurred however a negligible amount of cross-linker seems to have reacted with the polymer. Were the investigations with maleic acid to continue it would seem pertinent to find a balance between the two, by seeking a solvent in which PVA is sparingly soluble. As such the damage will be minimised but it will still be possible to swell the surface of the PVA a little, thus allowing cross-linker ingress, giving a surface-modified region.

The mechanism of cross-linking is accepted as that given by Gohil *et al.* [120]. The analytical techniques used in this work have not been able to determine conclusively whether or not it is correct, however given the body of other work on reactions of species with PVA it is safe to assume that the mechanism is as predicted [2, 108]. Nonetheless it would be helpful to confirm that it is the case, and also to establish what role (if any) the acetate groups play in the cross-linking.

An interesting point worthy of further consideration is that of the possibility of phase separation between maleic acid and PVA in the as-cast films. The issue of homogeneity of the blend has not been commented on by previous authors, yet the

AFM and DSC data in this work hint at a two phase structure. This is something which could be elucidated by performing more DSC scans and also by varying the maleic acid content of the films and recording the resulting AFM images. It is significant as if there is a maleic acid -rich and PVA-rich phase then it suggests a limit as to how much cross-linker can be present within bulk PVA.

UV induced cross-linking of PVA (using sodium benzoate as a photo sensitizer) has shown some promise however there are still fundamental issues remaining. It is not entirely certain whether there is an inherent limit with the method as to how deep cross-linking is able to proceed, though the results in this thesis suggest a surface-specific limit. This could of course be an advantage, however proper characterisation of such a depth along with control of the cross-link density within the modified region are both remaining goals.

Further work would focus on altering the power, frequency and exposure time of the films to UV radiation in order to try and establish relationships between these variables and the fraction of PVA samples cross-linked. Secondly it would be beneficial to perform an analysis of the cross-linking mechanism. Although Delville *et al.* [130] proposed several schemes for the photolysis of sodium benzoate no one has proved any of them conclusively, and an analysis (e.g. via mass spectrometry) of any species produced (and possibly diffused out) during the cross-linking would be extremely helpful.

An overall comparison can be made between the broad principles of using graft species or cross-linking to improve the surface solvent resistance of a film. From the results obtained in this work grafting is seen to be far more successful, as though cross-linking a film can render it insoluble it is often able to swell to a large degree - thus permitting the transport of solvent molecules deep into the bulk region of a film. If cross-linking were carried out to such a density that the potential for any swelling was removed then surface cross-linked films would likely perform to at least as good a degree as grafted films.

Surface crystallization

The data contained in chapter 6 presents strong evidence for surface-specific crystal formation in PVA. Clear evidence was presented of the onset of crystallization by around 60°C, with prolific crystal growth having occurred by 100°C. At such temperatures the bulk crystal fraction appears to be unchanged (as shown by XRD traces) whilst the AFM images show that the surface fraction increases far beyond the level of the bulk.

It is supposed that such crystals grow more easily at the surface owing to a lower surface T_g (due principally to the free volume available for conformational changes at the surface), however the experiments to characterise the surface T_g of PVA have proved inconclusive. More accurate AFM heating stage data could be obtained although it would be helpful to try and obtain the surface T_g via another means (e.g. ellipsometry [52]). In addition it would be pertinent to ascertain the pre-existing moisture level in the as-spun films (since any moisture has the potential to act as a plasticiser for PVA).

Surface crystallization did not occur in all areas of the film equally, suggesting that it begins as a heterogeneous nucleation process by some defect or otherwise on the surface. The crystals typically grew into a 'wheat-sheaf' type morphology, presumably due to preferential growth outwards (from the nucleation point) along an axis and then lateral dendritic growth from the main growth directions. Beyond a certain temperature and / or annealing time (typically around 140°C) the crystals began to fragment and breakdown. This is possibly as a result of bulk crystals developing from underneath and enveloping the surface crystals as they grow [7].

