

All Dielectric Composites for Metamaterial Applications

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Abstract

This thesis describes my work on manufacturing of all dielectric polymer/ceramic composites for electromagnetic property customisation at microwave frequencies. Electromagnetic wave manipulation can be achieved with the help of transformation optics concept and metamaterials with desired permittivity and permeability properties. The use of all-dielectric metamaterials, in particular, offers a novel solution to broadband, low loss microwave devices.

In this work, polymer/ceramic composites were studied to provide materials with a wide range of permittivity that can be customised precisely by optimised manufacturing routes. Thermoplastic perfluoroalkoxy (PFA) and thermoset epoxy were mainly used as polymer matrices and ferroelectric powders such as barium titanate used as ceramic fillers. Different composite types were fabricated by spraying, casting and 3D printing, with each manufacturing method carefully studied to produce stable and uniform composite quality. The microstructures of these composites were examined by microtomy and SEM and the dielectric properties were assessed by impedance and waveguide measurements for different microwave frequency ranges.

Controllable dielectric constants from 3 to 18 with high accuracy in epoxy/BT composites were achieved at 12 - 18 GHz. These composites were then used to fabricate advanced microwave devices such as the power divider lens to demonstrate my capability of permittivity customisation. Simulations for these advanced applications were done in Comsol Multiphysics and were compared to the experimental results.

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Contents

1	Introduction	19
2	Literature Review	24
2.1	Metamaterials	24
2.1.1	Definitions of Metamaterials	24
2.1.2	Classification of Metamaterials	25
2.1.3	Applications of metamaterials	31
2.2	Nanocomposites with customised material properties	35
2.2.1	Physical connotation of permittivity	36
2.2.2	Mixing formulas for dielectric composites	42
2.2.3	Polymer Matrix	47
2.2.4	High dielectric constant fillers	53
2.2.5	Ceramic dielectrics	53
2.3	Processing of Polymer-Ceramic Nanocomposites	60
3	Experimental Techniques	70
3.1	Processing Routes	70
3.1.1	Spray Deposition	70
3.1.2	Casting	74
3.1.3	3D Printing	75
3.2	Characterisation Techniques	76
3.2.1	Characterisation of dielectric properties	76

3.2.2	X-Ray Diffraction	85
3.2.3	Particle size and electrophoresis analysis	86
3.2.4	Scanning electron microscopy	87
3.2.5	Fourier Transform Infrared Spectroscopy	88
3.2.6	Thermogravimetric/Differential Thermal Analyzer	89
3.2.7	Surface Profilometer	90
3.2.8	NanoFocus μ Surf	90
3.2.9	Rheometer measurements	91
3.2.10	Raman Spectroscopy	91
3.2.11	Wavelength-dispersive X-ray Spectroscopy	92
4	Dielectric properties of sprayed PFA/BT composite films at microwave frequencies	96
4.1	Introduction	96
4.2	Sample Processing	98
4.2.1	Materials	98
4.2.2	Suspension preparation	103
4.2.3	Spray deposition	107
4.3	Results and Discussion	110
4.3.1	SEM	110
4.3.2	Thermogravimetric and Differential Thermal Analysis . . .	114
4.3.3	Surface roughness	116
4.3.4	Dielectric measurements	118
4.4	Conclusion	122
5	Dielectric properties of Epoxy based block materials at high frequencies (12-18 GHz)	128
5.1	Introduction	128
5.2	Experimental	130

5.2.1	Materials	130
5.2.2	Sample preparation	140
5.3	Results and discussion	144
5.3.1	Permittivity measurements	147
5.3.2	Mixing rules	157
5.4	Conclusion	163
6	Advanced applications	170
6.1	Anisotropic Dielectrics	170
6.1.1	Introduction	170
6.1.2	Simulation	173
6.1.3	Experimental	174
6.1.4	Results and discussion	175
6.1.5	Conclusion	180
6.2	Power Divider Lens	180
6.2.1	Introduction	180
6.2.2	Experimental	183
6.2.3	Simulation	191
6.2.4	Results and discussion	195
6.2.5	Conclusion	203
7	Conclusions and Suggestions for future work	210

List of Figures

1.1	A ray tracing diagram showing how rays are diverted in the cloaking material contained in region $R_1 < r < R_2$ (the inner and outer radius of the two spheres) without 'seeing' the hidden object [1]	20
2.1	Four types of materials categorized by different ϵ_r and μ_r values: (1)double positive materials are the most commonly seen conventional materials; (2) epsilon negative materials, in which $\epsilon_r < 0$ and $\mu_r > 0$, include metallic compounds employed in plasmonics devices such as gold and silver; (3) double negative materials refer to conventional metamaterials with negative refractive index; (4) mu negative materials, in which $\epsilon_r > 0$ and $\mu_r < 0$, involve current loops [3]	26
2.2	A left-handed media sample made of copper split ring resonators and copper wire strips on fiber glass circuit board (picture taken from [9])	29
2.3	(A) A field line in free space with the background Cartesian coordinate grid shown. (B) The distorted field line with the background coordinates distorted. (Picture taken from [12])	32
2.4	2D microwave cloaking structure [14]	33
2.5	A rectangular slab of negative index material bends light to a negative angle with the surface normal according to Snell's law [10]	34

2.6	(a) Macroscopic illustration of individual control over ϵ and μ , by changing the volume fraction of nano particles with different electromagnetic properties such as ferroelectrics and ferrites (the red and blue dots) in the spraying suspension when building up the film thickness on the substrate during the spraying process as indicated in (b)	36
2.7	Sinusoidal voltage applied to a capacitor (picture taken from [18])	38
2.8	(a)Phase diagram for a perfect capacitor (b)Phase diagram for a lossy capacitor (picture taken from [18])	38
2.9	Time dependence of polarization (picture taken from [20])	39
2.10	Variation of ϵ' and ϵ'' with frequency (picture taken from [18]) . .	41
2.11	Dielectric relaxation (picture taken from [18])	42
2.12	Cole-Cole diagram of a dielectric material (picture taken from [18])	42
2.13	the unit cell of BaTiO ₃	55
2.14	unit-cell distortion of the polymorphs	56
2.15	(a)Dielectric constants along different axis ϵ_a and ϵ_c , as function of temperature (b)Spontaneous polarization P_s , as function of temperature (picture taken from [54])	57
2.16	Dielectric constant versus temperature of BaTiO ₃ (picture taken from [56])	58
2.17	Grain size dependence of relative permittivity of BaTiO ₃ at 25 and 70 °C (picture taken from [55])	59
2.18	polymer processing methods (picture taken from [58])	61
2.19	Film capacitor fabrication using a comma roll coater (picture taken from [61])	62
2.20	Component parts of a single-screw extruder (picture taken from [64])	63
2.21	Spraying method to manufacture layered coatings with customised properties (QUEST application funded by EPSRC)	64

3.1	A picture of the spraying apparatus used in this work	71
3.2	The manufacturing process for sprayed films	71
3.3	A picture of the spraying apparatus in the lab	74
3.4	picture of the 3D printers	75
3.5	Diagram illustrating the suitability of each measurement technique according to frequency and the loss in the materials [6]	77
3.6	Complex impedance Z and the impedance phase angle θ [7]	78
3.7	Simple RC circuit approximation [10]	79
3.8	Schematic of the waveguide measurement	80
3.9	Picture of waveguide in connection with VNA used in this work .	80
3.10	Schematic of the split-post dielectric resonator [16]	83
3.11	Resonant frequency and quality factor change after insertion of dielectric sample [17]	84
3.12	Resonant frequency versus dielectric constant for the 15GHz split- post dielectric resonator [19]	85
4.1	Low and high magnification SEM images of the as-received barium titanate powder	101
4.2	XRD plots of as-received barium titanate nano-powder, (a) is the overall scan from 10 to 80 degrees and (b) is a detailed scan near 45 degrees which corresponds to the location of (200) peaks and where the characteristic peak splitting would occur for tetragonal crystal symmetry.	102
4.3	Raman spectrum of as-received barium titanate powder at room temperature	103
4.4	(a)Size measurement comparison between as received BT particles and BT particles after deagglomeration; (b)Intensity percentage comparison of particle sizes between two measurements separated by 6 days after deagglomeration	105

4.5	Pictures taken (a) immediately after the PFA:BT(v/v)=0.1 composite suspension was ultrasonicated with Dispex A40;(b) after 30 min of sitting still; (c) after 1 h of sitting still; (d) overnight . . .	106
4.6	Plots of weight and volume of fluids pumped-out of the syringe at flow rate of 2ml/min and 4 ml/min respectively.	106
4.7	Illustration of spraying process (diagram from Patrick Grant's group)	108
4.8	Pictures of sprayed large-area composite films at various compositions. It can be seen that the films' surface roughness gets worse as the barium titanate loading increased.	109
4.9	Picture of the in-house designed hot press system	110
4.10	Sprayed large-area films (a) were cut into roughly 40mm x 40mm little squares (b) which were stacked and pressed in a hot-press into a compact block (c and d) for high frequency measurement .	111
4.11	A typical heating process for hot pressing PFA-5vol%BT sprayed film	111
4.12	Optical images of a cross-section of a hot-pressed PFA-5vol%BT block showing no air gaps between the layers but distinguishable boundaries	112
4.13	Comparison of SEM images at high and low magnification of poor and high quality sprayed films proving the importance of parameter optimisation in the spraying process.	112
4.14	SEM images of cross-sections of PFA-BT composite films at (a) BT:PFA (v/v)= 0.05 (b) BT:PFA (v/v)= 0.1 (c) BT:PFA (v/v)= 0.2 (d) BT:PFA (v/v)= 0.3 four different compositions at magnification 5000x.	113

4.15	SEM images of microtomed film samples revealing BT particle agglomerates: (a) a low magnification image showing how the film sample was embedded in the epoxy resin and the inhomogeneity of particle distribution within the film and (b) a higher magnification image of one cluster of BT nanoparticles	114
4.16	TG/DTA measurements of sprayed PFA film	115
4.17	TG/DTA measurements of composite films with different compositions	116
4.18	Nanofocus μ surf measurement of a sprayed PFA film showing (a) 3D image of the film surface (b) 2D image of the film surface and (c) profile of the surface quality along the red line marked on the 2D image	117
4.19	Illustration of the parallel capacitor structure	118
4.20	(a) Dielectric measurements at low frequencies for PFA / BT composite films with varying volume ratios of barium titanate ;(b) dielectric constant and loss tangent of PFA / BT composite films at 10 kHz plotted against BT volume fraction and fitted using the Lichtenecker equation	119
4.21	(a) Dielectric measurements at high frequencies for PFA / BT composite blocks with varying volume ratios of barium titanate; (b) dielectric constant and loss tangent of PFA / BT composite films at 15 GHz plotted against BT volume fraction and fitted using the Lichtenecker equation	122
4.22	Comparison of low frequency and high frequency dielectric constants of sprayed PFA-BT composite films	123
5.1	Dielectric constant of $(\text{Ba}_x, \text{Sr}_{1-x})\text{TiO}_3$ single crystals as a function of temperature for different contents of barium [19]	132
5.2	SEM images of as-received BT(a), BST (b) and CT (c) powders .	133

5.3	Particle size measurements for as-received BT and BST powders with evidence of agglomeration shown as small additional peaks .	133
5.4	XRD scan for BST powders from 20° to 110° with a blow-up of a high angle peak (310) where tetragonal peak-splitting is most likely to be detected	135
5.5	Linear fittings of $\cos^2\theta$ - a and $(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta})$ - a plots showing that Nelson-Riley function gives a better converged a value - $3.97 \text{ \AA}$.	135
5.6	Atomic ratio calculation of Ba/Sr in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ formula from WDS for as-received and heat-treated BST powders respectively with an average value of 1.97 and 2.07 and standard deviation of 0.33 and 0.28 accordingly	136
5.7	Varied degrees of agglomeration seen in SEM images of epoxy composites with as-received BT and BST powders at high and low magnifications	141
5.8	Process flow diagram for preparing uniform epoxy/BST composites	142
5.9	Almost agglomerate-free cross-sections of epoxy-5vol%BST and epoxy-30vol%BST composites after surface treatment with silane GPTMS	143
5.10	Comparison of FTIR results of as-received GPTMS, GPTMS after 15 min of hydrolysis and GPTMS condensed for 15 min at 110°C after the hydrolysis	145
5.11	Comparison of FTIR results of as-received BT powders, BT powders dried directly after GPTMS surface treatment, and BT powders washed by EtOH twice after GPTMS surface treatment . . .	146
5.12	Comparison of FTIR results of as-received BST powders, BST powders dried directly after GPTMS surface treatment, and BST powders that was washed by EtOH twice after GPTMS surface treatment	146

5.13	Ten repeated measurements of one epoxy-15vol%BT sample to examine the instrumental error	147
5.14	Comparison of waveguide measurements made in Oxford and in Exeter of epoxy-BT composites with various BT loadings to ascertain the legitimacy of Oxford measurements. A vacuum degassing process was introduced to the sample preparation to achieve higher and stable results	148
5.15	Optical microscope images of undegassed epoxy/BT composite samples across different compositions with clear evidence of entrapped air	149
5.16	Optical microscope images of degassed epoxy-10vol%BT and epoxy-30vol%BT composite samples with no sign of air bubbles	149
5.17	Dielectric constant (top) and loss tangent (bottom) at scanning frequency 12 to 18 GHz for epoxy/BT composites with BT volume fractions from 0 to 43 %	151
5.18	dielectric constant of all epoxy/BT composites at 15 GHz plotted against BT loadings from 0 to 43 vol%	152
5.19	SEM images of (a) epoxy-5vol% BT (b) epoxy-15vol% BT (c) epoxy-25vol % BT (d) epoxy-35.5vol% BT samples	153
5.20	Dielectric constant and density measurements for epoxy-30vol%BST composites in five groups: A. composites made from untreated BST powders; B. composites made from GPTMS-treated BST powders; C. composites made from heat-treated BST powders; D. composites made from heat-treated and GPTMS-treated BST powders; and E. composites made from heat-treated, GPTMS-treated and acetone washed BST powders	154
5.21	Split-post and samples ready for measurements at 15 GHz	156

5.22	Epoxy/BT composites with BT loadings from 0 to 30 vol% dielectric constant data fitted with various mixing rules	158
5.23	Schematics of the two-phase separated-structure (a) assumed for the Maxwell-Garnett model and aggregated-structure (b) assumed for the Bruggemen model [11]	161
6.1	Laminated block formed by layers of two different dielectrics. When the electric field is applied in X and Z directions, the macroscopic dielectric properties will be different	171
6.2	Parallel (left) and perpendicular (right) structures in a waveguide representing the aforementioned two electric field orientations . .	171
6.3	Wiener bounds for a two-phase mixture with $\epsilon_m = 2.7$ (ABS) and $\epsilon_f = 6.4$ (ABS/BT composite) respectively. The calculated maximum and minimum effective dielectric constants for a 50/50 mixture of these two materials are 4.55 and 3.8 as marked on the graph	172
6.4	Comsol model of waveguides sandwiching (a) 6 perpendicular stripes sample and (b) 12 parallel stripes sample; In the layered sample structure, the ABS phases are highlighted to distinguish from the ABS/BT phase.	174
6.5	Picture of printed waveguide samples with perpendicular (left) and parallel (right) periodic structures. Samples were hand-polished to fit tightly into the waveguide after printing	175
6.6	SEM images of printed mixture sample (a) the ABS and ABS/BT interface after microtomy at low magnification (b) a relatively homogeneous distribution of BT particles in the ABS/BT composite phase at higher magnification	175
6.7	Waveguide measurements of pure ABS and pure ABS/BT composite samples at 12 - 18 GHz. The reference data are consistent with the values assumed in simulation	176

6.8	Simulation result (electric field normal) for 6 layer perpendicular structure at 12 GHz; the wave propagates opposite to y direction. The entire waveguide structure is 42 mm long with a 2 mm thick sample inserted in the middle. The wavelength in air equals to 25 mm.	177
6.9	Simulation result (electric field normal) for 12 layer parallel structure at 12 GHz; the wave propagates opposite to y direction. The entire waveguide structure is 42 mm long with a 2 mm thick sample inserted in the middle. The wavelength in air equals to 25 mm. . .	177
6.10	Comparison of simulated and measured S11 and S21 parameters in dB for the 6 layer perpendicular structure	178
6.11	Comparison of simulated and measured S11 and S21 in dB for the 12 layer parallel structure	178
6.12	Simulated and measured dielectric constant for perpendicular and parallel structure samples were extracted using the NRW method	179
6.13	A simulation to show that a modified Maxwell fish eye lens functions as a power divider (by Rhiannon Mitchell-Thomas and Oscar Quevedo-Teruel)	182
6.14	The proposed lens profile (a) the discretization plot (b), and the dielectric constant specification of individual layers listed in the chart (by Rhiannon Mitchell-Thomas and Oscar Quevedo-Teruel)	182
6.15	Pictures of the set of PTFE moulds used to cast the power divider lens	183
6.16	Pictures of the manufactured lens before (a) and after (b) lathing	185
6.17	Pictures of the completed lens showing good interface quality between layers as well as good dimensional precision	185
6.18	Graph comparing the target and measured dielectric constant of individual layers of the lens	186

6.19	First lens test in Exeter using a monopole source	188
6.20	Second lens test in the University of Queen Mary in an anechoic chamber using waveguide excitation with absorbing materials to block space waves	189
6.21	Schematics of the third lens test set-up (a) and picture of the modified waveguide inner structure before the metal top was sealed back on (b)	190
6.22	The modified waveguide fixture with lens and a metal cover (a); the second lens test with the no cover in anechoic chamber in the University of Queen Mary (b)	190
6.23	3D COMSOL model of the first lens test using a monopole source, which is highlighted in (b)	192
6.24	3D COMSOL model of the second lens test using a waveguide transmitter. The rectangular port is highlighted in (b) with a piece of absorber blocking part of the outlet	193
6.25	3D COMSOL model of the third lens test using modified waveguide source (highlighted in (b)) creating a transition section for better energy channelling between the waveguide and the lens	195
6.26	Experimental result of the first lens test using the a monopole transmitter (a)(b) Ez amplitude (V/m) plot and instantaneous Ez field plot measured at a plane of $z = 3$ mm at 15 GHz, (c)(d) and 18 GHz	196
6.27	Simulation results of the first lens test using the monopole transmitter (a)(b) Ez amplitude (V/m) plot and instantaneous Ez field plot measured at plane of $z = 3$ mm at 15 GHz, (c)(d) and 18 GHz	197
6.28	Arc scan from -60 to 60 degrees of normalised Ez amplitude of experiment and simulation results at 15 GHz and 18 GHz at radius of 70 mm and 90 mm	199

6.29	Experimental result of the second lens test using a waveguide source. (a)(b) Ez amplitude (V/m) plot and Instantaneous Ez field plot measured at plane of $z = 3$ mm at 15 GHz (a)(b) and 18 GHz (c)(d)	201
6.30	Simulation result of the second lens test using waveguide source: (a)(b) Ez amplitude (V/m) plot and instantaneous Ez field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d) . .	202
6.31	Experimental results of the third lens test using a modified waveguide source with no cover. (a)(b) Ez amplitude (V/m) plot and instantaneous Ez field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d)	203
6.32	Simulation result of the third lens test using modified waveguide source with no cover: (a)(b) Ez amplitude (V/m) plot and Instantaneous Ez field plot measured at plane of $z = 3$ mm at 15 GHz (a)(b) and 18 GHz (c)(d)	204
6.33	Experimental result of the third lens test using a modified waveguide source with metal top. (a)(b) Ez amplitude (V/m) plot and instantaneous Ez field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d)	205
6.34	Simulation result of the third lens test using a modified waveguide source with metal top. (a)(b) Ez amplitude (V/m) plot and instantaneous Ez field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d)	206

List of Tables

2.1	Dielectric constants of selected polymeric substances [42]	48
2.2	Major industrial fluoroplastics [42]	52
2.3	Common seen processing methods for polymeric materials [58] . .	61
4.1	Dielectric constants of some polymeric substances [17]	100
4.2	Viscosity reference for BT/PFA suspensions with different volume ratios before and after ultrasonication	107
4.3	Comparison between nominal sample composition and TGA weight residue	115
4.4	Dektak measurements of sprayed PFA film	116
5.1	Dielectric measurements at high frequencies reported in the liter- ature for BST with various strontium contents x	132
5.2	Split-post measurements at resonant frequencies between 10 and 15 GHz and waveguide measurements for the same materials at 15 GHz as comparison	157
5.3	List of morphology factor n values found in the literature	162
5.4	polarizability factor α_n for various particle shapes	162
6.1	Composition of epoxy/BT composites used for manufacturing in- dividual layers of lens	184
6.2	Maximum element size setting for all dielectric domains in COM- SOL model	192

Chapter 1

Introduction

Customisation of electromagnetic properties or refractive indices is a key element of transformation optics, a mathematical technique that is used to design artificial materials in order to manipulate the emission, propagation and absorption of EM radiation. Transformation optics was first introduced in [1] and [2] based on the form-invariant property of Maxwell's equations under coordinate transformations. By transforming the electromagnetic properties, specifically permittivity and permeability, in an original coordinate space in a specific way onto a new coordinate system, the way that waves propagate through materials can be tailored. Such a concept offers a powerful tool to explore the realisation of various optical effects and devices, most remarkably the 'invisibility cloak' (illustrated in Figure 1.1). The transformation optics method is, however, ineffective if artificial materials with desired permittivity and permeability properties are not available due to limitations in fabrication methods to produce the complex locally changing properties required[3].

The implementation of transformation optics usually goes hand in hand with the employment of metamaterials. Conventional metamaterials are often realised using metallic resonant structures. However, the strong dissipation and narrow bandwidth limitations observed in artificial materials that show the negative re-

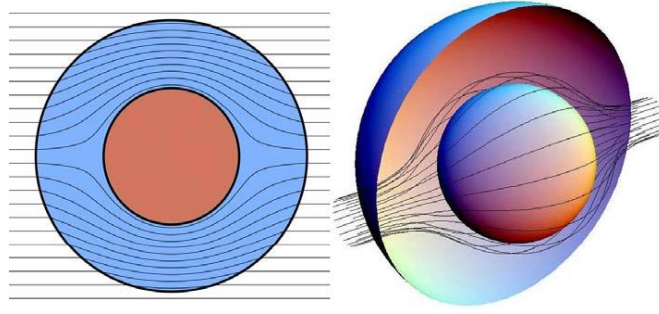


Figure 1.1: A ray tracing diagram showing how rays are diverted in the cloaking material contained in region $R_1 < r < R_2$ (the inner and outer radius of the two spheres) without 'seeing' the hidden object [1]

fraction severely restricts their application [4–6]. Therefore, an alternative way to realise the power of transformation optics using only positive refractive index materials has also been actively sought [7–10]. The objective of my DPhil project is to investigate and manufacture dielectric materials with a wide range of relative permittivity values, as part of the wider goals of 'The Quest for Ultimate Electromagnetics using Spatial Transformations (QUEST)' project (<http://www.quest-spatial-transformation.org/>) that requires such a capability in EM customisation to design transformation optics devices at microwave frequencies.

Polymer/ceramic composites have been chosen to fabricate dielectric materials with controlled permittivity values. The attractive features of these polymer/ceramic composites include low-cost, good processibility and ease of scaling-up. High dielectric constant ceramic fillers embedded homogeneously in low dielectric constant polymer matrix offer a rather large dynamic range of dielectric constant variation, depending on the maximum loading of fillers that can be achieved, which is favourable for the purpose of electromagnetic customisation. However, accurate control of dielectric properties in three dimensions poses enormous challenges for materials processing. The selection of polymer and ceramic materials used in this work was complicated by consideration of key factors, including:

- 1) routes to manufacture

- 2) stable dielectric properties, including dielectric constant and loss
- 3) microwave testing methods

To achieve the maximum possible dielectric constant enhancement of the composites, ferroelectric ceramics of barium titanate (BT) and barium strontium titanate (BST) which are known for their high dielectric constant were used in this work. For ceramic fillers, because the dielectric properties of the ferroelectric ceramics are dependent on composition, particle size and frequency, careful preliminary research work in powder properties was important to choose the most suitable ceramic fillers. The choice of polymer matrix decides the manufacturing method and consequently the shape of the composites. Several manufacturing methods, including spraying, casting and 3D printing, were studied in this work to accommodate the reliable fabrication of different polymer/ceramic systems, Chapter 5 and 6. These manufacturing processes were optimised to ensure stable dielectric properties in isotropic composites at various compositions. Microstructural characterisation techniques were utilised to confirm the control over dielectric properties of a microscopic scale. To provide reference data on the frequency dependence of their dielectric properties, the dielectric properties of these different polymer/ceramic composites were measured at two frequency bands within the microwave range, the low frequency band from 100 Hz to 1 MHz and the high frequency band from 12 to 18 GHz. A master curve of the dielectric constant of polymer/ceramic composites was generated to calculate and to predict the corresponding composition of composites at a given dielectric constant, i.e. to achieve dielectric constant customisation, Chapter 5. Various mixing rules were investigated to provide best curve fitting to the experiment data.