Given that films annealed for two hours at 120°C led to the formation of a high number of surface crystals such films were produced and their water vapour uptake assessed. Overall the saturated water vapour uptake was unchanged, however the kinetics of uptake showed a marginal improvement for the surface treated samples. Control of the crystal fraction within the surface layer will likely be the controlling

factor for improving solvent resistance. Also whilst crystals have been visible on the surface it is not immediately clear how deep such crystals are (as only $\sim 4\text{nm}$ protruded above the surface - see figure 6.15) and the crystal size will impact on the dissolution kinetics. An investigation of the whole typical crystal dimensions (possibly using SAXS) would be beneficial.

Other surface modification routes

Other possible routes for surface modification not examined in this work include layer-by-layer assembly, controlled heat treatments, γ -radiation, plasma ablation, electron-beam and bi-continuous coatings.

Degree of hydrolysis

A general feature of interest is the influence of the degree of hydrolysis. As stated partially hydrolysed (87-89%) PVA has been the most commonly used form in this work. The impact of this partial degree of hydrolysis is already thought to reduce the crystallinity compared with fully hydrolysed PVA [9]. However the presence of the acetate units is also possibly affecting the ability of PVA to accept graft chains and be cross-linked via species such as maleic acid. Further work could also repeat many of the experiments contained herein, but by varying the degree of hydrolysis a better understanding of the impact of the acetate portion could be obtained.

Industrial viability

The methods proposed in this thesis are currently at differing stages of industrial scale-up viability. Dealing firstly with the grafting method, at present this system is relatively slow requiring two days processing at room temperature. It is also limited in size since it is a batch (rather than continuous) process. If the graft molecules could be attached via a different means (i.e. not capping them with the -trichlorosilane groups) then they could potentially be attached via a quicker grafting route (e.g. plasma activation), though care would need to be taken to avoid substrate damage.

Surface specific cross-linking is a little quicker, however the treatment still requires two hours at 130°C to activate the cross-linking reaction (this is a result of the cross-linking chemistry chosen). The deposition of the cross-linking molecules has been possible by spin-coating however on a larger scale another deposition method such as spraying would be needed.

Surface crystallization appears to take place within 20 minutes at 120°C (see table 6.1) and nucleation happens spontaneously across the surface. This bodes well as scale up to a much larger film size should be straightforward - the film need only be given enough thermal energy and nucleation and growth will occur in a matter of minutes.

Chapter 8

Glossary

AFM = Atomic Force Microscopy

at% = Atomic Percent

ATR = Attenuated Total Reflectance (a specific form of FTIR measurement)

DCA = Dynamic Contact Angle analysis

DMSO = Dimethyl sulphoxide

DSC = Differential Scanning Calorimetry

eV = electron volt

FTIR = Fourier Transform Infrared Spectroscopy

IUPAC = International Union of Pure and Applied Chemistry

λ = Wavelength

M_n = Number Average Molecular Weight

M_w = Weight Average Molecular Weight

n-decyl = n-decyltrichlorosilane

MA = Maleic acid

M_n = number average molecular mass

M_w = weight average molecular mass

NMR = Nuclear Magnetic Resonance Spectroscopy

PDMS = Poly(dimethyl siloxane)

PE = Polyethylene

PEO = Poly(ethylene oxide)
PET = Poly(ethylene terephthalate)
PF-decyl = 1H,1H,2H,2H-perfluorodecyltrichlorosilane
PF-octyl = 1H,1H,2H,2H-perfluorooctyltrichlorosilane
PS = Polystyrene
PTFE = Poly(tetra fluoroethylene)
PVA = Poly(vinyl alcohol)
PVAc = Poly(vinyl acetate)
RH = relative humidity
RMS = Root Mean Square
rpm = Revolutions per minute
SFM = Scanning Force Microscopy
 T_c = Crystallization Temperature
 T_g = Glass Transition Temperature
 T_m = Polymer Melting Temperature
TGA = Thermogravimetric Analysis
XPS = X-ray Photoelectron Spectroscopy
XRD = X-ray Diffraction
wt% = Weight Percent

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