Once confidence over the control of dielectric properties of the composites I made was achieved, this capability was tested by exploring advanced applications of anisotropic dielectrics and a gradient-indexed lens design, Chapter 6. The

anisotropic dielectrics were made of laminated dielectric layers with two different dielectric constant values by 3D printing. By aligning the layers in different orientations, the effective dielectric constant of the system was shown to be different. A gradient-indexed all dielectric lens consisting of 11 concentric layers of discretized dielectric constant was designed by partners in QMUL. The lens was a proof-of-concept device modified from a Maxwell fish eye lens [8] and functioned as a power divider lens dividing incoming beam into two sub-beams. Both test devices were simulated in COMSOL Multiphysics and the results compared with the experimental data.

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Chapter 2

Literature Review

In this literature review, I summarise the significance and possibility of developing polymer-based dielectric composites for metamaterial applications. The background of metamaterials is introduced briefly and investigation on nanocomposite system is given regarding both ceramic loadings and polymer matrices. Eventually some routine processing methods for polymers based composites are covered and the specific spraying method adopted in this project mentioned.

2.1 Metamaterials

2.1.1 Definitions of Metamaterials

1. “Metamaterials are artificial materials engineered to have properties that may not be found in nature. Metamaterials usually gain their properties from structure rather than composition, using small inhomogeneities to create effective macroscopic behaviour.” (From Wikipedia, 2012)

2. “Metamaterials are a new class of ordered composites that exhibit exceptional properties not readily observed in nature. These properties arise from qualitatively new response functions that are: (1) not observed in the constituent materials and (2) result from the inclusion of artificially fabricated, extrinsic, low

dimensional inhomogeneities.” (by Valerie Browning and Stu Wolf in the DARPA Metamaterials program in 2001 [1])

3. “Metamaterials are artificial electromagnetic (multi-) functional materials engineered to satisfy the prescribed requirements. The prefix meta means after, beyond and also of a higher kind. Superior properties as compared to what can be found in nature are often underlying in the spelling of metamaterials. These new properties emerge due to specific interactions with electromagnetic fields or due to external electrical control.” (the Metamorphose Network of Excellence funded by the European Union, 2006 [1])

Definition 2 is probably the one has agreed by most scientists, nevertheless some people may think it too specific. The definition of metamaterials could go as wide as ‘materials that do not exist naturally’, although not many people would appreciate such an inclusive conclusion. For instance, materials that are modified by doping to supply the desired properties satisfy the definition of metamaterials but do not necessarily fit our understanding of metamaterials. The essence of most metamaterials’ definitions agrees on two points [1]: 1. not observed in nature and 2. not observed in its constituent materials.

2.1.2 Classification of Metamaterials

It will not be easy to classify a topic as huge as metamaterials. However, I attempt to summarise in this review by enumerating the most well-known branches of metamaterials. We talk about metamaterials in an electromagnetic setting where the interaction between waves and materials is the main interest, and permittivity ϵ and permeability μ are two key parameters that determine wave propagation in this material. Therefore, we can rely on the combinations of these two quantities to categorize metamaterials explicitly. To start with, we shall resort to the effective permittivity (real part of epsilon ϵ_r) and effective permeability (real part of mu μ_r) diagram in which materials fall into four quadrants

representing four different properties, as described in Figure 2.1. To make cases simpler, we confine the situation to isotropic materials in which ϵ and μ are independent of each other (we will discuss cases where these two quantities interact later). Veselago had a comprehensive description of these four properties in his paper in 1967 [2] (written first in Russian in 1967 then translated into English in 1968). A premise is that when we talk about permittivity and permeability of materials, we automatically regard these parameters as effective values for the whole system. For this assumption to hold, the artificially designed structures in metamaterials have to be of a size (both the size of individual elements and the spacing) much smaller than the wavelength of incident radiation.

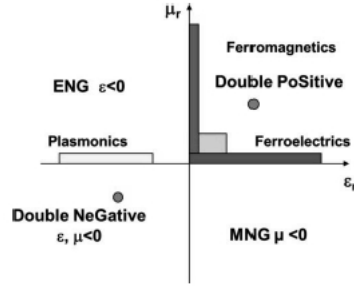


Figure 2.1: Four types of materials categorized by different ϵ_r and μ_r values: (1) double positive materials are the most commonly seen conventional materials; (2) epsilon negative materials, in which $\epsilon_r < 0$ and $\mu_r > 0$, include metallic compounds employed in plasmonics devices such as gold and silver; (3) double negative materials refer to conventional metamaterials with negative refractive index; (4) mu negative materials, in which $\epsilon_r > 0$ and $\mu_r < 0$, involve current loops [3]

Double Positive Medium

In the first quadrant in Figure 2.1, both permittivity and permeability are positive ($\epsilon > 0$, $\mu > 0$), under which conditions the refractive index $n = +\sqrt{\epsilon\mu}$ is positive and wave propagation is permitted. Most conventional materials (natural and artificial) fall into this area. Artificial dielectrics, to usually describe man-made electric metamaterials with sub-wavelength metal fillers embedded in homogeneous background, are necessary especially when a gradient of indices is

required in the materials [4]. Another proposed method to obtain graded-index metamaterials is to attain control over permittivity and permeability of materials by carefully designing composite systems with specific choice of matrix and loadings as well as their ratios. Examples of applications of graded-index metamaterials include conventional Luneburg lens and more novel inventions such as optical cloaks [4].

Single Negative Metamaterials (SNG)

In quadrants II and IV, either permittivity or permeability is negative but not both. When the signs of permittivity and permeability are opposite, the refractive index n is imaginary indicating no wave propagation. In the second quadrant, $\epsilon < 0$ while $\mu > 0$, plasmas and fine wire structures belong to this zone (We call such metamaterials ENG in short of epsilon negative media). In the fourth quadrant, $\epsilon > 0$ while $\mu < 0$, microstructured magnets and split rings exhibit such characteristics (We call these materials MNG in short of mu negative media).

Negative Index Materials (NIM) OR Left-Handed Media

The third quadrant ($\epsilon < 0, \mu < 0$) is where metamaterialists' enthusiasm and passion are centred. When both permittivity and permeability are negative, the refractive index n has to take the negative square root of the product of ϵ and μ , $n = -\sqrt{(\epsilon\mu)}$, thus the materials will show negative refractive index.

Ever since Veselago first established the possibility of materials having both negative permittivity and permeability in 1967, considerable work and many publications have been dedicated into research on negative index metamaterials. What exactly is so special about this negative index materials ? Firstly, back then materials with such properties had never been known to exist with the suspected reason that such materials probably violated some fundamental

physics law. When light incident on a NIM, it will bend to the same side as the incident beam which contradicts to the Snell's law. Veselago modified the Snell's law and proved in theory that such materials can exist. Secondly, for these two parameters to move into negative values, they are going to be dispersive — varying in accordance with frequency, possess shorter bandwidth compared to their positive counterparts and to makes things even worse, the frequencies in which electronic and magnetic resonant phenomena occur simply do not overlap [5]. All these facts indicate that it won't be a easy task to achieve negative index materials. Be that as it may, the interesting properties and enormous potential behind these negative index metamaterials still provide sufficient impetus for scientists to carry on.

Exotic metamaterials with negative refractive index open a door to a whole new land of possibilities, e.g.backward waves (some periodic structure has such effect too), reversed Doppler effect and reversed Cerenkov effect [1, 6]. There are four seminal papers that should be included in the description of the history of NIM. After Veselago's demonstration in theory of the possibility of negative permeability and permittivity, there was not much progress in experiments until approximately 30 years later. Despite Veselago's lack of faith in the existence of negative permeability materials, they do exist in the antiferromagnets MnF_2 and FeF_2 or certain insulating ferromagnets [7]. However the negative permeability with low loss does not coexist in nature with negative permittivity. Smith *et al.* (2000) proposed a composite medium in which they adopted a peculiar structure of a periodic array of split ring resonators (SRR) and continuous wires to achieve negative ϵ and μ [8]. This split ring resonator design was initiated by Pendry in 1999, a very special structure that achieved negative μ at one frequency.

The next big stride was taken by Shelby *et al.* (2001) who successfully verified negative refractive index [9] using a similar structure in Figure 2.2. This structure

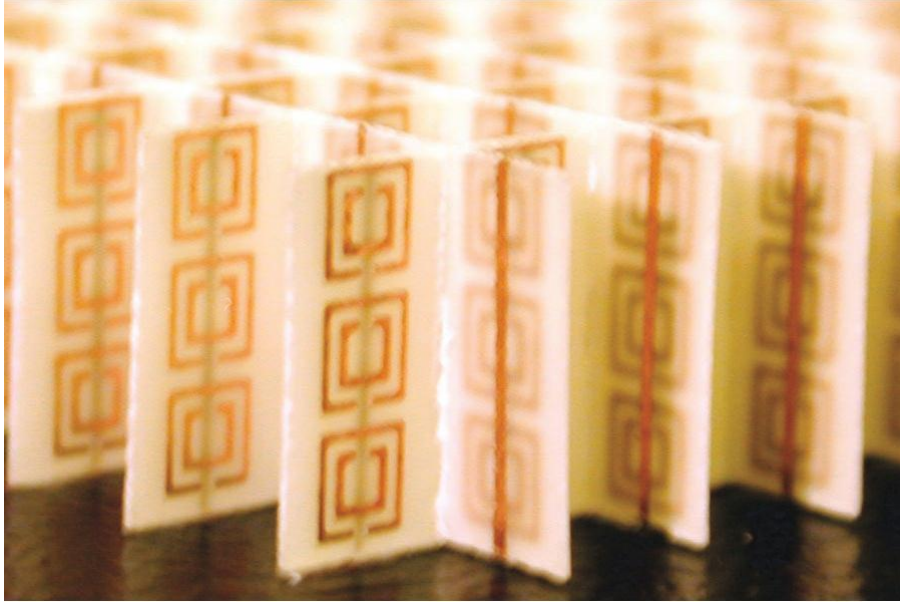


Figure 2.2: A left-handed media sample made of copper split ring resonators and copper wire strips on fiber glass circuit board (picture taken from [9])

was cut into a prism shape and placed between two circular aluminium plates. The angle of a transmitted beam through the prism was detected and found to be from an expected but unusual direction thus confirmed the prediction of Maxwell's equations that n takes negative square root of the product of ϵ and μ when they are both negative. Finally, the last missing piece in the puzzle, the lack of practical applications, was suggested by Pendry in 2000 with his perfect lens [10], which will be discussed in detail later.

In addition to SRR structures, there are other options to realise negative index in metamaterials. Examples include photonic crystal, transmission line structures and chiral metamaterials. It is disputable whether photonic crystals should be categorised as metamaterials. Photonic crystals, also known as many other names such as photonic bandgap materials or electromagnetic bandgap structures, gain the name for their artificially designed structure satisfying Bragg reflection in every direction thus being capable of trapping electromagnetic fields (similar to the way band gaps work for electrons). In order to satisfy the Bragg equation, the lattice spacings of the structure have to be same order as the magnitude of

the incident wavelength, which differs from general metamaterials whose structures have to be much smaller than the operating wavelength as to qualify as a homogeneous medium.

Bi-isotropic and Bi-anisotropic Metamaterials

Now let us consider the situation where permittivity and permeability do interact with each other, that is, electric fields can cause magnetic polarization while magnetic fields can induce electric polarization, i.e., magnetoelectric coupling. Bi-isotropic and bi-anisotropic materials are used to describe materials that exhibit such cross-polarization (electric to magnetic coupling and magnetic to electric coupling). The difference between the two is that if the electromagnetic responses of such materials are dependent on the direction of the exciting field or their permittivity and permeability are in a tensor form, we call them bi-anisotropic materials. On the contrary, if the electromagnetic responses are independent of the exciting field or their permittivity and permeability are in a scalar form, we refer to them as bi-isotropic materials.

Chiral metamaterials

When metamaterials are made of chiral elements, they are referred as chiral metamaterials in which the effective parameter k becomes non-zero and the refractive index is presented to be $n = \sqrt{\epsilon\mu} \pm k$. This equation suggests a simpler route for realising negative refractive when both ϵ and μ being negative is no longer a requisite, as long as the $k > \sqrt{\epsilon\mu}$. Study of chiral metamaterials in microwave regions stimulus application areas such as antennas, polarizers and waveguides [11].

2.1.3 Applications of metamaterials

Metamaterials are a class of materials that achieve their exceptional physical properties by meticulous design of structure such that we gain good control over the interaction between incident electromagnetic waves and materials. Following this logic, it is not exaggerating to say that the gate towards a whole world of new possibilities is opened up by metamaterials as it extends its potential application to every field concerning EM wave propagation. I shall only list the three main areas here where metamaterials stand the greatest chance of making a difference in practice.

Cloaking devices

Invisibility cloaking was believed to only live in Harry Potter fiction before two seminal papers published on the same issue of *Science* in 2006 by Pendry [12] and Leonhardt [13] respectively, the foundation of transformation optics. The idea of spatial transformations (STs) is to enable new ways of manipulating the emission, propagation and absorption of EM radiation by the spatial arrangement of materials with different properties. STs utilize a symmetry property of EM fields based on the fact that Maxwells equations remain the same under coordinate transformations: when an EM wave travels along a straight line in original Cartesian space displayed in a uniform square mesh, it will follow a distorted mesh while in distorted coordinates. STs are used to explain ideas such as invisibility cloaking and other optical illusions. According to Fermat's principle, light rays take the shortest path in dielectric media, and the path length is defined by the refractive index n of this media. When we have a media whose refractive index is not homogeneously distributed (as we distort the space anisotropically) but varies spatially, the shortest optical path will no longer be straight lines but are curves, as shown in Figure 2.3. Using spatial transformation, the original homogeneous space is allowed to transform into inhomogeneous space which is

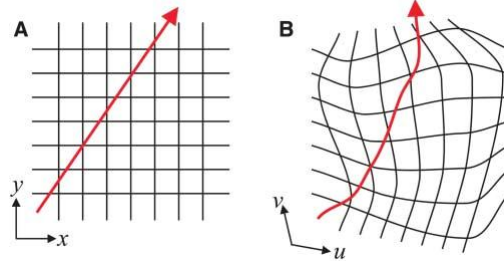


Figure 2.3: (A) A field line in free space with the background Cartesian coordinate grid shown. (B) The distorted field line with the background coordinates distorted. (Picture taken from [12])

capable of guiding incident waves around the object intended to be shielded from view without being affected by the object itself. For this theory to work, permittivity and permeability have to vary from point to point in the space in question. That is to say, materials with a range of extreme values of permittivity and permeability have to be designed. The first proof of concept demonstration was conducted at microwave frequency and published in 2006 in *Science* [14]. The group chose a series of concentric SRR structure to give a profile of permittivity and permeability that satisfied the parameters given by spatial transformation modelling (Figure 2.4). A conducting cylinder was placed at the inner radius of the cloak. This conducting cylinder has the strongest scattering to be concealed in such a cloaking geometry. However, a few drawbacks were revealed. The cloaking device only worked at a narrow frequency band because of the resonant nature of metamaterial used, and natural absorption, dissipation and dispersion are problems impairing the performance of cloaking device. Up to date, cloaking across a broad spectrum of frequencies has yet to be developed.

It is worth mentioning though that since 2009, there has been a rising trend in developing ground plane cloaks [15] (also known as carpet cloaking) which perform quasi-conformal transformations rather than non-conformal ones as was employed in the original cloak. The advantage of ground plane cloaks is that they avoid magnetic resonant elements and sticks to an all dielectric structure with

the benefit of broad band performance.

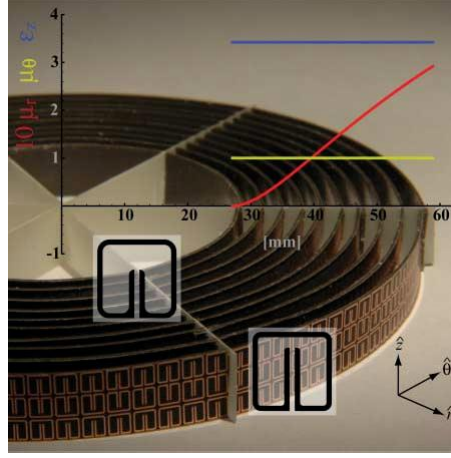


Figure 2.4: 2D microwave cloaking structure [14]

Perfect imaging

Perfect imaging, or perfect lens or superlens, represents the idea of subwavelength imaging beyond the diffraction limit of conventional lenses. Optical lenses are of vital importance to scientists, who use every effort to design and polish lenses perfectly in hope of pushing their resolution to the maximum. Nevertheless, this inherent diffraction limitation to all lenses means that they cannot focus light onto an area smaller than a square of half a wavelength. The physics rationale is that conventional lenses only transfer information conveyed by far field radiation, while the near field radiation consisting of evanescent waves decays exponentially in any medium with positive permittivity and permeability. Based on his research on metamaterials, Pendry raised the solution of using NIM to make a perfect lens that would compensate evanescent waves as well [10].

The principal conclusion given by Pendry is that by making lens with negative index materials, the resolution of lens would no longer be limited by the wavelength restriction. A schematic was employed to illustrate how such lenses work to focus light even in a flat slab shape as shown in Figure 2.5. When light is

propagating through this negative index material, evanescent waves are enhanced in amplitude, thus making it possible to refocus the light. The material require-

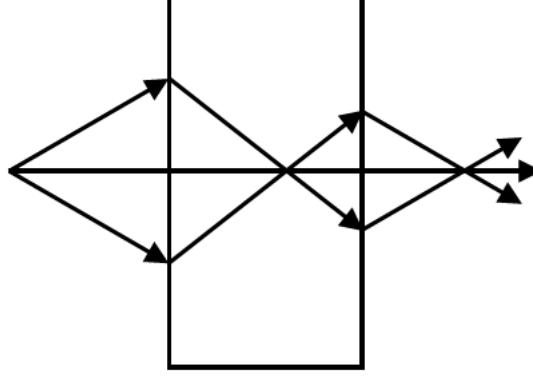


Figure 2.5: A rectangular slab of negative index material bends light to a negative angle with the surface normal according to Snell's law [10]

ment presented by Pendry for a perfect lens to work is actually very stringent. The material is required to have permittivity and permeability value of -1 resulting in a refractive index of -1 at the same time. What is more, it needs to be lossless. Therefore, 'perfect lens' cannot be perfect in practice. This does not necessary mean that it is an unrealistic goal to improve the resolution towards subwavelength. In fact, in electrostatic near field limit, for transverse magnetic (TM) polarization, negative permittivity suffices for achieving a superlens that has much better resolution. It has been experimentally proved that a thin slab of silver superlens can achieve a resolution as high as 60 nanometer half-pitch (or $\lambda/6$) [16]. Even better resolution is made possible by the novel design of multilayer superlens put forward by Ramakrishna *et al* [17]. Nevertheless, loss remains a major issue to be tackled for any practical achievement.

Antenna design

Metamaterials are used in antenna design application to improve the performance of electrically small antennas. Antennas' function is to launch energy into space and has to be at least half the wavelength of incident radiation to work

efficiently. Conventional antennas can get very lengthy in order to function properly bound by its size requirement, which severely hinders the development of antennas. Metamaterials incorporated antennas carry out further miniaturization in antenna industry, developed to be applied in wireless communication such as portable interaction with satellites, wide angle beam steering.

2.2 Nanocomposites with customised material properties

In the practical and industrial realisation of various ST devices such as low profile directive conformal-antennas, cloaking devices and electrically small antennas, metamaterials with a wide profile of customized permittivity and permeability are desired. In our project, nanocomposites with selected matrix and high permittivity or permeability loadings are manufactured so that their physical properties can be adjustable at will. For example, in a layered structure, refractive index variation through the thickness can be designed when layers with chosen values of permittivity or permeability or both are stacked together. A schematic illustrating such customization is shown in Figure 2.6. In this section, we will start with an introduction to basic physical principles behind permittivity and permeability parameters, then investigate specific materials with appealing parameters that may be useful in our project. I will end this section with a detailed review on electromagnetic mixing formulas with an emphasis on the role individual components play in determining the composite refractive index. Despite this section covering fundamentals of both parameters, my project mainly focused on the dielectric property customisation of composites, i.e. using ferroelectric fillers to adjust the permittivity values of the composites.

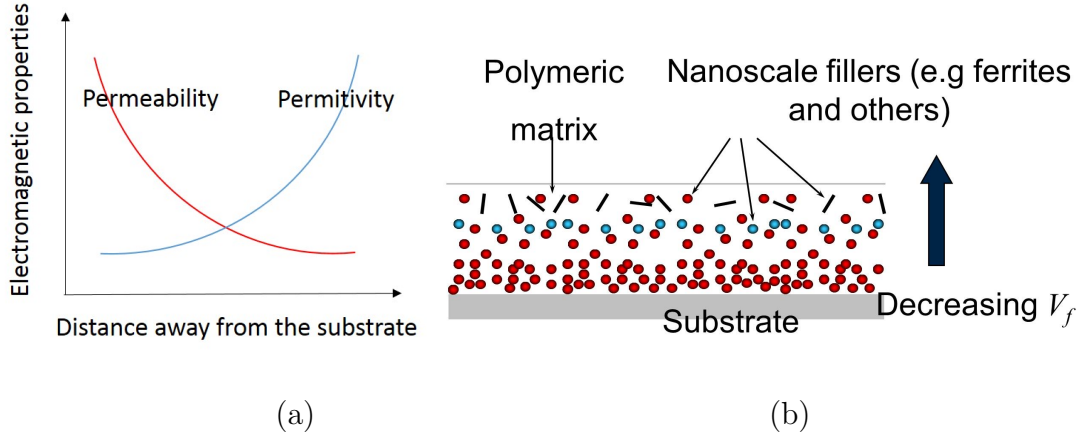


Figure 2.6: (a) Macroscopic illustration of individual control over ϵ and μ , by changing the volume fraction of nano particles with different electromagnetic properties such as ferroelectrics and ferrites (the red and blue dots) in the spraying suspension when building up the film thickness on the substrate during the spraying process as indicated in (b)

2.2.1 Physical connotation of permittivity

Permittivity and permeability, denoted respectively in Greek letters ϵ and μ , are two parameters used to describe and measure the response of a medium towards electric and magnetic fields. Together, they determine the phase velocity of electromagnetic radiation propagating in the materials (Equation 2.1). This explains why ϵ and μ are significant in the field of electromagnetism.

$$v = c/n, \epsilon\mu = 1/v^2 \quad (2.1)$$

Materials are divided into two main classes: **conductors** and **insulators** (or **dielectrics**), depending on whether electrons are free to roam around as in conductors or are bound as in dielectrics. When a static electric field is applied to a dielectric, electrical polarization will arise, denoted as α . From a macroscopic scale, all the individual polarization together combine to give the overall

polarization $\mathbf{P}$. It relates to the electric displacement $\mathbf{D}$ as follows:

$$\mathbf{D} = \epsilon \mathbf{E} + \mathbf{P} = \epsilon_0 \epsilon_r \mathbf{E} \quad (2.2)$$

Here permittivity ϵ is the bridge connecting the macroscopic parameter electric displacement to microscopic polarization. ϵ_0 is the permittivity of vacuum, with the value of $8.85 \times 10^{-12} \text{ C}^2 / \text{N} \cdot \text{m}^2$. The relative permittivity ϵ_r is also called the dielectric constant.

Complex permittivity

In the cases of alternating fields, when a sinusoidal voltage (Figure 2.7) is applied to a capacitor, the phase difference between I and U remains to be 90° for a perfect capacitor where there is no loss but a varying angle of δ emerges in the real capacitor (Figure 2.8). The behaviour of a.c circuits can be described using complex quantities. For a perfect capacitor where there is no loss, it follows that

$$\mathbf{I} = \dot{Q} = \dot{\mathbf{U}}C_0 = j\omega C_0 \mathbf{U} \quad (2.3)$$

For a real capacitor where a lossy component is included, a complex relative permittivity $\epsilon^* = (\epsilon' - j\epsilon'')$, where ϵ' and ϵ'' are respectively the real part and imaginary part of the relative permittivity, should be introduced to account for the effect.

$$I = j\omega \epsilon_r^* C_0 \mathbf{U} = j\omega \epsilon_r' C_0 \mathbf{U} + \omega \epsilon_r'' C_0 \mathbf{U} \quad (2.4)$$

The current is made up of two parts, one capacitive (i.e. lossless) and the other in phase with $\mathbf{U}$ and thus lossy. The loss tangent $\tan \delta = \frac{\epsilon''}{\epsilon'}$ as can be seen in Figure 2.8(b), in which ϵ' reflexes the energy storage ability of the materials while ϵ'' is related to loss.

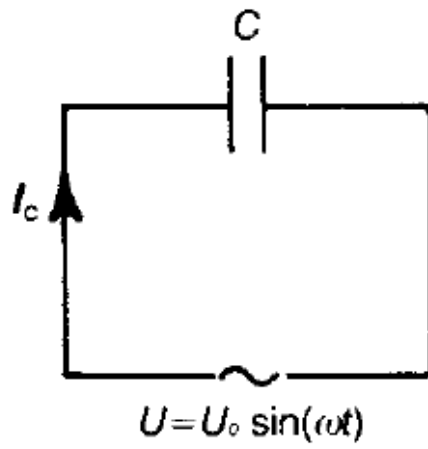


Figure 2.7: Sinusoidal voltage applied to a capacitor (picture taken from [18])

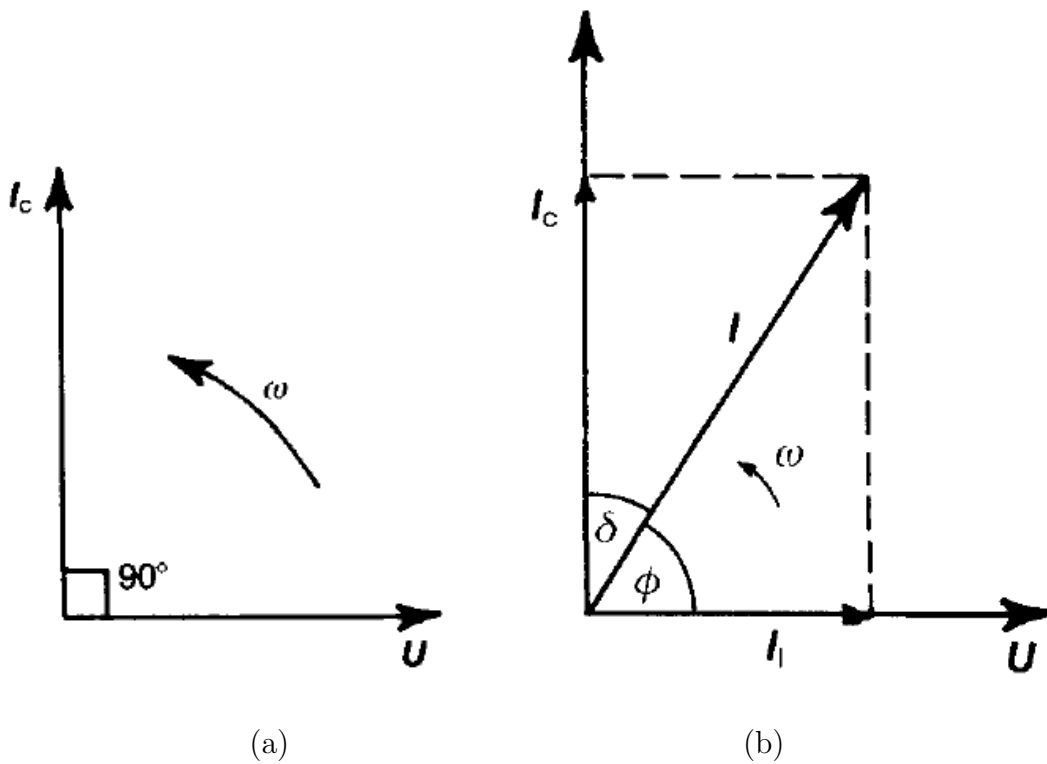


Figure 2.8: (a)Phase diagram for a perfect capacitor (b)Phase diagram for a lossy capacitor (picture taken from [18])

Polarization mechanisms in dielectrics

When an electric field is applied to dielectrics, the resulting polarization comprises two parts according to the time constant of the response: one polarization arises instantaneously (denoted as $\mathbf{P}_\infty$); and the other is time-dependent denoted as $\mathbf{P}_s$) [19], as seen in Figure 2.9.

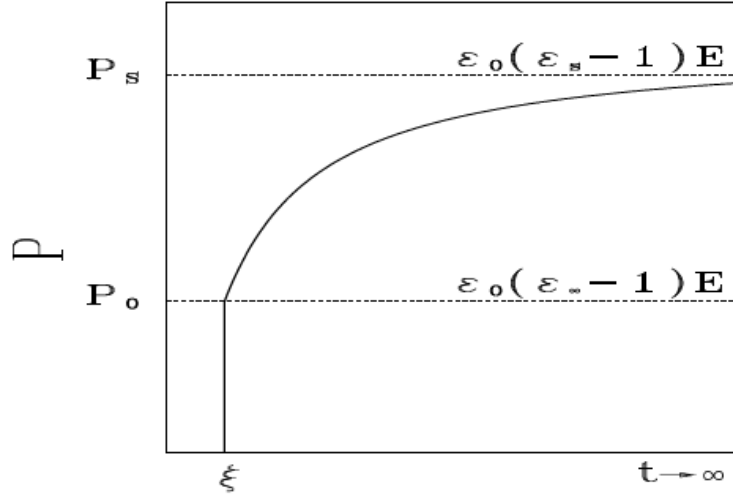


Figure 2.9: Time dependence of polarization (picture taken from [20])

These two polarizations define the static dielectric constant at very low frequencies and the upper limit dielectric constant at high frequencies, known as ϵ_s and ϵ_∞ respectively.

The reason for the difference in response is different polarization mechanisms. Polarization over a wide range of frequencies is either a relaxation or resonance process. At high frequencies above 10^8 Hz, dipole moments express resonance behaviour showing no lag time in response. At frequencies below 10^8 Hz, dipole moments respond to applied fields in a finite time. Various dipole moments in materials account for these relaxation and resonance processes. For example, light components such as electrons are less bound and free to move around thus can respond instantly to applied fields even at very high frequencies. Large

molecules on the other hand are massive and require a certain amount of time to reach polarization positions. The following polarization mechanisms, with their characteristic frequency ranges, are observed in materials.

Electronic polarization This process occurs when a neutral atom is placed under electric field. Influenced by the field, the positively charged core (the nucleus) and a negatively charged electron cloud surrounding it would be pushed to opposite ends and result in electronic polarization. It exists in all materials and lasts up to the highest frequencies.

Atomic polarization In the case of ionic crystals, atomic or ionic polarization occurs when the average position of positive and negative ions changes under external electric fields.

Dipolar relaxation Dipolar polarization or orientational polarization depicts the situation where molecules with permanent dipole moments experience a torque in applied fields. This torque encourages otherwise randomly located molecules to reorient themselves in the field direction. The distortion is not instantaneous, and hence is a relaxation process.

Space-charge relaxation Space-charge or interfacial polarization comes into play when materials are heterogeneous and possess different phases or permittivity zones. It is not caused by locally bound charges but by mobile charge carriers such as free ions which would migrate a certain distance upon the application of external fields, especially common in electrode interfaces of capacitors. This process only subjects to very low frequencies.

A dielectric permittivity (both real and imaginary) spectrum versus frequency is given to summarise these polarization and relaxation mechanisms (Figure 2.10).

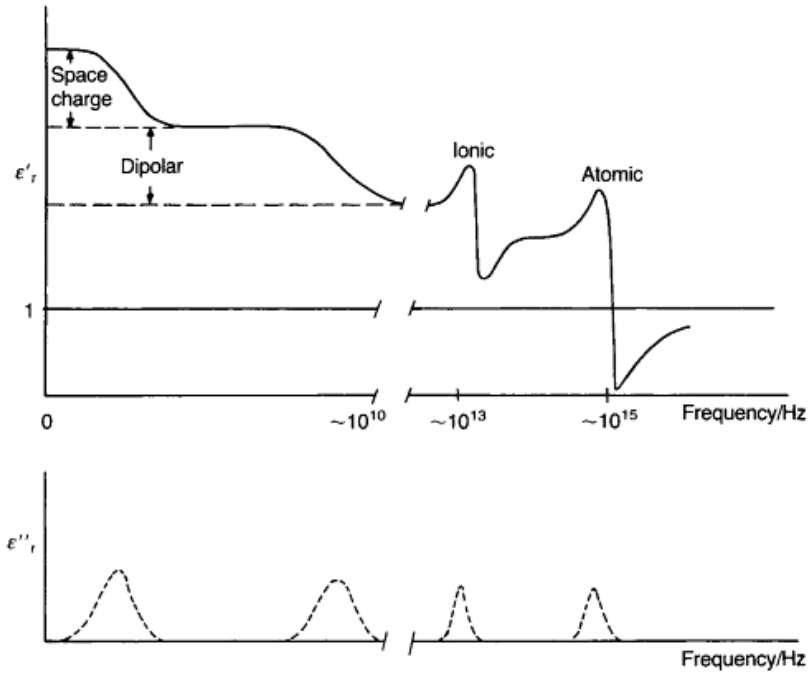


Figure 2.10: Variation of ϵ' and ϵ'' with frequency (picture taken from [18])

Dielectric relaxation and Debye model

Orientation of molecular dipoles is a slow process compared to electronic or atomic polarizations which happens up to 10^{12} Hz. As we have previously discussed in Figure 2.9, only when sufficient time is allowed after the application of electric field for the molecular dipoles to reach their equilibrium will a maximum polarization be achieved (corresponding to ϵ_s). If the dielectric constant is measured instantly after the application of electric field, then we will see the low point of dielectric constant (corresponding to ϵ_∞). Somewhere in between these extreme values, a dispersion is bound to exist connecting high and low dielectric constants. Such relaxation behaviour is pioneered by Debye who gave the Debye dispersion equation for dielectrics with single relaxation time constant τ shown in Equation 2.5.

$$\epsilon^* = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1 + j\omega\tau) \quad (2.5)$$

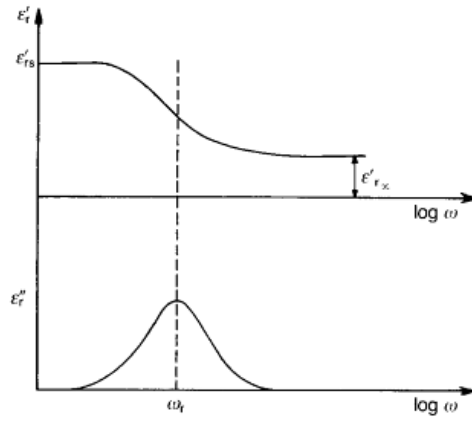


Figure 2.11: Dielectric relaxation (picture taken from [18])

In Argand plane, the Debye model can be presented as in Figure 2.11, known as Cole-Cole diagram, a powerful tool in impedance spectroscopy [19].

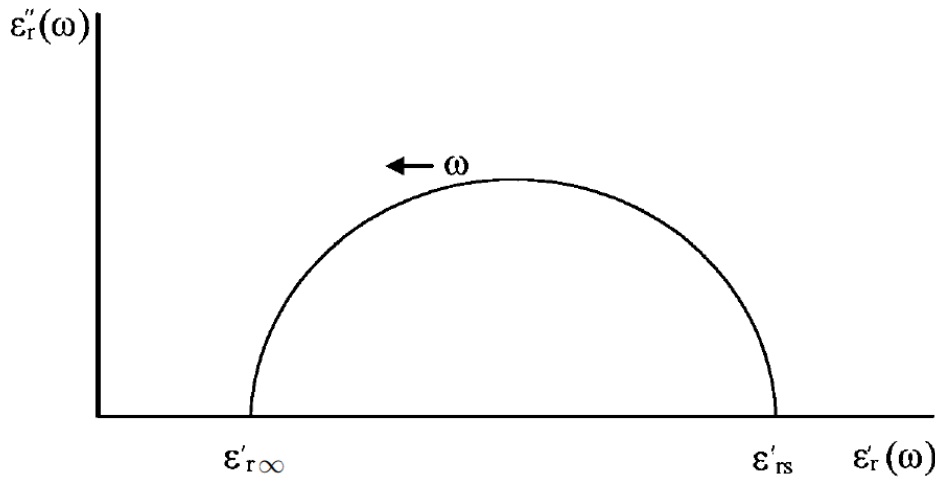


Figure 2.12: Cole-Cole diagram of a dielectric material (picture taken from [18])

2.2.2 Mixing formulas for dielectric composites

To give an accurate prediction of the effective dielectric constant of a composite system is by no means an easy task. In fact, it has been such a demanding job that no theoretical or experimental formulas at present can offer a generic prediction with tolerable accuracy. All sorts of factors have a role in determining the composites' dielectric constant, ranging from less complicated elements of fillers'

volume fraction and dielectric constant of each component to more sophisticated elements of fillers' shape and size, interfaces between components, porosity and even temperature or humidity. Efforts to solve the conundrum have exploited solutions from different angles: effective medium theory, percolation theory and simulational methods are employed to account for experimental results. It has gradually been realised that a fixed equation has trouble in providing a wide applicability and a common practice to amend equations by adding variables (normally to include morphology influence from fillers) emerges with popularity. However, the scarcity in the literature of experimental data to support these mixing rules means that no dominant one could be agreed. In this section we shall introduce some of the most popular formulas involved in literature, classical and empirical, and review each one's applicability and drawbacks.

Classical formulas

The Clausius-Mossotti relation is probably the first formulae developed to relate a macroscopic property (*e.g.* dielectric constant ϵ) to a microscopic property (*e.g.* the molecular polarization α)[21]. In Equation 2.6, ϵ_{eff} indicates the effective dielectric constant, ϵ_e is the dielectric constant of environment materials, α represents polarization of individual inclusion and n is the number of dipoles. It was deduced based on a two-phase homogeneous model. The Clausius-Mossotti relation stands for a perfect situation that have very limited application in reality. More rigorous equations were subsequently invented.

$$\frac{\epsilon_{eff} - \epsilon_e}{\epsilon_{eff} + 2\epsilon_e} = \frac{n\alpha}{3\epsilon_e} \quad (2.6)$$

The Maxwell-Garnett equation was directly evolved from the Clausius-Mossotti equation by replacing the polarization factor with dielectric constant, as shown in Equation 2.7, where f denotes the frequency. The Maxwell-Garnett equation usu-

ally gives a good fitting for composite dielectric constant of polymer/ceramic systems at low loadings (i.e. dilute mixtures). Maxwell-Garnett is a non-symmetric model where matrix and filler do not have an equal contribution to the composite dielectric constant [22]. The model describes small spherical particles embedded in continuous matrix. For mixtures with non-spherical particles, a more generalised effective medium model was proposed by adding a depolarization factor A to include the morphology influence [23][24]. The modified equation is shown in Equation 2.8. One major limitation to the Maxwell-Garnet model is that it only applies to dilute mixtures and minor dielectric constant differences between components. For high filler loadings or high dielectric constant ceramic fillers, the model usually ends up being quite a disappointment. The epoxy/alumina composite dielectric constant ($\epsilon_{epoxy} \approx 3$ and $\epsilon_{alumina} \approx 6$) tested by Frost *et al.* [25] showed good agreement with the prediction, but when using high dielectric constant filler of barium titanate ($\epsilon \approx 6000$), a strong deviation between experiment data and prediction of this model occurred. Similar cases are experimental data of polymer/ceramic fillers systems such as $\text{SrTiO}_3/\text{PEEK}$ [26] and epoxy/ BaTiO_3 [27].

$$\epsilon_{eff} = \epsilon_e + 3f\epsilon_e \frac{\epsilon_i - \epsilon_e}{\epsilon_i + 2\epsilon_e - f(\epsilon_i - \epsilon_e)} \quad (2.7)$$

$$\epsilon_{eff} = \epsilon_e \left[1 + \frac{f(\epsilon_i - \epsilon_e)}{A(1 - f)(\epsilon_i - \epsilon_e) + \epsilon_e} \right] \quad (2.8)$$

The Bruggeman formula [28] is believed to be the most representative formula based on effective medium theory (EMT). It was the first EMT formula employing the idea of percolation and predicted a threshold value. The Bruggeman formula takes two forms of appearance: one symmetric and one asymmetric (Equations 2.9 and 2.10). The symmetric model (Equation 2.9) is for a random distribution of spherical fillers while the asymmetric equation is deduced by a differential approach based on the theory of dispersion of spherical fillers coated by the

host material [29]. It worth noting that Bruggeman formula does not give the solution of an explicit ϵ_{eff} , severely restricting its application as a non-linear equation must be solved to get the value of ϵ . The major advantage of the Bruggeman equation is that it holds its validity till relative high filler content. It remains valid till a high loading of 50 vol % as long as a percolation path is not established [23]. Experimental results where Bruggeman equation gave satisfactory fitting for polymer/ceramic composites with high loading content and substantial discrepancy in components' dielectric constants can be found in the literature [30] [25].

$$(1 - f) \frac{\epsilon_m - \epsilon_{eff}}{\epsilon_m + 2\epsilon_{eff}} + f \frac{\epsilon_i - \epsilon_{eff}}{\epsilon_i - 2\epsilon_{eff}} = 0 \quad (2.9)$$

$$\frac{\epsilon_i - \epsilon}{\epsilon^{\frac{1}{3}}} = (1 - f) \frac{\epsilon_i - \epsilon_m}{\epsilon_m^{\frac{1}{3}}} \quad (2.10)$$

Lichtenecker logarithmic mixing law The Lichtenecker formula stemmed from the famous 'power-law' approximation with a general form shown in Equation 2.11. The rationale behind this equation is simply averaging the permittivity by volume weights [22]. The variable β could vary from -1 to 1 depending on the shape and orientation of fillers [31]. Several well-known formulas with specific β values are the Birchak formula ($\beta=1/2$), Looyenga formula ($\beta=1/3$) and the limiting case of the Lichtenecker formula ($\beta \rightarrow 0$, representing a mixture with randomly distributed nearly spherical fillers [32]) shown in Equation 2.12. A modified form of the Lichtenecker formula was proposed and tested to give consistent fitting in many cases. The modified Lichtenecker formula is shown in Equation 2.13, in which a empirical parameter k was utilized to bring in the interaction between matrix and filling materials. Unlike the morphology parameter A in the modified Maxwell-Garnett formula which is only determined by the filler material, the value of k depends on both components and a value of 0.3 seen suited for most well-dispersed polymer-ceramic composites [33] [34]. There is no conclusion

about which particular composite mixtures the Lichtenecker formulas are applicable to. The dielectric constant of a SrTiO₃/PEEK composite studied by Nisa *et al.* was proved to fit the best with the Lichtenecker formula [26] and so was the performance of epoxy/BaTiO₃ composites by Cho *et al.* [27] and also by Ramajo *et al.* [35]. Some other cases such as the COC/BST composite tested by Hu *et al.* turned out to be well predicted using a modified Lichtenecker formula with $k \approx 0.43$ [36].

$$\epsilon_{eff}^\beta = f\epsilon_i^\beta + (1-f)\epsilon_e^\beta \quad (2.11)$$

$$\epsilon_{eff} = \epsilon_i^f \epsilon_e^{(1-f)} \quad \text{or} \quad \log \epsilon_{eff} = f \log \epsilon_i + (1-f) \log \epsilon_e \quad (2.12)$$

$$\log \epsilon = \log \epsilon_e + v_i(1-k) \log(\epsilon_i/\epsilon_e) \quad (2.13)$$

More empirical options

Predicting the effective dielectric constant of a heterogeneous composite system is of a highly empirical nature. Thus all modelling theories as well as formulas are bound to be imperfect and recognised to have characteristic strengths and limitations. It is generally believed that all mixing rules are bound to lose their validity when the content of loading fillers is too high (poor dispersion and porosity increase in the composites are most likely to be the cause). We shall introduce a couple of more empirical equations which were generalised and tested in experiments and deemed to be effective for particular conditions.

The Yamada equation was proposed from a study of the binary system of PZT powder with PVDF matrix [37]. Unlike most models initiated by researchers, the Yamada equation carries two independent variables, loading volume fraction V_c and morphology factor n which is determined purely empirically (Equation 2.14). This shows the emphasis of morphology on the effective dielectric constant in Yamada's model. Bai *et al.* applied the Yamada formula to fit the composite dielectric constant of P(VDF/TrFE)/PMN-PT [38]. A matched fitting was

achieved with $n = 10.6$ comparable to the value of 8.6 given by Yamada himself.

$$\epsilon_{eff} = \epsilon_p \left[1 + \frac{nV_c(\epsilon_c - \epsilon_p)}{n\epsilon_p + (\epsilon_c - \epsilon_p)(1 - V_c)} \right] \quad (2.14)$$

The Jayasundere-Smith equation shown in Equation 2.15 was derived from modifying the well-known Kerner equation by including neighbouring molecule interactions [39]. The model is based on calculation of the dielectric constant of piezoelectric dilute composite system. It is valid for estimating the dielectric constant of polymer-ceramic composites where $\epsilon_i \gg \epsilon_m$, but not for situations where $\epsilon_i < \epsilon_m$ [40]. However, when the dielectric constant of the ceramic loading exceeds 1000, the Jayasundere-Smith equation can barely notice any change. Experimental proof of the Jayasundere-Smith equation in fitting the polymer/ceramic composite dielectric constant can be found in the literature [27].

$$\epsilon_{eff} = \frac{V_p\epsilon_p + \epsilon_c V_c \left(\frac{3\epsilon_p}{\epsilon_c + 2\epsilon_p} \right) \left[1 + \frac{3V_c(\epsilon_c - \epsilon_p)}{\epsilon_c + 2\epsilon_p} \right]}{V_p + V_c \left(\frac{3\epsilon_p}{\epsilon_c + 2\epsilon_p} \right) \left[1 + \frac{3V_c(\epsilon_c - \epsilon_p)}{\epsilon_c + 2\epsilon_p} \right]} \quad (2.15)$$

2.2.3 Polymer Matrix

In light of virtues such as light-weight, ease of processing, high dielectric strength, superb mechanical properties that polymers manifest, they are considered the superior matrix choice for high dielectric constant (high-k) composites which attracts enormous interests for their great potential in electronic applications, such as transducers, piezo-sensors, hydrophones, telecommunication devices and capacitors [41].

Material	Dielectric Constant
PTFE [Poly(tetrafluoroethylene)]	2.1
PP (Polypropylene)	2.2
PE (Polyethylene)	2.3-2.65
PS (Polystyrene)	2.4
ABS (Acrylonitrile-butadiene-styrene)	2.6
Modified PPO (Polyphenylene oxide)	2.7
PC (Polycarbonate)	3.0
PET [Poly(ethylene terephthalate)]	3.0-3.3
Acrylic resins	3.0
PBT (Polybutylene terephthalate)	3.1
PPS [Poly(phenylene sulfide)]	3.2
PEEK [Poly(ether etherbetone)]	3.3
LCP (Liquid-crystal polymer)	3-4
Acetal copolymers	3.7
PVC [Poly(vinyl chloride)]	4.0
PA 66 (Polyamide 66)	4.6
PVF [Poly(vinyl fluoride)]	8.2-8.5
PVDF (Polyvinylidene fluoride)	8.2-9.5

Table 2.1: Dielectric constants of selected polymeric substances [42]

Polar and non-polar polymers

Generally speaking, polymers have relatively low dielectric constants when compared to other dielectrics, for instance ceramics. But there is a certain degree of variation in dielectric constant within different types of polymers. In table 2.1, the dielectric constants of some common polymers are listed.

To better understand such variation we are going to discuss polymers under polar and non-polar regimes. Nonpolar polymers represent the simplest case where permanent dipoles do not exist. Examples like PE or other similar assemblies of $-\text{CH}_2-$ usually reveal relatively low dielectric constants where polarization is mainly electronic. For polar polymers, permanent dipoles exist in the polymeric chains but the resulting net effect depends on whether individual segments reinforce or balance each other out. For example in PTFE, alternating $-\text{CF}_2-$ groups balance each other exactly so it has a low dielectric constant. The opposite case is PVC, whose C-Cl dipole moments are additive in a zigzag conformation, so it

has a high dielectric constant.

Factors influencing the dielectric constant in polymers

The dielectric constant itself is a frequency variant parameter, as seen in Figure 2.10. Given the complex long chain structure of most polymers, some other factors also have an impact on the dielectric constant of polymers. Effects of additives, temperature and frequency etc. all have influence on dielectric constant.

During the processing of polymers, additives like plasticizers, antioxidants, stabilizers exert huge importance. However, these residual chemicals could result in elevation of dielectric constant of polymers. On the optimistic side, polymers are usually ideal candidates of matrix materials for composites processing. Choosing conducting fillers like carbon blacks could result in a dramatic increase in the dielectric constant of such polymer-based system. Added carbon blacks would be surrounded by a polymeric insulating layer and induce considerable effect of interfacial polarization. With a 30-60 weight percent of carbon black particles, the composite's dielectric constant could be enhanced to more than 100. Besides carbon blacks, high dielectric constant ceramic particles are also good options (BaTiO_3 etc.). The inhomogeneity in such materials brings in large interfacial polarization and consequently big jump in ϵ . Details about composite systems will be addressed more comprehensively later.

Commercially available polymers

Commodity polymers are extensively applied in industry covering a wide range of properties. Most of these polymers are synthetic although polymers with natural origin are employed as well. Normally we categorise synthetic polymers into

plastics, elastomer (or rubber) and fibers. Priority here goes to plastics which is of the greatest interest to our research.

Plastics generally can be classified into following three groups: 1. Commodity or bulk resins, including PVC, PE, PP and PS; 2. Engineering plastics which offers improved mechanical, electrical and thermal properties; 3. High-performance resins reveal superior characteristics especially for performances at high temperatures.

We will mainly address engineering plastics here. Regular service engineering plastics include [42]:

1. *ABS* is a copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. For most applications, ABS can be used between -25 and 60 °C. Although ABS is mainly used for mechanical purposes, it also has fairly constant electrical properties over a wide range of frequencies. ABS polymers are also resistant to aqueous acids and alkalis. They are soluble in esters, ketones, and ethylene dichloride.

2. *PCs* Polycarbonate has a glass transition temperature of ~ 150 °C. Unlike most thermoplastics, polycarbonate is capable of a large degree of deformation without cracking thus can be processed at room temperature using sheet metal techniques.

3. *PAs* Polyamides include a number of polymers distinguished by the number of carbon atoms. Crystalline polyamides have high tensile strength and impact strength as well as abrasion resistance. They are resistant to non polar solvents but can be dissolved in polar solvents.

4. *Polybutylene terephthalate (PBT)* PBT is a semicrystalline thermoplastic with heat resistance up to 150 °C. It has good mechanical properties and is resistant to solvents. 5. *Polyethylene terephthalate (PET)* PET is a thermoplastic polymer resin from the polyester family. Depending on processing history, PET may exist in both amorphous and semicrystalline states.

High-Performance Plastics include polymeric materials that exhibit superior resistance to elevated temperatures, chemicals and mechanical forces. These plastics are usually suitable for service at temperatures > 150 °C. Many polymers can be attributed to this group: Poly(p-phenylene oxide) (PPO) or poly(p-phenylene ether) (PPE), Polysulphone (PSU), Polyether ether ketone (PEEK), Polyetherketone (PEK), Polyimide (PI), Polyamide-imide (PAI), Polyphenylene sulfide (PPS), Polyacrylates, Polyetherimide (PEI), Polyoxymethylene (POM), Fluoroplastics. Among them, fluoroplastics are a rather unique group in which several monomers are used in synthesis. The first fluoropolymer discovered was PTFE in early 1950s. The uniqueness of fluoropolymers is determined by two factors: strong bond between fluorine and carbon and shielding of carbon backbone by fluorine atoms. The group of fluoroplastics have high chemical inertness, low friction coefficient and several of them have very high melting points, particularly PTFE and perfluoroalkoxy (PFA) resins. Some of them are excellent dielectrics and most of them show high resistance towards common solvents, UV radiation and chemicals. The main fluoroplastics are listed in Table 2.2.

ETFEs exhibit an excellent balance of physical, chemical, mechanical and electrical properties. They can be readily processed by melt-processing techniques (e.g. extrusion, injection molding etc.). PVDF homopolymer is a semicrystalline polymer with a degree of crystallinity varying from 35 to over 70 percent, and there are four distinct crystalline forms in PVDF. The dielectric constant of PVDF can be as high as 17 in some samples, accompanying a high dielectric loss

Abbreviation	Name
ETFE	Copolymer of ethylene and tetrafluoroethylene
ECTFE	Copolymer of ethylene and chlorotrifluoroethylene
EFEP	Terpolymer of ethylene, tetrafluoroethylene and hexafluoropropylene
FEP	Copolymer of tetrafluoroethylene and hexafluoropropylene
MFA	Copolymer of tetrafluoroethylene and perfluoromethylvinyl ether
PCTFE	Poly(chlorotrifluoroethylene)
PFA	Copolymer of tetrafluoroethylene and perfluoropropylvinyl ether
PTFE	Poly(tetrafluoroethylene)
PVDF	Poly(vinylidene fluoride)
PVF	Poly(vinyl fluoride)
THV	Terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride

Table 2.2: Major industrial fluoroplastics [42]

factor as well. PCTFE shows excellent mechanical properties, chemical resistance and optical properties. The drawback of PCTFE is its low thermal stability in the molten state. PVF exhibits high resistance to weathering, satisfactory mechanical properties and chemical resistance. High dielectric strength and dielectric constant are also observed in PVF.

Several popular matrix choices found in literature are:

1. epoxy ($\epsilon \approx 3 \sim 4.5$) forming composites with ceramics BaTiO_3 , alumina and PMN-PT etc. [25, 33, 35]
2. PVDF ($\epsilon \approx 8.9$) where ceramic fillers were PZT, BT etc. [37, 43, 44]
3. P(VDF/TrFE) ($\epsilon \approx 17$) used to form extra high dielectric constant composites with PMN-PT [38]
4. PTFE ($\epsilon \approx 2.1$) in composite mixtures with ceramic fillers of $\text{Sr}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$, CaTiO_3 etc. [45, 46].

2.2.4 High dielectric constant fillers

High ϵ fillers to combine with the polymer matrix mainly consists of four types: metals, ceramics, carbon based materials and organic fillers [23]. Each option has its advantages and inevitable drawbacks. By using conductive fillers such as metals or carbon nanotubes, a sharp increase in dielectric constant can be achieved near the percolation threshold which is normally extremely low for conductive fillers. In these cases, the mechanical properties of the polymer matrix would not be severely affected by addition of fillers, which is highly desirable for processing and industrial applications. Real cases include a very high dielectric constant of 200 realised in an epoxy/silver composite [47], a dielectric constant of 400 in Ni/PVDF [48, 49] as well as abundant data in CNT realm [50–52]. On the downside, employment of metals would introduce high dielectric loss which makes them unsuitable for certain electromagnetic applications such as signal transmission. The problem with carbon nanotubes is their long chain structure and high surface energy, causing easy entanglement and it is thus difficult to disperse them uniformly into polymers. Ceramic fillers are the most conventional and widely applied option for polymeric composites. Advantages range from predictable dielectric constant, low loss and easy fabrication. Drawbacks are fast deteriorating mechanical properties for composites when the filler loading gets very high.

2.2.5 Ceramic dielectrics

Ceramic dielectrics occupy a significant position in a range of industrial applications such as power storage and telecommunication. Computer and communication technology inject great impetus for the development of ceramic dielectrics or insulators. The advancement in telecommunication systems calls for dielectrics to operate at higher frequencies and the increased complexity of components demands miniaturization in device manufacturing. This section describes the functionality of ceramic dielectrics, examining initially their polarization mecha-

nisms. Then we will uncover factors that control the dielectric constant in these materials based on a representative model—BaTiO₃. Finally, more high-k ceramic dielectrics are probed as potential candidates.

Spontaneous polarization

The most efficient and self-evident way to analyse the physical behaviour of a ceramic material requires the knowledge of its crystal structure. As to dielectric behaviour, the distinction between instant and spontaneous polarizations (or polar and non-polar ceramics) will suffice. Of the 32 crystal classes, 11 are centrosymmetric i.e. non-piezoelectric. Of the remaining 21 non-centrosymmetric classes, 20 are piezoelectric and of them 10 are polar [18].

Piezoelectric crystals are those undergo polarization when they are stressed and conversely become strained when an electric field is applied. The 10 polar crystal types are also pyroelectric as well as piezoelectric, so polarization is induced when the temperature changes. A limited number of pyroelectric materials possess an additional property that applied fields could reverse their spontaneous polarizations. We term such materials as ferroelectric materials, in analogy to ferromagnetism.

BaTiO₃—the prototype ferroelectric ceramic

Barium titanate is the first ceramic material in which ferroelectricity was observed and most exhaustively studied as well. BaTiO₃ is like a textbook for the study of ferroelectricity. First of all, let us examine the crystal structure and microstructure of BaTiO₃, see Figure 2.13. The crystal structure of BaTiO₃ belongs to the perovskite structure ABO₃. When BaTiO₃ is in the cubic phase, each barium ion is surrounded by 12 oxygen ions. Together they form a face-centered cubic lattice. Titanium atoms are in octahedral interstitial positions crowded with six oxygen

ions. The octahedral interstices are quite big due to the large size of barium ions, especially for small titanium ions. This gives titanium ions the liberty to wobble in the interstices. It is believed that the minimum-energy positions are off-center in the direction of each oxygen ions next to the titanium ion [53]. When titanium ions fall into these minimum-energy sites, spontaneous polarization would be induced for each Ti^{4+} . Since each Ti^{4+} possess a +4 charge, this polarization is quite considerable and accounts for the BaTiO_3 's high dielectric constant.

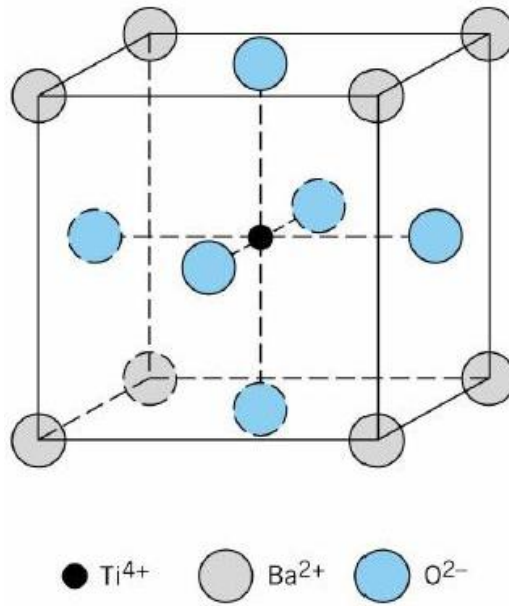


Figure 2.13: the unit cell of BaTiO_3

Temperature dependence of dielectric constant of BaTiO_3 The temperature effect on dielectric constant is revealed through the phase transition in BaTiO_3 . There are four phases for BaTiO_3 : cubic, tetragonal, orthorhombic and rhombohedral, with transition temperatures near 130°C , 0°C and -90°C respectively. Permanent dipoles exist in all phases but cubic. In the tetragonal phase, the dipole moment is along the c direction while the polar axis is parallel to a face diagonal in the orthorhombic structure and parallel to a body diagonal in rhombohedral structure, see Figure 2.14. Therefore, 130°C becomes a critical point where above it barium titanate loses its ferroelectricity at temperature. We

term it the Curie temperature or Curie point (T_c). The polarization and dielectric response to temperature change were pointed out by Merz in 1949 [54] and are demonstrated in Figure 2.15. It is well illustrated that as a phase transition happens accompanying temperature change, the degree of spontaneous polarization is affected and consequently the dielectric constant in different directions. In the cases of polar crystal structures (tetragonal, orthorhombic and rhombohedral), the polarizations are high anisotropic. Take the tetragonal structure for instance, the relative dielectric constant along the c-axis in a tetragonal BaTiO_3 single crystal is only $\epsilon_c \approx 400$, whereas in the two perpendicular directions $\epsilon_a = \epsilon_b \approx 4000$. Generally speaking, the dielectric constant in a polycrystalline system takes the average of values from different directions. The relative permittivity of approximately $\epsilon_r \approx 1500\text{-}2000$ observed at room temperature is in good agreement with the average theory [55]. The dependence of dielectric constant on temperatures is shown in Figure 2.16 for a barium titanate grain size of $25\ \mu\text{m}$. It is evident that the dielectric constant peak occurs at the Curie point.

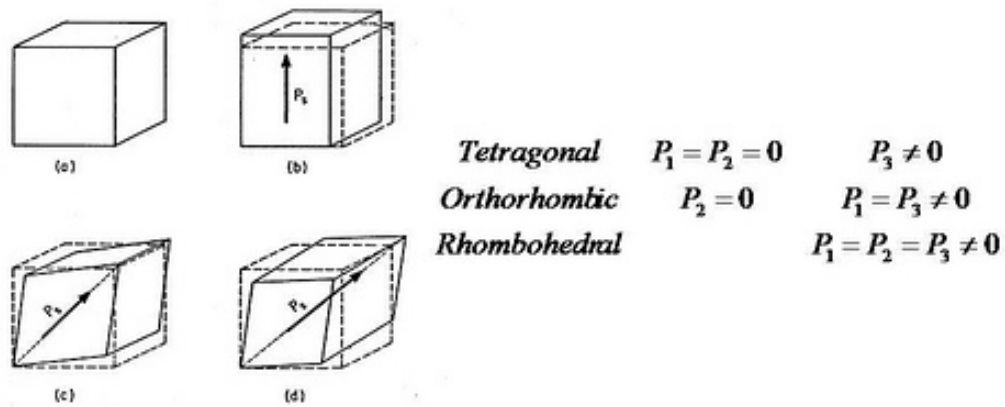
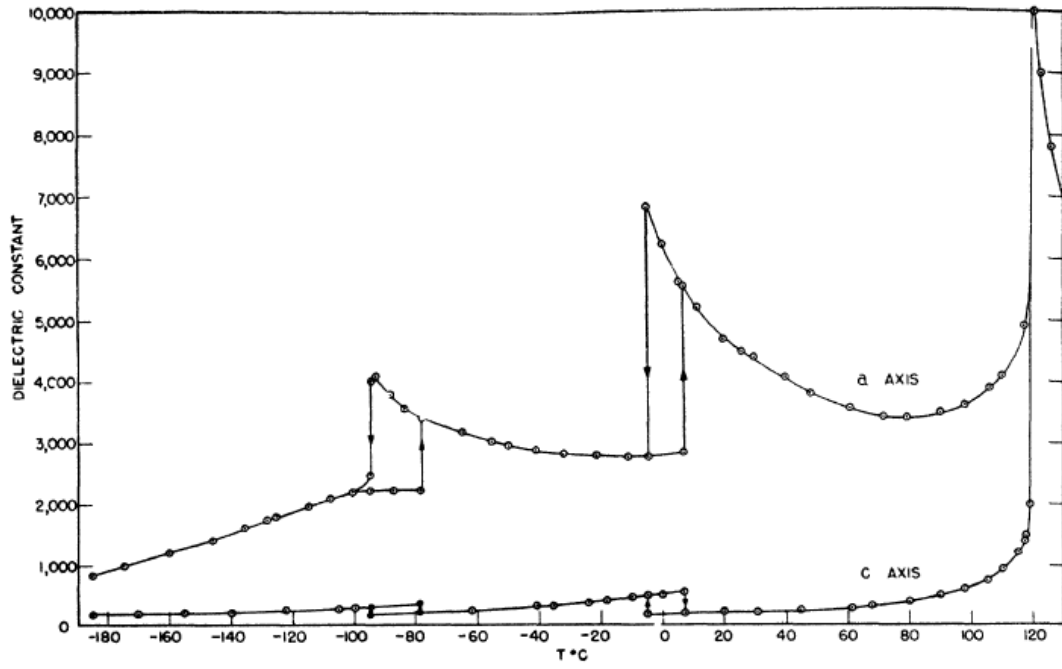
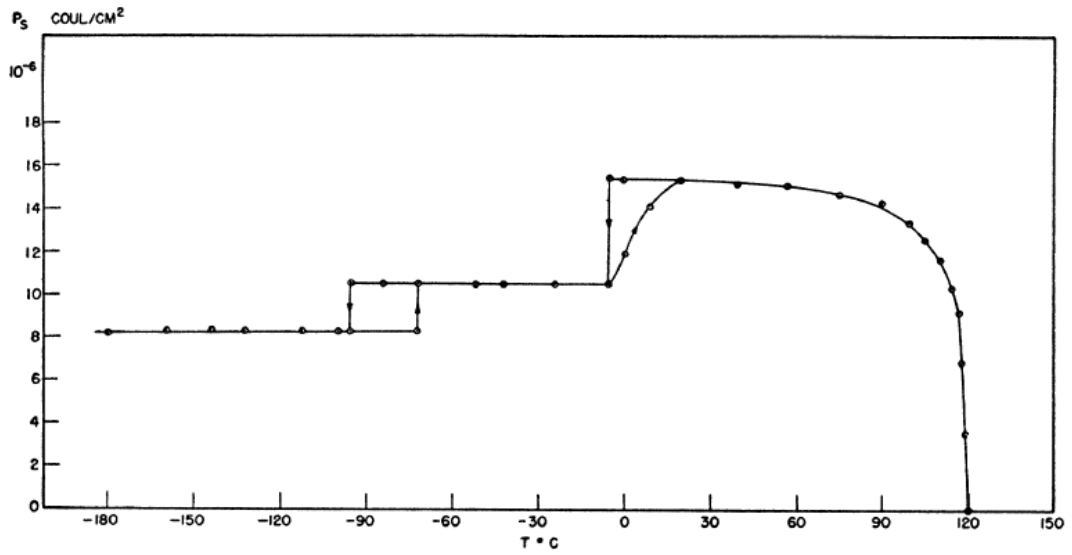


Figure 2.14: unit-cell distortion of the polymorphs

Size effect on dielectric constant of BaTiO_3 The strong dependence of grain size on the phase transition and dielectric behaviour of barium titanate is well acknowledged. In light of the massive demand for devices to go lighter and



(a)



(b)

Figure 2.15: (a) Dielectric constants along different axis ϵ_a and ϵ_c , as function of temperature (b) Spontaneous polarization P_s , as function of temperature (picture taken from [54])

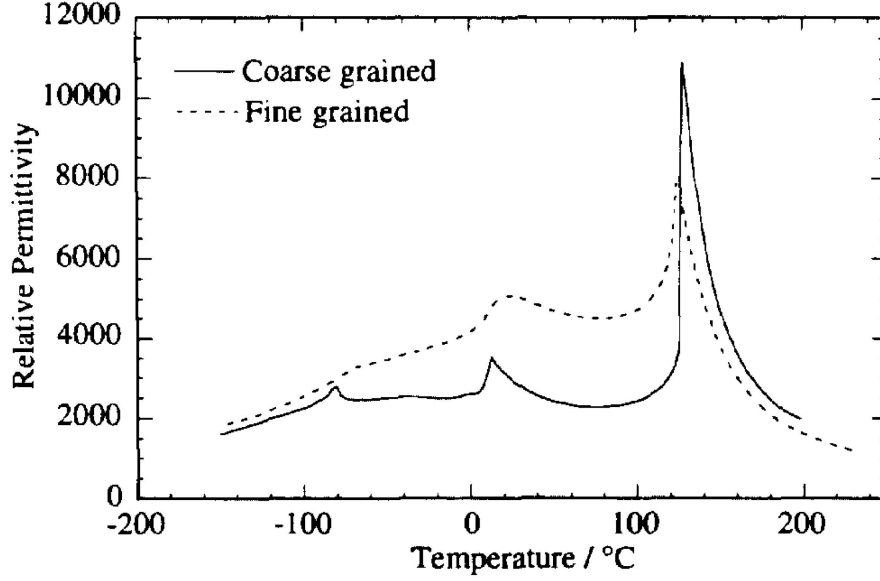


Figure 2.16: Dielectric constant versus temperature of BaTiO₃ (picture taken from [56])

smaller, the tendency to develop micro and even nano barium titanate powders is inevitable. The effect grain size has on dielectric behaviour of barium titanate has been studied extensively. To shed light on the quality change size reduction introduces to dielectric constant, a coarse comparison can be found in Figure 2.16, where compared to coarse grained (grain size $> 10 \mu\text{m}$) barium titanate particles, fine grained (grain size $< 1 \mu\text{m}$) see an overall increase in relative permittivity along the temperature range. In the quantitative sense, the relative dielectric constants of various grain size barium titanate particles were measured at 25 and 70 °C by Hennings, in Figure 2.17. From the plot it is evident that dielectric constant of barium titanate particles experiences an initial increase till a peak value and then dropped abruptly when particle sizes decrease from *ca.* 100 μm to *ca.* 0.2 μm . A pronounced maximum value of $\epsilon_r \approx 5000-6000$ occurred at approximately 0.7-0.8 μm . The high permittivity values appeared in the experiments were interpreted using domain wall contribution theory, where the striking increase in the density of 90° domains contributed to dielectric constant elevation when the grain size was reduced to approximately 1 μm . It is believed that no ferroelectric domain could exist below 1 μm as the grain size was sim-

ply too small to contain any, explaining the drop in dielectric constant after the peak. The size effect also manifests itself through influencing the cubic-tetragonal phase transition temperature (Curie temperature). For bulk barium titanate, the cubic-tetragonal transition takes place at approximate 130 °C. However, a shift of Curie point to much lower temperatures (e.g. room temperature) was spotted when the grain size was decreased. Uchino *etal.* reported a critical particle size of 0.12 μm at which the cubic-tetragonal transition happened at room temperature [57]. The reported critical particle size agreed well with the data shown in Figure 2.17, indicating that the dielectric constant peak of BT could be a result of cubic-tetragonal phase transition due to shift in Curie temperature. It is worth mentioning that the critical size is also subject to various parameters such as processing methods (e.g. hydrothermal, sol-gel) and impurities.

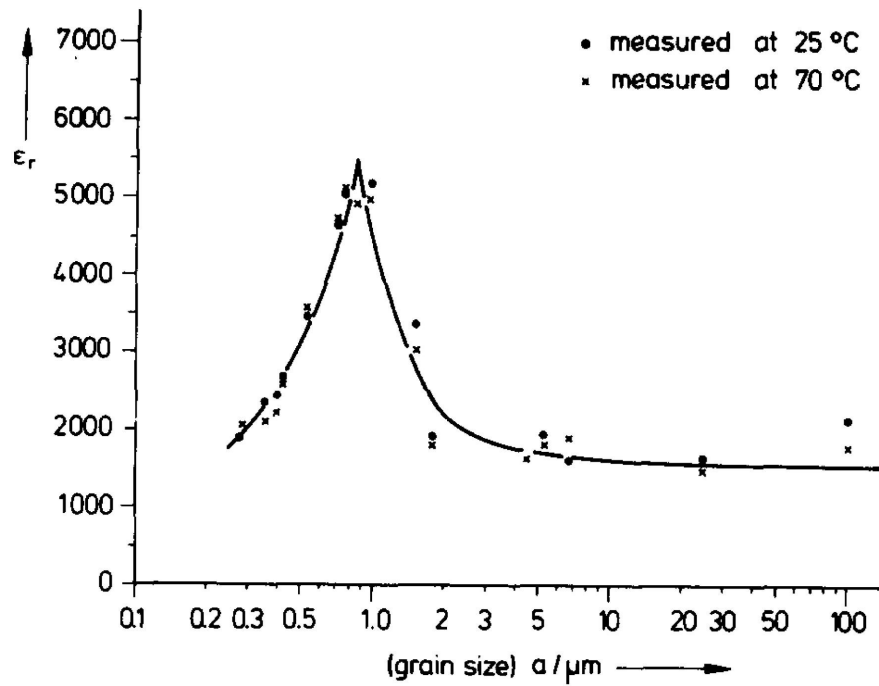


Figure 2.17: Grain size dependence of relative permittivity of BaTiO₃ at 25 and 70 °C (picture taken from [55])

high-k ceramic materials

Dielectrics with dielectric constants exceeding 1000 are based on ferroelectric materials and are sensitive to factors like temperature and frequency than low permittivity dielectrics. BaTiO₃ and modified barium titanate dielectrics are the most widely applied high permittivity ceramics. Approaches to modify barium titanate ceramics such as choosing appropriate crystal size and substituting barium and titanium ions with other elements sometimes can be surprisingly beneficial to ceramic properties. For example, substitutional zirconium, hafnium and tin lower the cubic-tetragonal transition temperature of barium titanate but raise the temperature of the other two transitions thus they almost coincide in the neighbourhood of 50 °C and show a particularly high dielectric constant. Other well-known ferroelectric materials include PZT (Pb[Zr_xTi_{1-x}]₂O₇, 0 ≤ x ≤ 1) which is a ceramic perovskite showing remarked piezoelectric, pyroelectric and ferroelectric properties. The dielectric constant of PZT ranges from 300 to 3850 depending on orientation and doping. PZT plays an important role in applications of ultrasound transducers, ceramic capacitors and STM/AFM actuators. Another ferroelectric ceramic widely used is lithium niobate (LiNbO₃) especially in the telecoms market (e.g. mobile telephones, optical modulators).

2.3 Processing of Polymer-Ceramic Nanocomposites

Thanks to the excellent processability of polymers, various processing methods are available for manufacturing polymer/ceramic composites. In light of particular requirements for industry such as high dielectric constant, low capacitance tolerance, low dielectric loss, good processability, temperature and chemical endurance and low cost, specific processing route can be chosen for particular components. As so far no single processing method could satisfy all the requirement

Shaping technique	References
Casting/freeze casting	Melcher and colleagues
Impregnation/infiltration	Satoa and colleagues
Tape casting	Cromme et al.
Coating (spraying, dip- or spin-coating, chemical vapor deposition)	Goerke and colleagues
Pressing (cold/warmuniaxial, coldisostatic)	Haug and colleagues
Injection molding	Zhang and colleagues
Extrusion	Mutsuddy and colleagues
Fiber drawing	Bunsell and colleagues
Blowing/foaming	Zeschky and colleagues
Machining	da Rocha et al.
Joining	Colombo and colleagues
Rapid prototyping	Friedel et al.
Ink jetting	Mott and colleagues
Electro-hydrodynamic-spraying/spinning	Nangrejo and colleague
Aerosol spraying	Xiao and colleagues
Self-assembly	Garcia and colleagues
Microcomponent processing (UV/X-ray lithography, nano-/microcasting, replication, microextrusion, embossing/forging)	Hanemann and colleagues
Microfluidics processing	Ye et al.
Emulsion processing	Bakumov et al.
Formation of nanostructures (tubes, fibers, wires, cables, belts, coils), directly by pyrolysis	Otoishi and colleagues

Table 2.3: Common seen processing methods for polymeric materials [58]

listed above, sacrifices and compromises are inevitable as long as the primary concerns are served. A list of common processing methods is provided below (Table 3.1)accompanied with an illustration of several most popular ones (Figure 2.18).

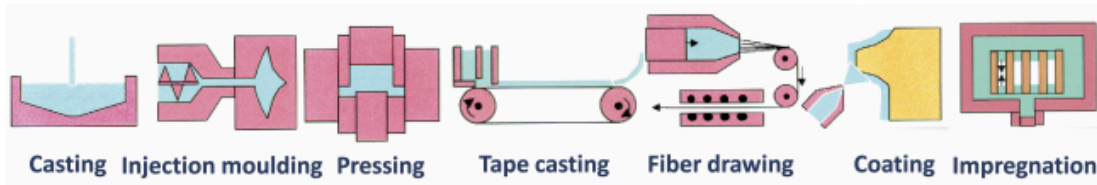


Figure 2.18: polymer processing methods (picture taken from [58])

Spin Coating

Spin coating has been extensively applied to processing polymer/ceramic composites, especially for the use of producing high capacitance thin films[59, 60]. It has two major drawback: substantial waste of raw materials and non-uniformity in the thickness of films [61]. The amount of solvent and spin coating speed work together to control the viscosity of the suspension and eventually the thickness of films. Thinner films are produced at higher speeds and when suspensions with lower viscosity are selected. The speed of spin coating was also believed to have an effect on the dielectric behaviour of product films by affecting filler agglomeration and porosity [62]. Because of these drawbacks, many researchers seek improved processes based on spin coating. One example is comma roll coating. Compared to spin coating, the obvious advantages of comma roll coating include no materials waste, uniform film thickness and high productivity [61]. A figure outlining a comma roll coater is shown in Figure 2.19.

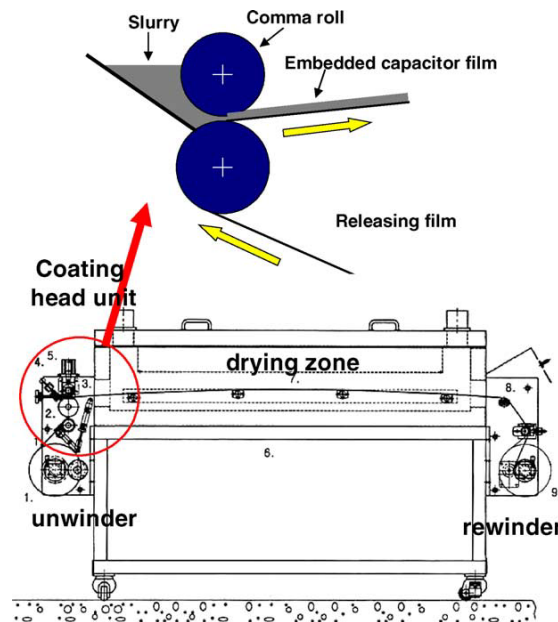


Figure 2.19: Film capacitor fabrication using a comma roll coater (picture taken from [61])

Extrusion

Extrusion is widely used for fabricating thermoplastic polymers for end products like wire insulation, tubing, profile, film and sheet [63]. The extrusion process consists of melting the polymer and then forcing it through a die. Extrusion is believed to be a continuous process that forms products in two dimensions. The x-y dimensions form the cross-section while the z dimension marks the length of extrudate. Since the product's cross-section is formed in a die, it will always maintain a constant cross-section. Depending on the intended use, there are different extrusion method to choose for example single and twin-screw types.

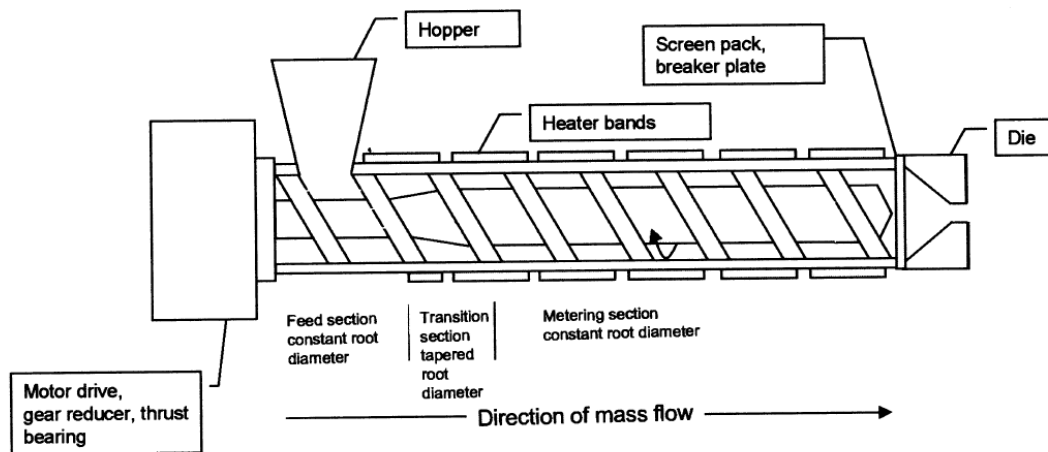


Figure 2.20: Component parts of a single-screw extruder (picture taken from [64])

Injection molding

Injection molding is a process to produce a complex part shape in a single operation. The most significant feature for injection molding is that it integrates many operations into one rapid and automatic operation. Injection molding machines and molds can be very costly because of the high pressure endured during the injecting process and the complexity of process controls. However, the single operation feature offsets this drawback and renders it economically viable.

Compression molding

Compression molding is regarded as one of the most conventional ways to process plastics. The whole process can be described as: plastic sources are placed on the bottom of one heated mold before the other half mold is lowered and pressure is applied. Under the influence of heat and pressure, plastics start to soften and flow to fill the mold. The mold is then reopened with the part completed. Commercial compression molding usually adopts high temperature and pressure to shorten the processing cycles.

Spraying

Spraying is a novel and economical processing method for liquid phase composites. It is useful especially in applications with high design complexity such as multilayer structures and curved surface coating. An illustration of spraying for the fabrication of multilayer coatings is shown in Figure 2.21. The ease of adjusting processing conditions and the potential for scaling up makes it attractive for industrial manufacturing. Successful experimental examples using spraying process to fabricate dielectric thin films can be found in literature [50, 65, 66].

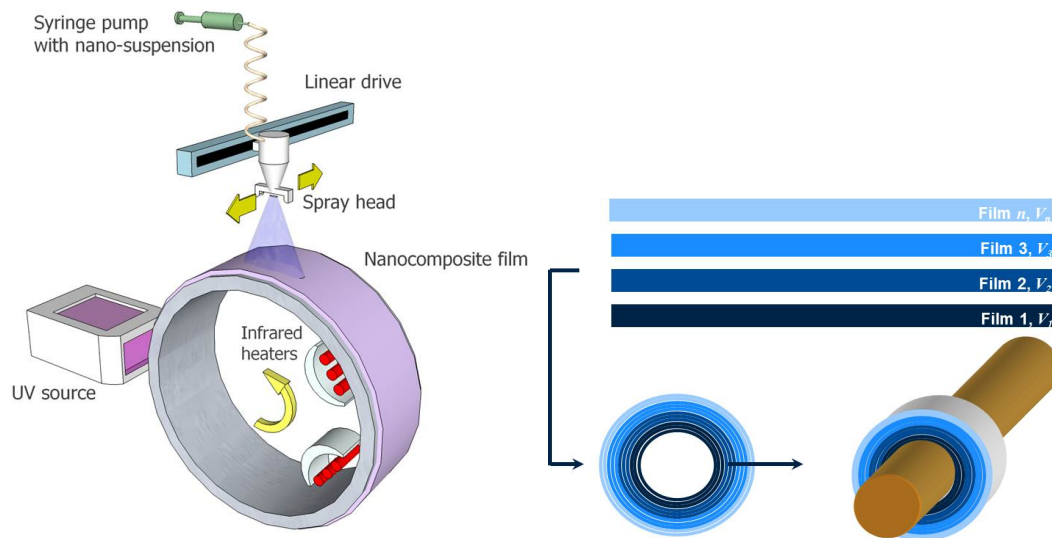


Figure 2.21: Spraying method to manufacture layered coatings with customised properties (QUEST application funded by EPSRC)

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Chapter 3

Experimental Techniques

3.1 Processing Routes

The main objective of this project is to explore suitable processing routes to manufacture dielectric composite materials with customised electromagnetic properties and geometries. In this work, three manufacturing techniques; spray deposition, casting and 3D printing were investigated for their distinct strengths and limitations to meet different material requirements. An introduction to these processing routes is given below.

3.1.1 Spray Deposition

Spray deposition is a convenient and cost-effective manufacturing technique for producing high quality polymer-ceramic composite films for various applications such as capacitors. The spraying system comprises a pneumatic nozzle, syringe pump and compressed air supply as marked in Figure 3.1. Minimal equipment maintenance is required and this method is suitable for efficient small quantity spraying when compared with spin-coating whose one major drawback is significant waste of precursor materials [1]. Pre-stabilised polymer-ceramic composite suspensions were fed by the syringe pump at a constant speed to the nozzle, at

the tip of which high pressure compressed air atomises liquid droplets into fine mists. The shape of the cone of the mists is adjustable by applying compressed air from different directions or at different pressures. Eventually the fine mists are projected onto a clean surface and deposit into a compact film structure. Depending on the types of polymer or monomers chosen, the final product could be cured either by heat or UV light. Both aqueous and non-aqueous composite suspensions have been demonstrated to be suitable for this spraying apparatus from the group's previous work [2, 3].

In this project, with the aim of customising the dielectric properties of these films, a polymer matrix material and high dielectric constant ceramic nanoparticle fillers were chosen as the composite feed. The key steps of the spraying process were identified as suspension preparation, spray deposition, heat curing and electrical conductor layer deposition as shown in the flow diagram in Figure 3.2.

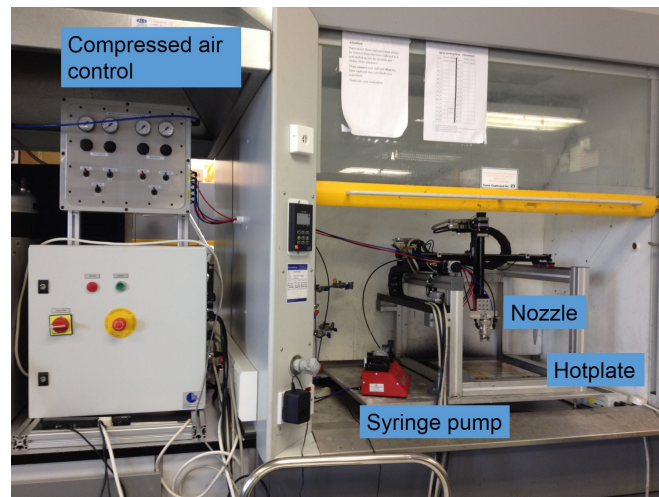


Figure 3.1: A picture of the spraying apparatus used in this work

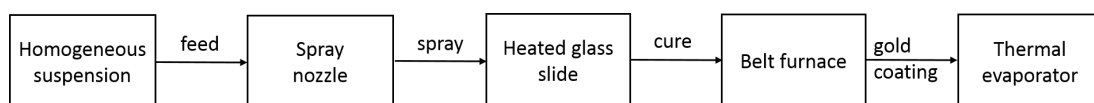


Figure 3.2: The manufacturing process for sprayed films

Spray parameter optimisation

The parameters critical to the spray process are highlighted in Figure 3.3. Optimisation of these parameters was required to produce good quality composite films. They include:

Nozzle tip size Lechler offers a series of nozzle tips with diameters ranging from 0.015 to 0.1 inch. Smaller diameters generate finer atomised particles but are more vulnerable to blockages. Blockages occurring in the middle of a spray process would be catastrophic to the film quality. Larger orifices also have the problem of creating rough surfaces due to the large atomised particles. In this work, middle range 0.023 and 0.031 inch orifices were tested for their applicability. Although the 0.023 inch orifice shows occasional blockage for very viscous suspensions, the situation can be improved by better particle de-agglomeration. It produced smoother and better surface quality films than the 0.031 inch orifice and therefore was mainly used in this work.

Nozzle head height The height from the nozzle head to the hotplate determines the area that is sprayed on when the mists are depositing on the hotplate. Because the atomised mist is less concentrated in the outer range of the cone than the core, a high nozzle height (up to 20 cm) could cause uneven film deposition on the glass slides whereas a low nozzle (down to 6 cm) head height although results in a more confined area of deposition on glass slides could also cause film flaking due to the high pressure. A nozzle head height of 10 - 15 cm has been proved to be optimal.

Atomisation pressure The air pressure controls the degree of atomisation and also needs to be set in accordance with the selected nozzle head height. Higher height values usually require a higher atomisation pressure, but a very high pressure is not desirable for building up film thickness due to film cracking

and flaking. For the nozzle head height I chose, an atomisation pressure of 300 - 400 kPa produces good quality films. Flaking and cracking are common if the height and pressure are not set in the optimal range. Use of a fan is optional to press the full cone into a flattened shape, but in this work the full cone pattern worked the best so the fan air option was not adopted.

X and Y length The dashed black and red lines in Figure 3.3 represent the spray pattern that the nozzle head moves along. The spray area can be adjusted by setting the X and Y length. The maximum length that the X and Y stage allows is 200 mm by 200 mm.

Pitch and margin The pitch and margin are the step sizes that the nozzle moves in Y and X directions respectively. The nozzle moves along the zig-zag red line pattern and the dashed black pattern as a one spray cycle. For glass slides, the spray pattern was set to be a straight line aligned with the glass slides and repeated for multi-layer deposition. For large area films, spray patterns are the zig-zag overlap shown in Figure 3.3 with pitch and margin values of 5 mm which was roughly the same as the diameter of the spray core.

Stage moving speed and suspension flow rate As experimented by previous students in the group, the X and Y stage moving speed of 50 mm/min and the suspension feed rate of between 2 to 4 ml/min were effective for film deposition therefore were chosen in this work.

Curing and post-process

Sprayed films were melt-processed in a furnace at 380 °C for about 30 min as described in previous work [3]. For impedance measurement films, two layer of gold of around 100 nm thick were deposited on both sides using Edwards Cryo Auto 306 thermal evaporator with a base vacuum of lower than 4×10^{-6} mbar

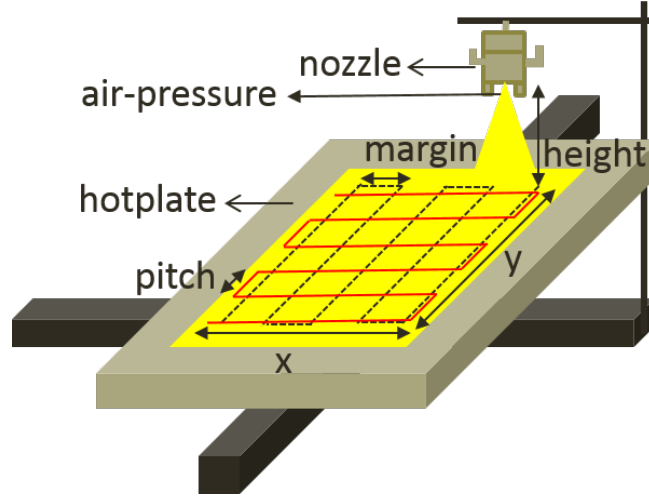


Figure 3.3: A picture of the spraying apparatus in the lab

for impedance measurements. For large area films, cured films were stacked and hot-pressed into 15.8 mm x 7.9 mm blocks suitable for waveguide measurements.

3.1.2 Casting

A casting route was used to prepare epoxy-based composite block materials. The advantages of casting include cost-efficiency, flexibility in sample geometry and suitability for use of a wide selection of ceramic powders. Depending on the viscosity of different epoxy resins, you can choose ceramic powder fillers with diameters ranging from nm to tens of microns while still maintaining a stable mixture. By mixing together epoxy resin and ceramic fillers homogeneously, we can tailor the dielectric properties of the composites by controlling the ratio of the two. During the mixing process, air bubbles tend to get trapped into the composites and lower the composite dielectric constant. Moreover, inhomogeneous distribution of these air bubbles causes inhomogeneous distribution of overall dielectric properties. To avoid this problem, a vacuum oven was introduced after the mixing. The mixed composites sit inside the vacuum oven of a negative pressure of -0.1 MPa at room temperature for less than 30 min until air bubbles stopped popping. After degassing, the mixture was poured into silicone or PTFE moulds

to be cured. Depending on the type of epoxy resin, the curing condition varies. In my case, the sample needed to be placed in a oven at 60 °C for at least 24 h as instructed by the supplier.

3.1.3 3D Printing

3D printers supplied by Makerbot (Figure 3.4) were used to prepare geometrically flexible samples using in-house customised filaments. 3D printing has attracted increasing attention in recent years for its superiority in geometry control and its efficiency in manufacturing. By feeding filaments into multiple nozzles which were pre-heated to high temperature, the materials were melt and extruded and built up complex geometries on a hotplace as the nozzles moving at high speed. The geometries to be printed were pre-drawn either using the company's own software or other drawing software such as CAD. In this work, in-house customised filaments with desired permittivity properties by extruding ABS and high permittivity ceramic powder mixture at selected ratios were made by Dmitry Isokov. The minimum step size for the 3D printing machines used in our work is 0.1 mm.

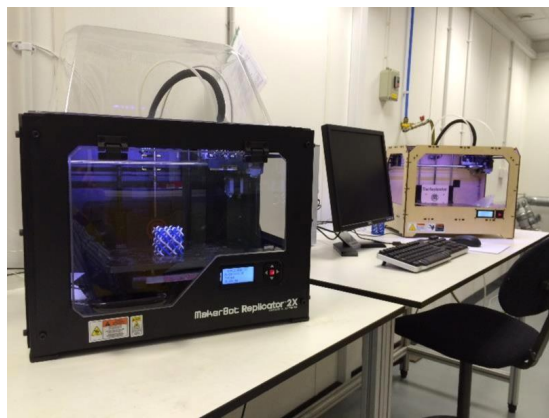


Figure 3.4: picture of the 3D printers

3.2 Characterisation Techniques

3.2.1 Characterisation of dielectric properties

Dielectric characterisation refers to measurements of the complex permittivity of dielectric materials and the evaluation of relative permittivity and loss tangent values from these measurements. The relationship between absolute permittivity, ε^* , relative permittivity, ε_r^* , (both complex values) and dielectric constant, ε_r , and loss tangent, $\tan\delta$, are:

$$\varepsilon^* = \varepsilon_0 \varepsilon_r^* \quad (3.1)$$

$$\varepsilon_r^* = \varepsilon_r' - j\varepsilon_r'' \quad (3.2)$$

$$\varepsilon_r = \sqrt{\varepsilon_r'^2 + \varepsilon_r''^2} \quad (3.3)$$

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} \quad (3.4)$$

where $\varepsilon_0 = 8.854 \times 10^{-12}$ [F/m].

In general, these measurement techniques can be divided into three categories; lumped-element capacitance measurement methods, transmission and reflection (T/L) methods and resonator methods [4, 5]. The lumped-element methods measures directly the impedance Z or admittance Y of the capacitor structure to calculate relative permittivity and loss using an impedance analyser, and is only applicable at frequencies below the GHz range. For higher frequencies, transmission and reflection methods measure the scattering matrix of the interaction of electromagnetic radiation with materials using a network analyser, from which the permittivity values are evaluated. The resonator method measures the resonant frequency f and quality factor Q and their shift after loading materials to be measured to calculate relative permittivity and loss tangent. It is an accurate measurement method for low loss materials but only provides discrete data points at single resonant frequencies. Exactly which method to choose mainly de-

depends on the required frequency range, the dielectric properties to be measured and the form of the materials (for example, film or bulk materials). Figure 3.5 is a diagram that summaries very well the selection of dielectric measurement techniques based on frequency and materials loss. In this work, the impedance measurement technique, waveguide measurement (T/L technique) and split-post resonator measurements were all used to characterise the dielectric properties of my polymer/ceramic composites with various shapes and over different frequency ranges.

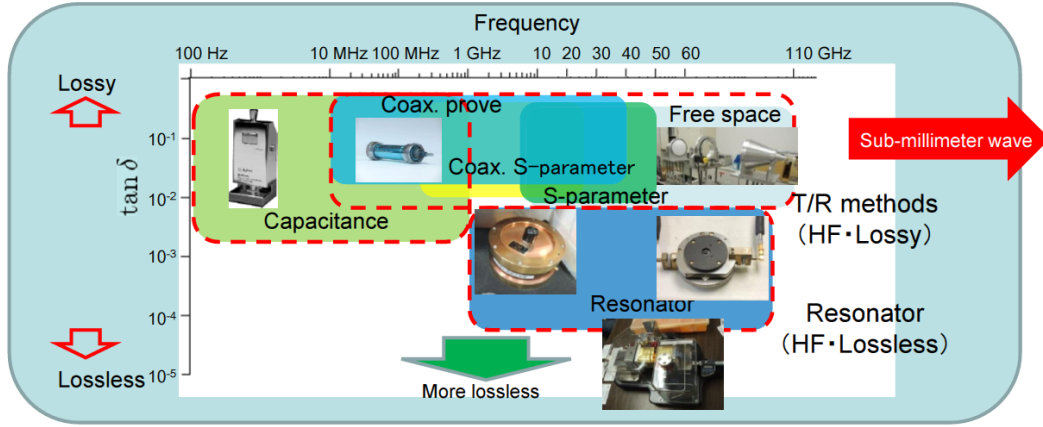


Figure 3.5: Diagram illustrating the suitability of each measurement technique according to frequency and the loss in the materials [6]

Impedance measurements

Impedance measurements were conducted on parallel capacitor structures formed by sandwiching polymer/ceramic composite thin films with Au electrodes at room temperature. The magnitude of the impedance, $|Z|$, impedance phase angle, θ , admittance, Y , and capacitance magnitude, C , were measured by an impedance analyser (Solartron SI 1260) by sweeping over a frequency range of 10 Hz - 1 MHz, with DC level set to 0 V and AC level set to 1 V. The Sample dielectric constant, ϵ_r , can be calculated using the simple formula:

$$\epsilon_r = \frac{Ct}{\epsilon_0 A} \quad (3.5)$$

where C is the measured capacitance, t is the thickness of the film and A is the area of the film under test. The relationship between complex impedance, Z , and the impedance phase angle, θ , is shown in Figure 3.6 and defined by equations 3.6 and 3.7.

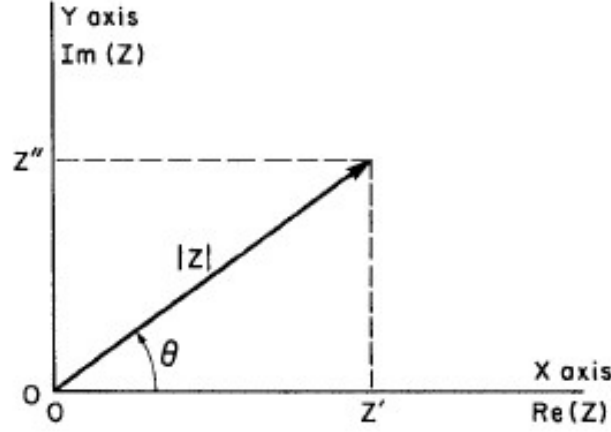


Figure 3.6: Complex impedance Z and the impedance phase angle θ [7]

$$Z^* = Z' - jZ'' \quad (3.6)$$

$$Z' = |Z|\cos\theta, Z'' = |Z|\sin\theta \quad (3.7)$$

The loss tangent, $\tan\delta$, can be calculated from [8]

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'} = -\frac{Z'}{Z''} = -\frac{1}{\tan\theta} \quad (3.8)$$

In impedance spectroscopy, the measured impedance of an electrode-material system can be approximated by impedance of an equivalent electric circuit made of ideal resistors, capacitors and inductors. The resistance in such a circuit represents a conductive path while the capacitance and inductance usually represent space polarization and specific adsorption and electrocrystallization reactions at the electrodes [9]. Impedance plot in a complex plane revealing response patterns is a useful tool in identifying the physiochemical processes in impedance spectroscopy [10]. A simple RC circuit approximation often seen in IS results for

solids and liquids is shown in Figure 3.7. It consists of a geometrical capacitance C_1 and a bulk resistance R_1 in parallel with it. The impedance of the system equals

$$Z = R_1 + \frac{1}{j\omega C_1} \quad (3.9)$$

With a system that exhibits capacitance with very little resistance in parallel

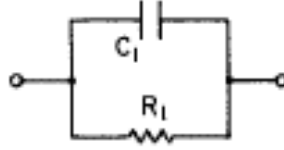


Figure 3.7: Simple RC circuit approximation [10]

($R \approx 0$, $\frac{Z'}{Z''} \approx 0$), the complex impedance plot would appear to be a straight line (as is the case for our polymer/ceramic composite measurements) instead of semi-circle (or part of semi-circle) with $\theta \approx -90$.

Waveguide measurements

For waveguide measurements at 12 - 18 GHz, a 15.8 mm x 7.9 mm cavity needs to be filled with materials to be tested. Sample thickness should be much less than the guided half wavelength but thick enough to generate reliable S-parameters. In this work, polymer/ceramic composite blocks with thickness between 1 mm and 2 mm were prepared depending on their dielectric constant. The waveguide was connected to a two port Vector Network Analyser or VNA (Agilent 8510C) with phase-stable cables. Electromagnetic signals coming out of one port were guided through the test material to the other port. S11 and S22 parameters are reflection coefficients for port 1 and port 2 respectively, while S12 is the transmission coefficient from port 2 to port 1 and S21 the transmission coefficient from port 1 to port 2. These four parameters compose the scattering matrix (or S-parameters). Figure 3.8 is the schematic of the testing set-up and Figure 3.9 is a picture of waveguide connected with VNA in the actual testing scene.

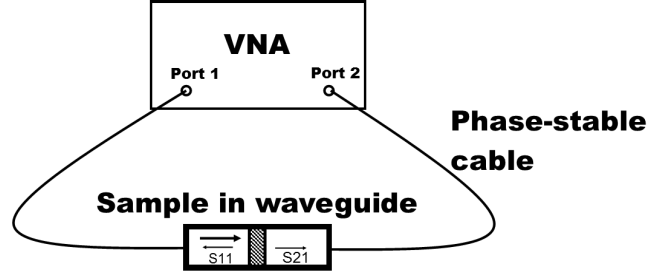


Figure 3.8: Schematic of the waveguide measurement

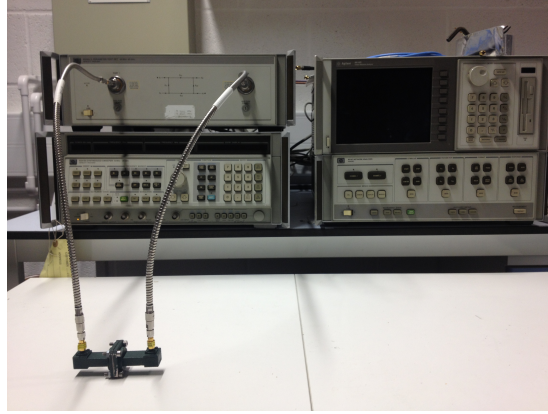


Figure 3.9: Picture of waveguide in connection with VNA used in this work

The S-parameters were then used to evaluate the dielectric properties of my samples using the Nicholson-Ross-Weir (NRW) method [5, 11–14]. The process is briefly described as follows:

For a material with thickness of d and complex relative permittivity and permeability

$$\varepsilon_r = \varepsilon'_r - j\varepsilon''_r \quad (3.10)$$

$$\mu_r = \mu'_r - j\mu''_r \quad (3.11)$$

The transmission coefficient is defined as

$$z = e^{(-\gamma d)} \quad (3.12)$$

where

$$\gamma = j\frac{2\pi}{\Lambda} = j\frac{2\pi}{\lambda_0} \sqrt{\varepsilon_r \mu_r - \left(\frac{\lambda_0}{\lambda_c}\right)^2} \quad (3.13)$$

$$\gamma_0 = j \frac{2\pi}{\lambda_{0g}} = j \frac{2\pi}{\lambda_0} \sqrt{1 - \left(\frac{\lambda_0}{\lambda_c}\right)^2} \quad (3.14)$$

The complex reflection coefficients at the boundaries of air and a solid material are Γ and $-\Gamma$

$$\Gamma = \frac{Z - Z_0}{Z + Z_0} \quad (3.15)$$

$$Z = j \frac{w\mu_0\mu_r}{\gamma} \quad (3.16)$$

$$Z_0 = j \frac{w\mu_0}{\gamma_0} \quad (3.17)$$

The relationship between the S-parameters and z and Γ is found to be

$$S_{12} = S_{21} = \frac{(1 - \Gamma^2)z}{1 - \Gamma^2 z^2} \quad (3.18)$$

$$S_{11} = S_{22} = \frac{(1 - z^2)\Gamma}{1 - \Gamma^2 z^2} \quad (3.19)$$

Defining the sum and difference between the scattering parameters as

$$V_1 = S_{21} + S_{11} \quad (3.20)$$

$$V_2 = S_{21} - S_{11} \quad (3.21)$$

if

$$X = \frac{1 - V_1 V_2}{V_1 - V_2} \quad (3.22)$$

Γ and z can be expressed with S-parameters

$$\Gamma = X \pm \sqrt{X^2 - 1} \quad (3.23)$$

$$z = \frac{V_1 - \Gamma}{1 - V_1 \Gamma} \quad (3.24)$$

An appropriate sign is chosen to ensure $|\Gamma| \leq 1$. Based on equations 3.15,3.16

and 3.17, the complex permeability value can be solved as

$$\mu_r = \frac{\lambda_{0g}}{\Lambda} \frac{1 + \Gamma}{1 - \Gamma} \quad (3.25)$$

where λ_{0g} and Λ , as indicated in equations 3.13 and 3.14, are guide wavelength for the empty and loaded waveguide.

$$\lambda_{0g} = \frac{\lambda_0}{\sqrt{1 - \left(\frac{\lambda_0}{\lambda_c}\right)^2}} \quad (3.26)$$

$$\Lambda = \frac{\lambda_0}{\sqrt{\varepsilon_r \mu_r - \left(\frac{\lambda_0}{\lambda_c}\right)^2}} \quad (3.27)$$

From equation 3.25 and 3.27, we can get

$$\varepsilon_r = \frac{\lambda_0^2 \left(\frac{1}{\Lambda^2} + \frac{1}{\lambda_c^2} \right)}{\mu_r} \quad (3.28)$$

where Λ can be obtained from the transmission coefficient using equation 3.12

$$\frac{1}{\Lambda} = \frac{j \ln(z)}{2\pi d} \quad (3.29)$$

In conclusion, as the transmission coefficient z can be obtained from S-parameters, Λ can be calculated by 3.29 and hence μ_r and ε_r can be determined by 3.25 and 3.28 respectively.

We should be aware of a couple of restrictions when applying the NRW method to extract permittivity and permeability values. This method assumes a uniform material where $S_{11} = S_{22}$ and $S_{21} = S_{12}$, so inhomogeneous materials such as materials graded along the propagation direction are not suitable for the NRW method. Secondly, although both the real and imaginary parts of the permittivity can be extracted from the rectangular waveguide measurement, it is deemed

inadequate for loss measurements when the imaginary part is very low ($\epsilon'' < 0.05$ according to [11]), i.e. very low loss materials. For these very low-loss materials, I used a resonator technique instead to accurately measure the loss.

Split post measurements

The split-post measurement is a non-destructive resonator technique to accurately measure the complex permittivity of dielectric substrates with low loss. Split-posts with resonant frequency of 10 GHz and 15 GHz manufactured by QWED were used in this work. The schematic of a split post dielectric resonator (SPDR) arrangement is shown in Figure 3.10. The fixture consists of a pair of thin dielectric resonators, metal enclosure and coupling loops. The small height of the metal enclosure allows a strong evanescent electromagnetic field in the active measurement area [15] and tends to be smaller for higher frequency measurements. The SPDR is connected to a network analyser for measurements. The signal magnitude can be tuned by adjusting the coupling loop, and the S_{21} peak should be kept around -40 dB for proper measurements. After insertion of

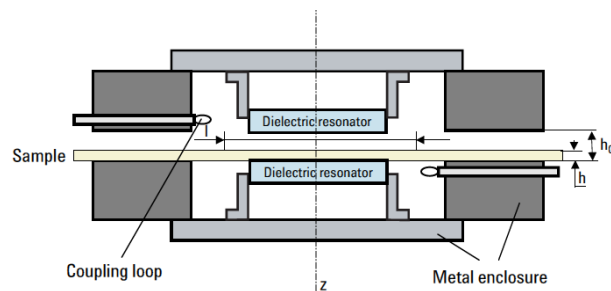


Figure 3.10: Schematic of the split-post dielectric resonator [16]

the dielectric sample, a shift of the resonant frequency can be observed on the S_{21} peak, as shown in Figure 3.11. The resonant frequency decreases from f_c to f_s and quality factor changes from Q_c to Q_s . Most advanced VNA machines are capable of 3dB bandwidth and provide Q-factors automatically, but for some old-model VNA machines that do not measure Q-factors, this quality factor can

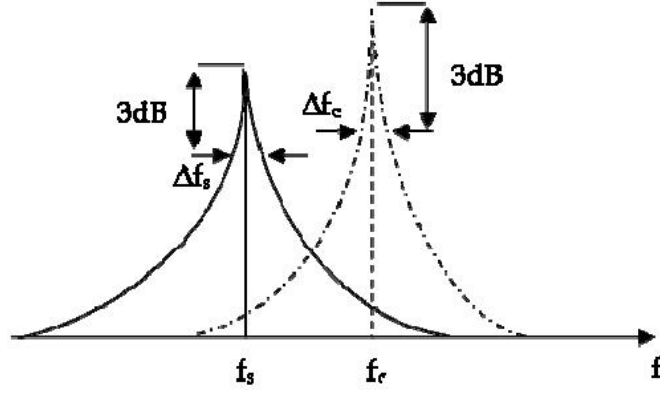


Figure 3.11: Resonant frequency and quality factor change after insertion of dielectric sample [17]

be calculated from the ratio of resonant frequency to the bandwidth, Δf , at half power (i.e. 3 dB).

$$Q_c = f_c / \Delta f_c, Q_s = f_s / \Delta f_s \quad (3.30)$$

By measuring the resonant frequencies, f_c and f_s , and quality factors Q_c and Q_s , with and without the sample, material dielectric constant and loss tangent can be calculated using an iterative method as described in [16, 18]. QWED provides the software to compute the dielectric constant and loss tangent with the input of these four measured parameters. The split-post technique offers an easy measurement, no special sample machining is required so long as the sample can fit into the fixture, and it can be used for film measurements. However, because the split post dielectric resonator is a single frequency measurement that only operates on the TE_{011} resonator mode. This limits the frequency range of the results, but because this mode only has an azimuthal component of electric field, hence the measurement is not affected by air gaps perpendicular to z-axis (for instance, when measuring stacked thin films) [16]. In addition, although the split-post measurement has minimum requirements on samples, it does have to reach a minimum size to cover the active area of the fixture, and the sample thickness needs to be chosen according to the dielectric constant. For the 15 GHz split-post arrangement, the sample has a minimum size of 14 mm in diameter and maximum

thickness of 0.6 mm, and the sample thickness needs to be reduced further for high ϵ_r or lossy materials. Reference sample thickness choice for different ϵ_r values are suggested in Figure 3.12, and the resonant frequency should not be lower than 13.5 GHz to avoid mode overlapping [19]. Typical SPDR real permittivity measurements have an uncertainty of less than $\pm 1\%$ providing a high accuracy in the sample thickness measurement and the loss tangent measurement uncertainty is $\pm 5\%$. It is worth noting that although resonator techniques are known as an accurate method for loss measurement, it is not very suitable for materials with high loss (for instance, loss tangents < 0.01 are suggested for split-cylinder measurements) where a significant decrease in the Q factor causes the resonator to fail to resonate properly [20].

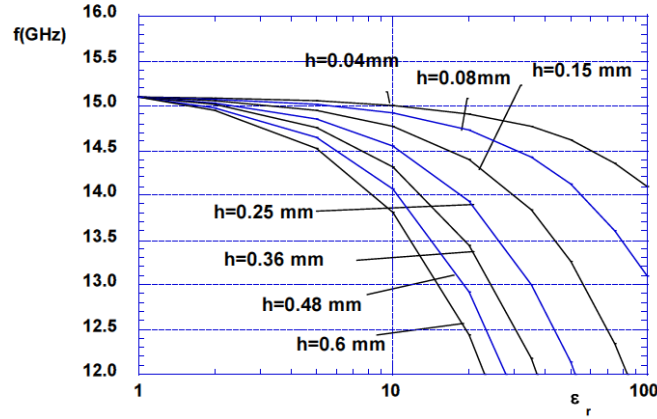


Figure 3.12: Resonant frequency versus dielectric constant for the 15GHz split-post dielectric resonator [19]

As well as a range of assessment techniques for dielectric properties, I have used different structural and microstructural techniques to study my composite samples.

3.2.2 X-Ray Diffraction

X-ray powder diffraction was used in this work to determine the crystal structure of ceramic powders. Ceramics with a specific composition and phase will possess a unique crystal structure with a distinct set of lattice parameters. When the

wavelength of the incident x-rays, λ , and the spacing of atomic planes that they impinge on, d , satisfy Bragg's law $n\lambda = 2d\sin\theta$, diffraction occurs where the reflected beams are constructively interfered and hence an intensified signal will be detected. By measuring these diffraction angles, the lattice parameters of the ceramic crystal structures can be determined. In this work, a Philips PW1729 X-ray generator with a PW1710 control unit using Cu $K\alpha$ radiation at 35kV and 50mA was used to characterise the crystal structures of the ceramic fillers. The step size ($2\theta^\circ$) was 0.05 and time per scan 0.5 s. Ceramic powders were spread evenly on a thin layer of glue that was sticking to one side of a glass slide. For more accurate and intense signals, powders were press-fitted into the XRD powder diffraction sample holder to give as much volume of material as possible.

3.2.3 Particle size and electrophoresis analysis

The particle size and zeta potential measurements were done on a Zetasizer Nano ZS (Malvern Instrument Ltd). It can accurately measure particle sizes dispersed in liquid within the range 0.3 nm - 10 μm and zeta potentials for particles within the range 3.8 nm - 100 μm .

The technique used for size measurement is Dynamic Light Scattering (DLS), in which the Brownian movement of particles in a liquid environment is measured and related back to the particle size by the Stokes-Einstein equation. The particle size measured by DLS is defined as the diameter of spherical particles that diffuse light to the same degree as the measured particles. When illuminating moving particles with a laser light, intensity fluctuations will be observed in the scattered light and are used to extract particle sizes. The technique used for zeta potential (ζ -potential) measurement is Electrophoretic Light Scattering. The zeta potential is defined using electric double-layer theory [21, 22]. Most liquids contain ions and when charged particles are dispersed in a liquid, ions with opposite charge in the liquid will be attracted to the surface of particles and an electric double

layer structure will be formed. The first layer is also called the Stern layer where ions are strongly bound to the surface of charged particles. The second layer is also referred as the diffuse layer, within which ions are only loosely attached. The outer boundary of the diffuse layer is referred to as the slipping plane. The potential between the bulk of the liquid and this slipping plane is defined as the zeta potential, and the value of the zeta potential is a reliable indication of the stability of the suspension. When particles possess very high positive or negative zeta potentials it indicates the existence of strong repulsion between individual particles and hence less likelihood of agglomeration. In the user manual of the Zetasizer it states that solutions containing particles with a zeta potential of more than ± 30 mV are considered stable. However, it has been reported in the literature that ± 15 mV is enough for particles to achieve electrostatic stability [23]. The Zetasizer Nano ZS measures the zeta potential by first applying an electric field to the liquid and measuring the electrophoretic mobility (U_E) of particles and then extracting the zeta potential using the Henry Equation [22].

Sample preparation is more stringent for size measurements than zeta potential measurements. To obtain the optimal conditions for testing, the suspension concentration has to remain low to avoid multi-scattering (when the light scattered by one particle gets scattered again by another). To visually control the sample concentration, the suspension should just develop 'a slightly milky appearance'. Sample concentration is then assessed automatically by the instrumental software. When using an unqualified sample, poor data quality will be indicated in the final report.

3.2.4 Scanning electron microscopy

Scanning electron microscopes were intensively used in my project, primarily to determine the microstructural distribution of ceramic fillers in the polymer matrix. Three SEM machines were used, JEOL JSM-840F, JEOL JSM-840A

and JEOL JSM-6500F. The equipment that was used the most was a JEOL JSM-840F which has a cathode emission gun and operates between 0.5 and 40 kV. The best resolution that can be achieved on this machine is 1.8 nm and is therefore adequate for nanoparticle observation. The JEOL JSM-840A was briefly used at the beginning of my project only to observe polymer structures. It uses a tungsten filament operating between 0.2 and 40 kV. Although it has a best resolution of 3.5 nm on high contrast samples, it was deemed inadequate for observing nanoparticles (*ca.* 60 nm in my case) in a polymer matrix. In addition to surface topography imaging using secondary electrons, some EDX (energy dispersive X-ray spectroscopy) analysis of ceramic particles was done by Gabriella Chapmann on the JEOL JSM-840A. The JEOL JSM-6500F was used when JEOL JSM-840F was out of action. It uses a low voltage field emission gun and operates between 1 and 30 kV. It has an adequate resolution for nanoparticle observation. For all of these scanning electron microscopes, a low operating voltage of 3 kV was used when observing samples involving polymers because of the low melting point and insulating properties. Whereas for ceramic particles, a higher voltage of 10-20 kV was used.

Depending on sample conditions, the sample preparation method varies. For film samples on top of glass slides, they were immersed into liquid nitrogen for a few seconds and then snapped while cold in order to get a clean fracture surface. The cross-section was then coated with a thin layer of Pt using a Cressington 208 HR sputter coater. For thicker films and for bulk composites, an alternative is to cut a small piece of sample and have it fixed inside epoxy pyramids. The pyramids were then cut by a diamond blade using microtome into very fine slices.

3.2.5 Fourier Transform Infrared Spectroscopy

A Varian Excalibur 3500 FTS FT-IR was used to examine chemical group specification and molecular fingerprinting in order to evaluate the effect of particle

de-agglomeration. FT-IR is an absorption spectroscopy where beams containing different frequencies shine on the sample and information on the amount of the beam absorbed is gathered. By repeating the process with different combinations of frequencies, the raw data is computer processed (the algorithm is a Fourier transform) to produce the light absorption for each wavelength. Spectra were taken in the mid-infrared region from 500 to 4000 cm^{-1} which accounts for fundamental vibrations and associated rotational-vibrational structure of many molecules. FT-IR samples were prepared by grinding and mixing 1 mg of the powder under test with about 299 mg KBr powder using a pestle and mortar, and the powder mixture was cold-pressed into a thin disc ready for measurement. For each measurement, a pure KBr disc of the same thickness is required as a reference sample which should be close to transparent, requiring the KBr powder to be dried thoroughly in an oven over 100 °C overnight prior to sample preparation.

3.2.6 Thermogravimetric/Differential Thermal Analyzer

The thermogravimetric and differential thermal analyses were conducted simultaneously on a Perkin Elmer Diamond TG/DTA machine. The flexibility of measuring weight loss and thermal information at the same time enables us to link weight loss to specific chemical reactions taking place at different temperatures. Both the ceramic pan (which can stand over 1000 degrees) containing a few mg of sample and the empty ceramic pan acting as an inert reference were heated up according to a preset programme from room temperature to 800 degrees at a rate of 10 C/min. The sample chamber is under constant nitrogen flush at 20 ml/min. For differential thermal analysis, the temperature difference between the sample and the reference was recorded and the differential temperature can be plotted against temperature to reflect any exothermic or endothermic reactions in the samples.

3.2.7 Surface Profilometer

A Veeco Dektak 6M Profilometer is a contact (stylus) method to measure the thickness and surface roughness of sprayed films. The sample stage moves under computer control while the stylus stays static and physically in contact with the surface to measure changes in the surface topography. A force of 2 mg was applied onto the film surface by the stylus. Measured parameters are ASH the average step height, arithmetic average roughness, R_a , and root mean squared roughness R_q which are defined as

$$R_a = \frac{1}{n} \sum_{i=1}^n |y_i| \quad (3.31)$$

$$R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2} \quad (3.32)$$

where y_i is the distance from the i th data point to the mean line.

3.2.8 NanoFocus μ Surf

A NanoFocus AG μ Surf confocal microscope was used to assess the surface quality of sprayed films. The NanoFocus μ Surf is a non-contact measurement for surface topography based on the white light confocal technique. A confocal head is mounted on a stable stand that is motor driven to move along the z axis and the sample is placed on a computer controlled x-y precision slide. The equipment provides high vertical and lateral resolution. An area of $800 \mu\text{m} \times 772 \mu\text{m}$ on the surface was measured in my work. 3D and 2D surface images were produced, based on which the areal roughness, S_a , was calculated. S_a is the average roughness defined as

$$S_a = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} |z(x_k, y_l)| \quad (3.33)$$

3.2.9 Rheometer measurements

The viscosity measurements in this project were performed on a Brookfield DV-III Ultra Rheometer. Single speed measurements reading viscosity and torque directly from the display were conducted for the sake of simplicity, and the objective was to obtain quick reference values for the viscosity of fluid samples. The rheometer set includes 6 spindles that cater for fluid samples with different viscosities. By selecting the suitable spindle that gives an acceptable torque reading (the reading for the torque should be between 10% - 90% for accurate measurement, ideally between 40% and 70%), and choosing an appropriate speed until the reading for the viscosity is stable, we can note down the displayed viscosity value normally displayed in SI system unit mPa·s and is convertible to cP as $1 \text{ mPa}\cdot\text{s} = 1 \text{ cP}$.

3.2.10 Raman Spectroscopy

Raman Spectroscopy was used to investigate the structural properties of barium titanate powders. Raman spectroscopy performs non-destructive chemical analysis based on measuring molecular vibrational modes. Raman scattering refers to the inelastic scattering when a laser beam in this visible, near infrared or near ultraviolet range interacts with molecules and is inelastically scattered with either a gain or loss of some energy. This energy change is characteristic of the molecule structure. To be Raman active, the molecular vibration must have some polarisation change in the process. A very important advantage of Raman Spectroscopy is that it requires very little sample preparation. It can measure materials in any form and any state. In this work, the Raman scattering was conducted on a Horiba Jobin Yvon LabRam Aramis equipped with two lasers (532 nm and 633 nm) to cater for a wide range of wavelength measurements. For barium titanate powders, the 532 nm laser was used to scan from 100 to 4000 wave numbers. No sample preparation was necessary, a small quantity of as-received barium titanate

nano-particles were laid out on a glass slide.

3.2.11 Wavelength-dispersive X-ray Spectroscopy

Wavelength-dispersive X-ray spectroscopy or WDS on a Jeol 6480 LV SEM was used to conduct quantitative chemical analysis on samples in this work. WDS gathers chemical compositional information about samples by counting the number of x-ray with specific wavelengths being emitted from samples under an energetic electron beam. The x-ray signal generated from the sample first impinges on an analysing crystal and get diffracted when the Bragg's law is satisfied. The diffracted x-ray is then detected by a proportional counter [24]. The main advantages of WDS are superior energy resolution (one order of magnitude higher than EDS) and high count rates [25]. On the other hand, WDS is more expensive, time-consuming and difficult to use. WDS adopts a serial detection system in which only pulses close to the selected Bragg angle get measured while EDS has a parallel detection system with a larger acceptance range, therefore in WDS only one line is measured a time whereas in EDS the whole spectrum can be recorded simultaneously. WDS requires a high standard of sample preparation. Flat and clean specimens were prepared by fine polishing. A number of points were sampled when analysing samples by WDS to generate good counting statistics.

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Chapter 4

Dielectric properties of sprayed PFA/BT composite films at microwave frequencies

4.1 Introduction

Polymer-ferroelectric composite films are widely used in the electronics industry for capacitors and other energy storage devices [1–3]. Combining the advantages of the easy processability, the high break down strength of polymers with the high dielectric constant of ferroelectric materials, polymer-ferroelectric composites offer a simple way to manufacture high permittivity materials with reproducible properties. In my work, the dielectric properties of thermoplastic perfluoro alkoxy (PFA) / BT nanocomposite films prepared by spray deposition were assessed using an impedance analyzer from 10 Hz to 1 MHz. Barium titanate BaTiO_3 (BT) is a widely available ferroelectric material with high dielectric constant, and is the most common choice for the ceramic filler material. BT shows a large dielectric relaxation at microwave frequencies whose origin is linked to its domain structure. The dielectric relaxation frequency depends on the ferroelectric domain size

and typically lies in the range 100 MHz to 10 GHz [4]. A relaxation frequency near 1 GHz has been experimentally demonstrated for BT with different domain sizes, where for instance the dielectric constant for samples with micron-sized domains dropped from 1900 at 10 kHz to 280 at 5.6 GHz [1]. It is expected that this frequency-dependent dielectric performance of BT will also be observed in polymer/BT composite materials.

Spray deposition technique has been shown in previous work in this group[5, 6] to be highly effective in producing small area films for energy storage demonstrators. In this work, the technique was developed further by scaling up to produce large area films (160 mm x 160 mm) with thickness exceeding 100 μm while still maintaining good surface quality.

Although data has been reported for the dielectric constant of polymer-ferroelectric composites at low frequencies (up to MHz), very limited reference data can be found for high frequency (above GHz) measurements of the same materials. In part this is due to sample preparation difficulties for the high frequency measurements [7]. For composite films, capacitance measurements using an impedance analyzer is the conventional way to obtain dielectric constant data [8–10], which unfortunately is only suitable for measurements up to 1 GHz as described in the previous chapter. In this work, the intention was to measure the dielectric properties of sprayed PFA/BT composite films at high frequencies (12 - 18 GHz) and to compare with those at low frequencies on the same materials. As discussed in the previous chapter, a waveguide technique to measure dielectric properties at high frequencies requires bulk materials of mm thickness. To meet this sample requirement, a carefully monitored hot pressing method was developed with the help from Claire Dancer to create reproducible samples from sprayed composite films for these high frequency waveguide measurements. Cured thermoplastic/BT composite films up to 120 μm thick were stacked and hot-pressed at a temperature just above polymer curing temperature to build up a sufficient sample thickness

for a reliable waveguide measurement without altering the microstructure of the material.

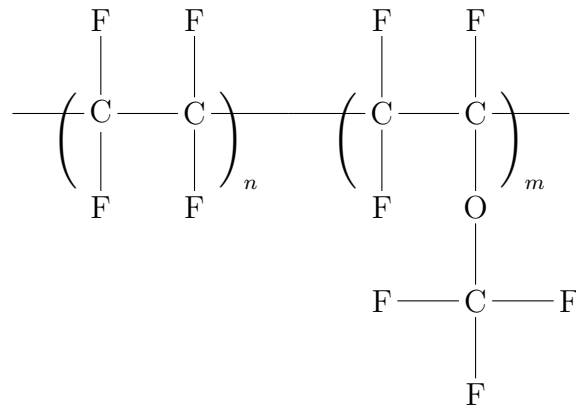
Industrial applications of polymer-ferroelectric composite films require accurate control and prediction of the dielectric performance. Several theoretical models have been used to predict the dielectric properties of composite systems, and their validity tested by curve fitting to experimental data [8, 11–15]. A comparison of different mixing rules will be introduced in the next chapter. It is worth noting that conclusions are rarely drawn on which model is superior to another in giving better fitting to this experimental data. The application of mixing rules can also be used to estimate the dielectric constant of the ferroelectric nanoparticles in a composite, since it is difficult to measure the dielectric properties of the nano-particles alone. In my work, the Lichtenecker equation was used to fit the measured dielectric constants of PFA/BT nanocomposite films at 10 kHz and 15 GHz to allow the estimation of the dielectric constant of the barium titanate nanoparticles.

4.2 Sample Processing

4.2.1 Materials

From the viewpoint of achieving high dielectric constant composite, a polymer with a high dielectric constant should be preferred as long as other manufacturing properties are favourable given that it is the dominant component in the composite. Table 4.1 lists the dielectric constant of some commonly used polymers. In this work, a thermoplastic polymer PFA with a mediocre dielectric constant of 2.1 was chosen due to manufacturing property consideration.

Perfluoroalkoxy



Thermopolymer perfluoroalkoxy (PFA) (3M Dyneon 6910GZ) whose chemical structure was indicated above was chosen as the polymer matrix for spraying. It comes as a *ca.*50 vol% PFA water suspension with PFA particle sizes around 80 nm. The water based suspension makes it an ideal candidate for a spraying process. Fluoropolymers are widely used in industry because of their good chemical resistance, high temperature resistance (as they normally have high melting points) and stable dielectric performance [16]. PFA has a reported stable dielectric constant of 2.1 in the frequency range tested and a high melting temperature (306 °C). The typical processing temperature for Dyneon PFA is between 360 and 390 °C, and above this temperature the polymer will decompose.

Barium titanate

Barium titanate (300nm, 99.9 %, tetragonal) supplied by Nanoamor was chosen for the spraying process. Barium titanate is a prototyped ferroelectric that offers a high dielectric constant. Its properties have been extensively studied and relatively well understood in the literature. As a typical ferroelectric ceramic, barium titanate's dielectric constant is dependant on both the temperature and the size of the particles. When choosing the most suitable particle size and phase, I had to consider these two determining factors; 1) the size of the particles must not be too big otherwise the orifice of the spray nozzle would be easily blocked, 2) the

Material	Dielectric Constant
PTFE [Poly(tetrafluoroethylene)]	2.1
PP (Polypropylene)	2.2
PE (Polyethylene)	2.3-2.65
PS (Polystyrene)	2.4
ABS (Acrylonitrile-butadiene-styrene)	2.6
Modified PPO (Polyphenylene oxide)	2.7
PC (Polycarbonate)	3.0
PET [Poly(ethylene terephthalate)]	3.0-3.3
Acrylic resins	3.0
PBT (Polybutylene terephthalate)	3.1
PPS [Poly(phenylene sulfide)]	3.2
PEEK [Poly(ether etherbetone)]	3.3
LCP (Liquid-crystal polymer)	3-4
Acetal copolymers	3.7
PVC [Poly(vinyl chloride)]	4.0
PA 66 (Polyamide 66)	4.6
PVF [Poly(vinyl fluoride)]	8.2-8.5
PVDF (Polyvinylidene fluoride)	8.2-9.5

Table 4.1: Dielectric constants of some polymeric substances [17]

particle size should give a dielectric constant as high as possible.

BaTiO₃ has four common phases, cubic, tetragonal, orthorhombic and rhombohedral, with transition temperatures near 130 °C, 0°C and -90 °C respectively. The cubic phase is the only one without any permanent dipoles, hence has the lowest dielectric constant of the four. At room temperature, the natural phase for bulk BaTiO₃ is tetragonal. However, as the grain size reduces, the Curie temperature of BaTiO₃ (the temperature at which the tetragonal to cubic phase transition takes place) can be shifted to a much lower temperature, even down to room temperature [18–20]. When the grain size is reduced to a certain value, no ferroelectric domains will be supported and only the cubic phase exists. Generally speaking, the dielectric constant of BaTiO₃ increases as the grain size is reduced. But this increase peaks at a sub-micron size, beyond which the dielectric constant starts dropping as a result of these two effects. This grain size dependence is illustrated in Figure 2.17. A maximum value of $\epsilon_r = 5000-6000$ occurred at a grain size of *ca.* 700-800 nm. Therefore, the BaTiO₃ powder we are looking for

should be tetragonal and with a particle size close to 700-800 nm to maximise its dielectric constant. However, the spraying process requires the particle filler to be as small as possible to avoid blockage. 300 nm BaTiO₃ powders is the smallest particle size that I can fine with tetragonal phase, therefore I decided to use 300 nm tetragonal BaTiO₃ powders.

The average size of the as-received barium titanate nano-powders and the degree of particle agglomeration were confirmed in the SEM images in Figure 4.1. In the higher magnification SEM image, we can see the barium titanate powders come in faceted irregular shapes with some variation in particle sizes. The barium titanate powders were sprinkled on top of carbon sticky pad glued to a cylindrical sample holder and then coated with 2.5 nm thick platinum before being inserted into the SEM.

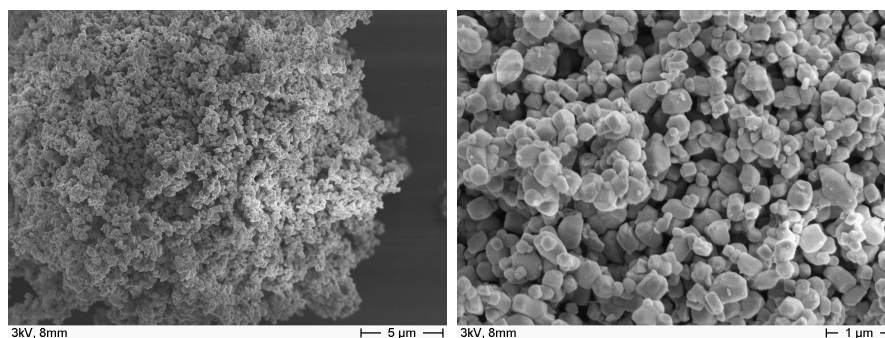


Figure 4.1: Low and high magnification SEM images of the as-received barium titanate powder

A combination of X-Ray diffraction and Raman spectroscopy were used to characterise the crystal structure of the barium titanate powders. It is known that conventional X-ray diffractometry proves to be inadequate for assigning cubic and tetragonal symmetries to very fine barium titanate nanoparticles due to line broadening and the lack of obvious beam-splitting of the (200) peak [21]. Therefore, as a complementary method, Raman spectroscopy was used to substantiate the manufacturer's claim of single phase of tetragonal barium titanate nanopowders used in our experiments. To prepare samples for X-ray diffractome-

try, sprinkles of BaTiO₃ powders were spread evenly on top of some glue sticking to one side of a glass slide. The glass slide was then cut into the right size to fit into the sample holder. When mounting the samples, it is important to make sure the top surface of the sample is flush with the top surface of the sample holder in order to obtain accurate peak positions. Two scans were performed on the as-received tetragonal 300 nm BaTiO₃ powders, one overall scan from 10 to 80 degrees and one detailed scan in the proximity of 45 degrees where the characteristic (200) peaks are located. The results are shown in Figure 4.2. The clear splitting between (200) and (002) peaks in the detailed scan proves the tetragonal symmetry in the barium titanate powders, which was further confirmed by the Raman spectroscopy results in Figure 4.3. The marked peaks at ~ 305 and ~ 710 cm⁻¹ are characteristic of the tetragonal phase [21, 22]. Here I am confident that the Nanoamor powder was mostly in the tetragonal phase.

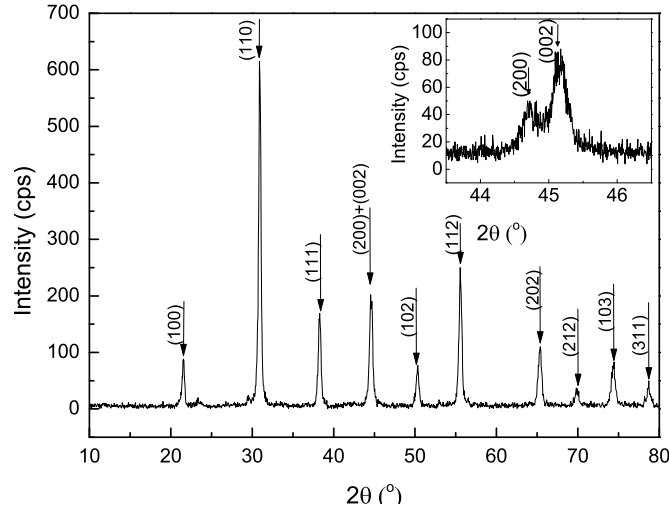


Figure 4.2: XRD plots of as-received barium titanate nano-powder, (a) is the overall scan from 10 to 80 degrees and (b) is a detailed scan near 45 degrees which corresponds to the location of (200) peaks and where the characteristic peak splitting would occur for tetragonal crystal symmetry.

Dispersant

Dispex A40 supplied by BASF, Germany is a well-known commercial product to disperse particles in water-based suspensions. To achieve highly stable and homo-

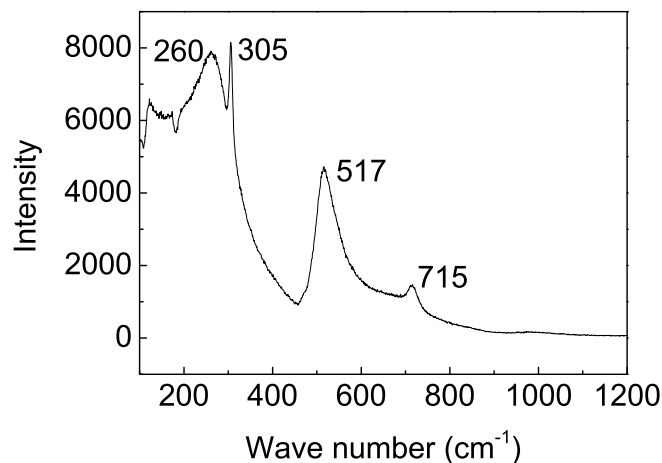


Figure 4.3: Raman spectrum of as-received barium titanate powder at room temperature

geneous particle dispersions, especially with high particle concentrations like the ones I wished to use, it is necessary to use a surfactant to facilitate electrostatic, steric or electrosteric stabilization. For non-polar solvents, the mechanism is normally steric stabilisation by surfactants that are high molecular weight polymers [23], whereas for polar solvents surfactants are usually made of polyelectrolytes which are ionised in solution and the charged polymers become attached to the particle surfaces to reach electrostatic stability [24]. The chemical nature of Dispex A40 is water solution of an ammonium salt of an acrylic polymer. Because of the rather short chain of the polymer molecule, it is conjectured to have an electrostatic rather than a steric stabilisation effect on the dispersion.

4.2.2 Suspension preparation

Composite suspensions with various BT loadings were prepared by high power ultrasonication of the PFA / BT water suspensions with the addition of Dispex A40 for approximately 1h in order to achieve homogeneous and stable suspensions by de-agglomerating the BT nanoparticles.

Deagglomeration is one of the biggest challenges for homogeneous dispersion of nano-particles in suspension. The smaller the size of the nano-particle, the big-

ger the surface area and hence the more susceptibility to particle agglomeration. The main consequences of particle agglomeration in my work are impaired stability of the final composite suspension and rapid particle sedimentation. In light of the high density of BaTiO_3 powders, particle sedimentation is expected to happen over time, but with well dispersed BaTiO_3 suspensions the sedimentation speed can be significantly reduced, therefore maintaining stable suspensions during a spraying process which usually lasts for less than 30 min. (According to Stoke's law, the settling velocity of small particles in fluid depends on the density of the particle and of the fluid, the radius of the particle and the dynamic viscosity of the fluid). Patchy electrical properties can be caused by particle agglomeration, especially at high loadings depending on the size of the agglomerates. Therefore, minimising particle agglomeration is the key to achieving stable composite suspensions, and hence good film properties.

The deagglomeration process was facilitated with two methods. A high power (maximum 750 watts) ultrasonic processor supplied by Sonics&Materials was used to break down any agglomerates mechanically, and an effective surfactant Dispex A40 was introduced to modify the surface chemical condition of ceramic powders to facilitate their bonding with the polymer matrix. To test the effectiveness of the deagglomeration process, the particle sizes for the as-received BaTiO_3 nanoparticles and after deagglomeration were measured by the Zetasizer. A few grams of barium titanate powder were dispersed in DI water with 2 wt% of Dispex A40. The suspension was then sonicated at 60 % of the maximum power by the ultrasonic atomizer for about 30 min. About 1 ml of further diluted suspension (until reached a faint milky colour) was pipetted into a disposable polystyrene cuvette which was then inserted into the Zetasizer for size measurement. For zeta potential measurements, a folded capillary cell was used instead. Size measurements were performed before and after deagglomeration process, and are compared in Figure 4.4 (a). To verify the stability of the deagglomerated powders, the sus-

pension was left still for 6 days and the particle size remeasured. The comparison graph is shown in Figure 4.4 (b). It was found that the barium titanate particle water suspension remained well dispersed after 6 days.

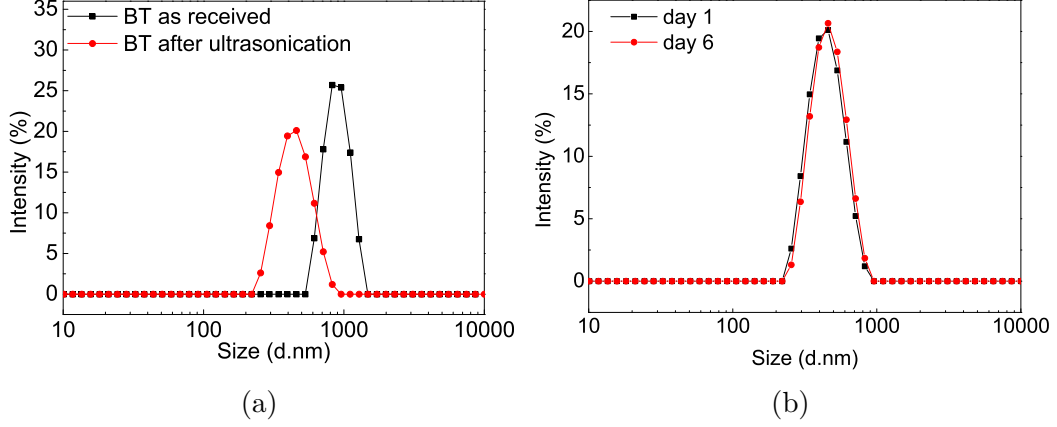


Figure 4.4: (a)Size measurement comparison between as received BT particles and BT particles after deagglomeration; (b)Intensity percentage comparison of particle sizes between two measurements separated by 6 days after deagglomeration

To assess the stability of PFA/BT composite suspensions, a sedimentation test was performed on a BT: PFA suspension with a volume ratio of 0.1. A beaker containing the well dispersed suspension treated by adding 2 wt% of Displex A40 and ultrasonication for about 1h was left still for sometime to observe visually the sedimentation process (Figure 4.5). It is seen from these pictures that the BT powders in PFA suspension start to sediment after 30 min of stillness and a thin layer of delamination can be clearly observed after 1 h. The sedimentation process was completed after sitting overnight. To quantify the suspension stability for the expected spraying session, de-agglomerated BT:PFA(v/v)= 0.1 suspensions were loaded onto the syringe pump and tested at two different pumping speeds, 2 ml/min and 4 ml/min. The pumped-out fluid was channelled into a beaker sitting on a precision balance which monitored the mass change of the fluid in real time. The volume of the pumped-out fluid can be read off the pump in real time as well. 60 ml of suspensions were pumped at each speed taking 15 min and 30 min respectively. The tracked data for the weight and volume change of the

pumped-out fluid against time is plotted in Figure 4.6, where the straight lines indicate constant weight or volume increments over the testing period and hence minimal particle sedimentation over this time period.

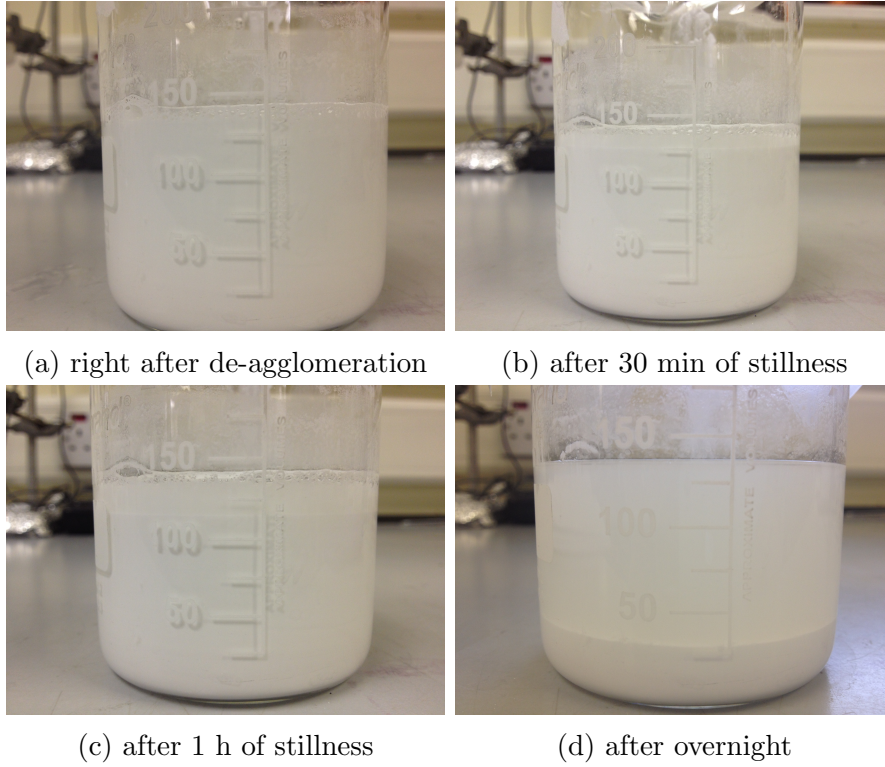


Figure 4.5: Pictures taken (a) immediately after the PFA:BT(v/v)=0.1 composite suspension was ultrasonicated with Dispex A40;(b) after 30 min of sitting still; (c) after 1 h of sitting still; (d) overnight

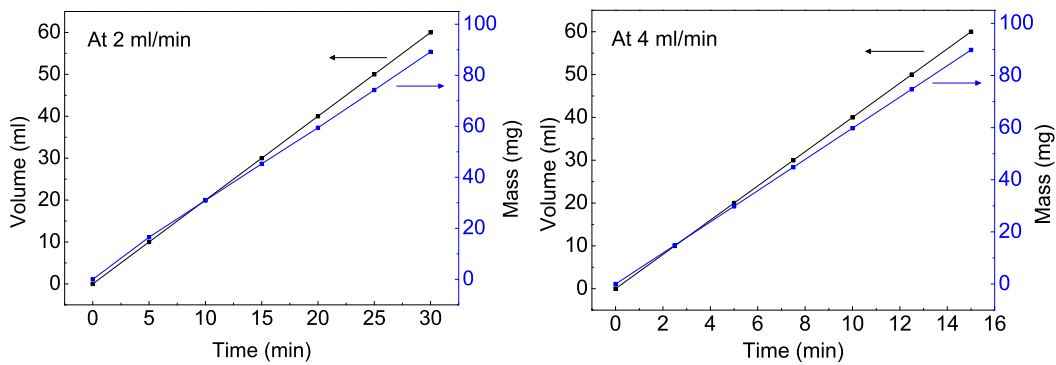


Figure 4.6: Plots of weight and volume of fluids pumped-out of the syringe at flow rate of 2ml/min and 4 ml/min respectively.

Addition or evaporation of water from the suspensions can adjust the viscosity of suspensions to encourage a smooth spraying process. Suspensions with high

Table 4.2: Viscosity reference for BT/PFA suspensions with different volume ratios before and after ultrasonication

Nominal volume ratio	Viscosity before ultrasonication	Viscosity after ultrasonication
BT:PFA = 0.05	16.2 mPas	66 mPas
BT:PFA = 0.1	14.8 mPas	64 mPas
BT:PFA = 0.3	-	95 mPas

viscosities were proven to be susceptible to causing blockage in the nozzle orifice. The viscosity values for some successfully sprayed suspensions are listed in Table 4.2 as reference.

4.2.3 Spray deposition

An illustration of the spray deposition process is shown in Figure 4.7. The stabilised suspensions were fed into the spraying nozzle through a syringe propelled by an electric pump. The nozzle atomised the liquid at the outlet with compressed air with pressure of ~ 300 kPa. The flow rate of the suspension was optimised to be $2\sim 3$ mL/min. The atomised liquid formed cone-shaped mists and deposited on the pre-metallised glass slides sitting on a hotplate. The hotplate temperature was set to be 95°C to facilitate water evaporation. The hotplate moved in a zigzag route on the x-y plane. A few layers were sprayed on top of each glass slide to build up the thickness. For each spraying session, films up about 100 microns thick can be deposited without significantly compromising the film surface roughness. The sprayed films were then loaded to a belt furnace for curing. The temperature inside the furnace was set to be 380 degrees and the moving rate was set so that the hold time was roughly half an hour, as optimised by previous students for optimal curing of the same polymer matrix [5].

The spraying process was scaled up for spraying large area films at a later stage of the project. Up to 160 mm x 160 mm PFA/BT composite films with BT volume fractions of 0.05, 0.1 and 0.2 were prepared (Figure 4.8). The sprayed

films all showed uniform structure by visual observation across the entire area. The thickness of the films was measured by micrometer to be approximately 100 μm . Float glass with dimensions 200 mm x 200 mm x 3mm which was supplied by Instrument Glasses was adopted as film substrate for its flat surfaces and uniform thickness. Moreover, the glass can withstand temperatures up to 400 °C as required by the curing process.

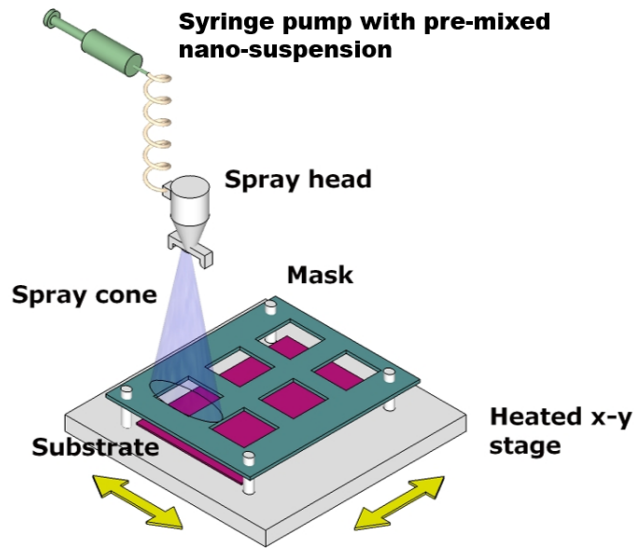


Figure 4.7: Illustration of spraying process (diagram from Patrick Grant's group)

Hot pressing

To prepare block samples suitable for waveguide measurements, 160mm x 160mm composite films with thickness $\sim 100 \mu\text{m}$ were cut into 40 mm x 40 mm square pieces and stacked. The stacks were placed in a heated die within a hot press system developed by Claire Dancer with an initial load of 25 Kgf evenly applied. The hot press system shown in Figure 4.9 includes the heater control that is channelled with the upper and lower heat bands wrapping around the aluminium dies, a load control that is connected with a load sensor placed on top of the aluminium dies, a linear variable displacement transducer (LVDT) that monitors the thickness change of the composite film stack, three thermocouples (two of

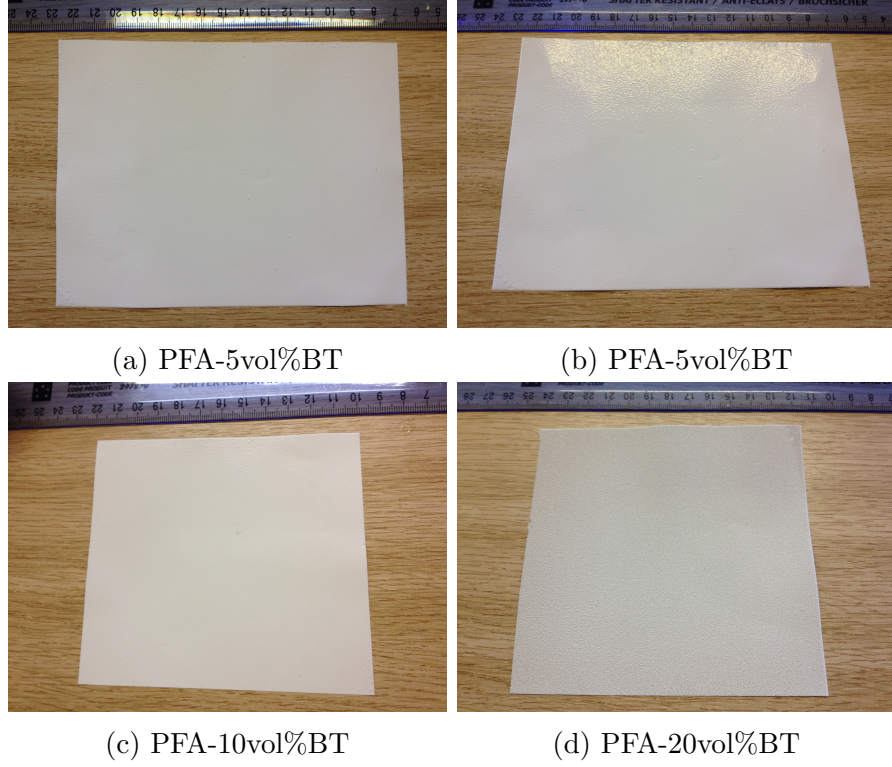


Figure 4.8: Pictures of sprayed large-area composite films at various compositions. It can be seen that the films' surface roughness gets worse as the barium titanate loading increased.

which were inserted into holes drilled in the upper and lower aluminium dies respectively, and one thermocouple can be sandwiched to the composite films stack to monitor directly the temperature of the films when necessary), and a computer monitoring system where all data are fed back to and analysed in Labview. The bonding process was carefully monitored by temperature measurements from thermocouples inserted in close proximity to the composite films and sandwiched inside the stack itself, together with displacement measurements of the pressurizing ram from LVDT to avoid excessive heating or pressing. The sample was heated to just above the PFA curing temperature of 306 °C and held for 5 - 10 min under pressure before the heaters were switched off and the sample cooled naturally. Approximately 16 layers of film were used to form a block of thickness 2 mm as required for waveguide measurements. The process is shown in Figure 4.10, and a typical heating cycle for hot pressing a PFA-5vol%BT sprayed film

was recorded and plotted in Figure 4.11. It can be seen in the graph that the film temperature did not exceed 308 °C, and the time over which the film stayed in temperature between 300 - 308 °C did not exceed 20 min to achieve good quality composite blocks. Figure 4.12 shows optical images of the cross-section of a typical hot-pressed PFA-5vol%BT block showing no signs of air gaps or excessive heating.

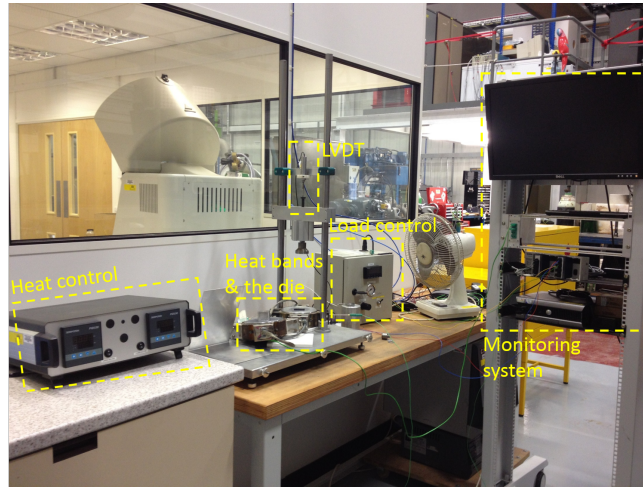


Figure 4.9: Picture of the in-house designed hot press system

4.3 Results and Discussion

4.3.1 SEM

The microstructure of the sprayed films were examined under SEM. Cross-sections of sprayed and cured pure PFA films were prepared by submerging them in liquid nitrogen and snapping them into half instantly after removed. The revealed cross-section along with the glass slide substrate were sandwiched between two parallel copper plates in a SEM holder. The fixture was then coated with a 2.5 nm layer of platinum. A comparison of typical good and poor quality sprayed PFA films is shown in Figure 4.13. Before optimizing the spraying parameters, films appeared to possess a certain number of trapped air bubbles, which would

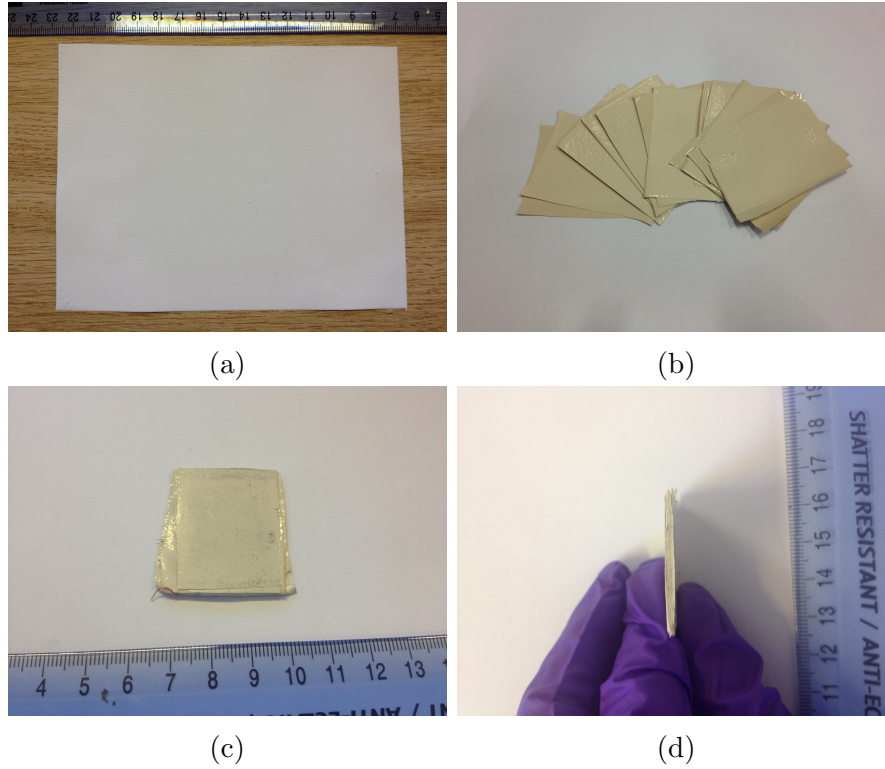


Figure 4.10: Sprayed large-area films (a) were cut into roughly 40mm x 40mm little squares (b) which were stacked and pressed in a hot-press into a compact block (c and d) for high frequency measurement

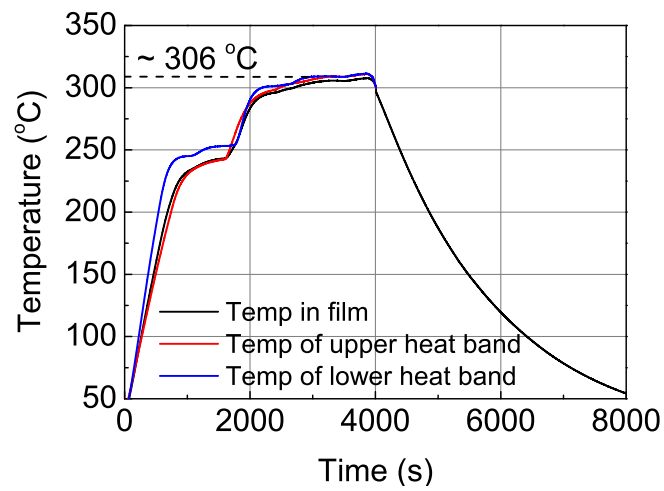


Figure 4.11: A typical heating process for hot pressing PFA-5vol%BT sprayed film

impair the structural and electrical performance of the films and could be avoided by careful control of the parameters described above.

SEM images of BT loaded PFA sprayed films with various compositions are

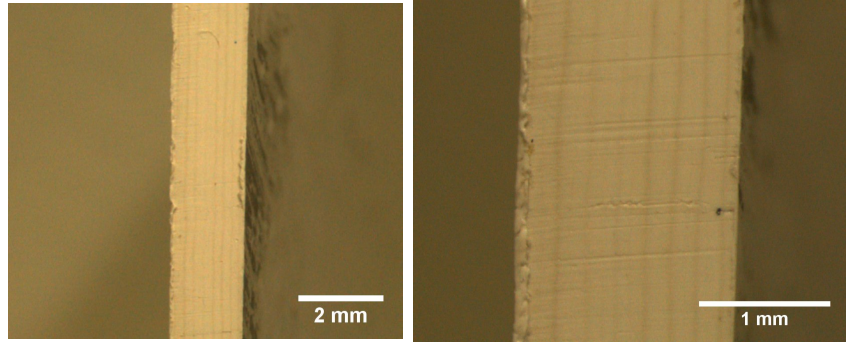
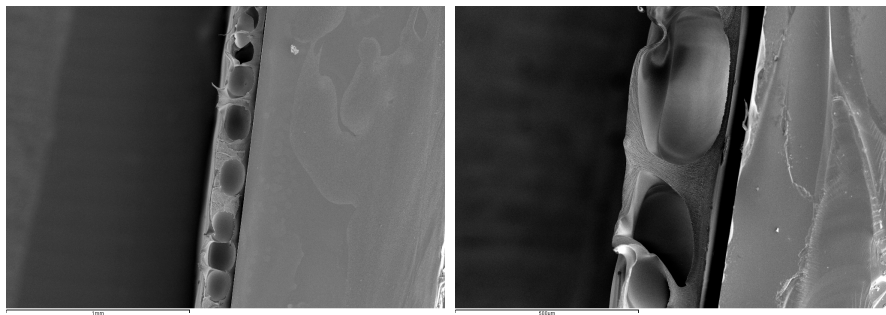
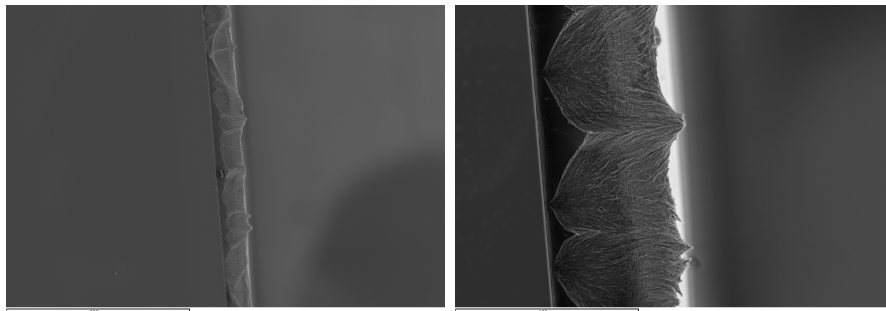


Figure 4.12: Optical images of a cross-section of a hot-pressed PFA-5vol%BT block showing no air gaps between the layers but distinguishable boundaries



(a) poor quality sprayed PFA film with trapped air bubbles



(b) good quality sprayed PFA film with a compact structure

Figure 4.13: Comparison of SEM images at high and low magnification of poor and high quality sprayed films proving the importance of parameter optimisation in the spraying process.

shown in Figure 4.14. At this magnification, a relatively well-distributed particle-polymer composite system was confirmed. Although generally there was judged to be an acceptable dispersion of the BT particles, pull-out of polymer chains during the fracture process prevented clear recognition of BT particle agglomerates. Moreover, for large area films or thick film samples, the method of snapping cold samples for cross-sectional analysis was no longer feasible due to weak attachment

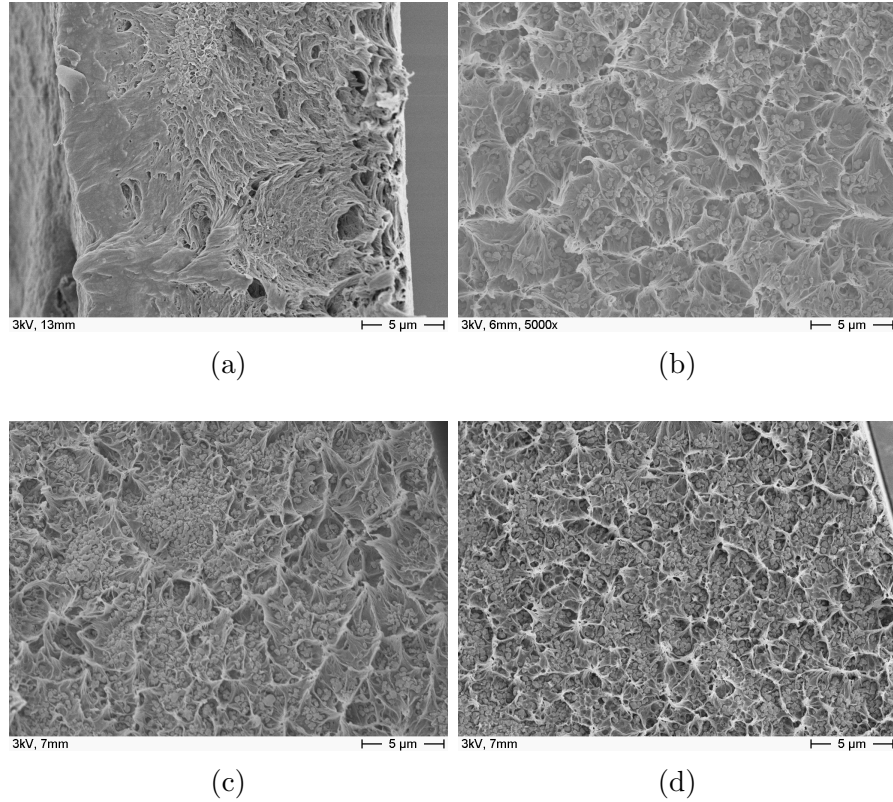


Figure 4.14: SEM images of cross-sections of PFA-BT composite films at (a) BT:PFA (v/v)= 0.05 (b) BT:PFA (v/v)= 0.1 (c) BT:PFA (v/v)= 0.2 (d) BT:PFA (v/v)= 0.3 four different compositions at magnification 5000x.

between the film and the glass substrate. Figure 4.15 shows SEM images at different magnifications of microtome-prepared cross-sections of a composite film with BT:PFA volume ratio of 0.1. The cured film sample was cut into a strip of roughly 1 cm long and 1 mm wide. The strip was then vertically embedded into epoxy resin in a pyramid-shaped silicone mould. The cured sample-containing epoxy block was mounted on a plastic cylinder and microtomed for a few slices just enough to reveal the cross-section of the film sample. In the images, BT clusters with diameters as big as $5\text{ }\mu\text{m}$ could be identified. Localised large nanoparticle agglomerates would result in not only patchy dielectric performance but also sedimentation of the composite suspension during the spraying process when large areas (long spraying times) were required.

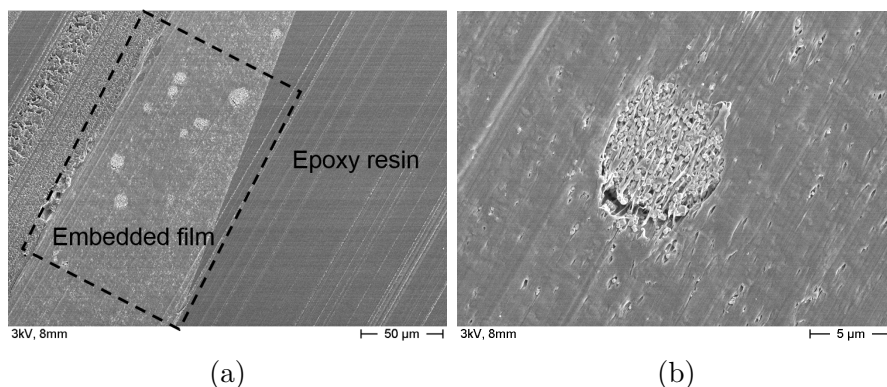


Figure 4.15: SEM images of microtomed film samples revealing BT particle agglomerates: (a) a low magnification image showing how the film sample was embedded in the epoxy resin and the inhomogeneity of particle distribution within the film and (b) a higher magnification image of one cluster of BT nanoparticles

4.3.2 Thermogravimetric and Differential Thermal Analysis

The curing process, and in particular the melting and decomposition temperatures of sprayed PFA were observed by differential thermal analysis where the heat changes in the sample are monitored during heating process. As is shown in Figure 4.16, ~ 2 mg of sprayed PFA film was heated from room temperature to 700°C . Two weight loss steps and three enthalpy changes are observed in the DT/TGA plot. The first enthalpy change happens around 185°C accompanied by approximately 6% of weight loss. This weight variation is related to volatilisation of solvents or lower molecular mass components including any plasticizer in the system. The second heat change happens around 306°C which corresponds to the melting point of PFA. At this temperature, the polymer chains of PFA will lose their crystalline structures and without causing significant weight variation. At temperatures higher than $\sim 450^{\circ}\text{C}$, a substantial heat change is observed along with a drastic weight loss. The strong exothermic process is due to the decomposition of PFA into volatile components and the residual weight is almost down to zero at the end of this process.

To test the thermal stability of the composite films, thermogravimetric anal-

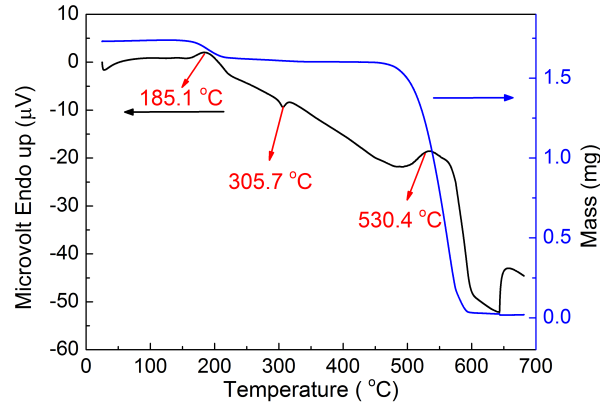


Figure 4.16: TG/DTA measurements of sprayed PFA film

Table 4.3: Comparison between nominal sample composition and TGA weight residue

Nominal volume ratio	Nominal wt% of BT	TGA wt%
BT:PFA = 0	0	2.32
BT:PFA = 0.05	12.0	11.5
BT:PFA = 0.1	21.4	23.2
BT:PFA = 0.2	35.2	33.3
BT:PFA = 0.4	52.1	45.2

yses of composite films with varying compositions were conducted on a Perkin Elmer Diamond TG/DTA machine (Figure 4.17). PFA was burned off at high temperature and the weight residue represented the BT powders in the composites. Some disagreement is observed between the TGA measurements and the calculated compositions during sample preparation, which is expected considering the particle agglomeration effect, compositional changes due to sedimentation during spraying and the extremely small samples that the TGA measurement is looking at. Table 4.3 list the nominal values of BT weight percentage compared with the weight residue results from thermogravimetric analysis. These experiments suggest that sprayed films could be manufactured with a BT loading rather close to the target figures.

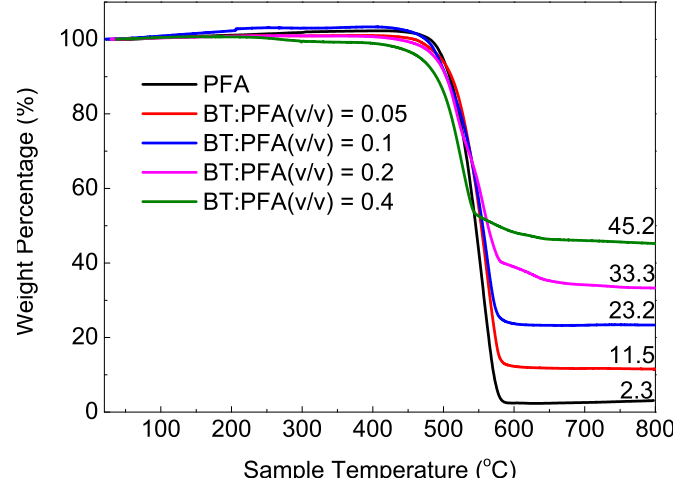


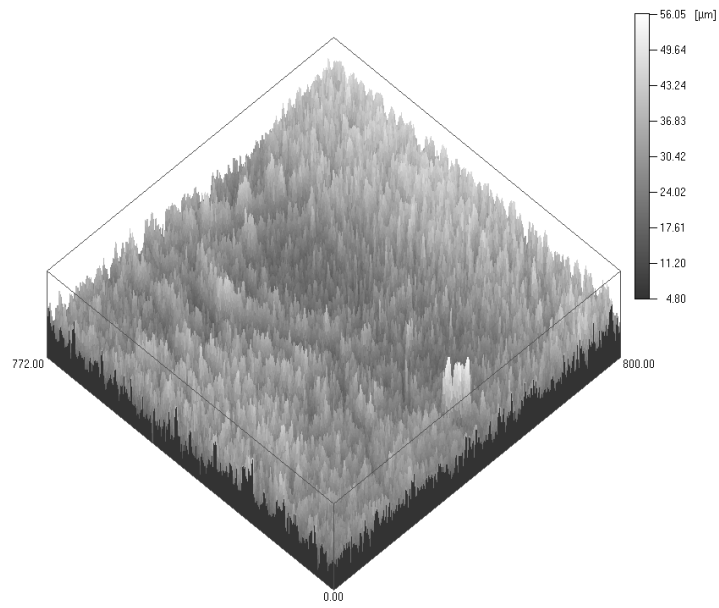
Figure 4.17: TG/DTA measurements of composite films with different compositions

Table 4.4: Dektak measurements of sprayed PFA film

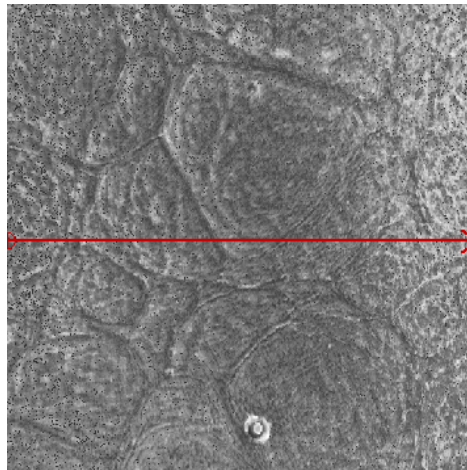
Items	Measurement 1	Measurement 2	Measurement 3
ASH(μm)	31.7	43.8	34.8
Ra(μm)	3.54	7.29	4.39
Rq(μm)	5.04	8.14	6.31

4.3.3 Surface roughness

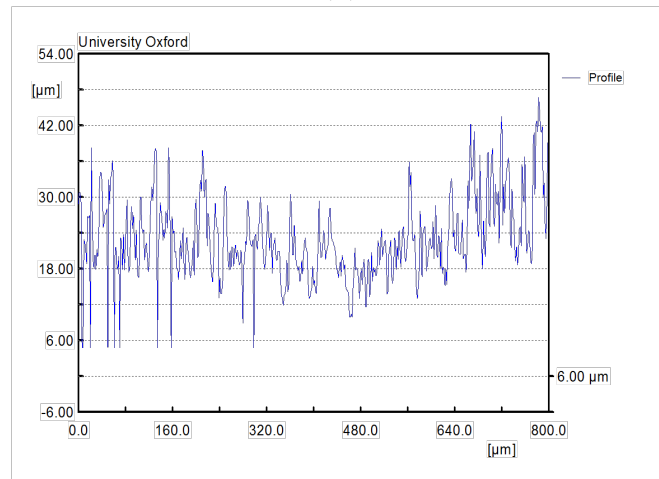
To get an idea of the surface quality of the sprayed films, the surface roughness of sprayed PFA films were measured by both Dektak and Nanofocus μsurf instruments. Three measurements were taken by the Dektak at different locations on the film and the results are listed in Table 4.4. The measured parameters are ASH (i.e. film thickness), surface roughness Ra and Rq. The Nanofocus μsurf measurement shown in Figure 4.18 on the other hand gives a 3D image of the surface, or a 2D height contrast image based on which areal roughness, S_a , values can be calculated and line profiles extracted. An areal roughness, S_a , of $4.94 \mu\text{m}$ was found for sprayed PFA film, i.e. reasonable agreement with the Dektak roughness values.



(a)



(b)



(c)

Figure 4.18: Nanofocus μ surf measurement of a sprayed PFA film showing (a) 3D image of the film surface (b) 2D image of the film surface and (c) profile of the surface quality along the red line marked on the 2D image

4.3.4 Dielectric measurements

Low frequency range

The dielectric properties of cured films at low frequencies were measured with an Impedance Analyser by creating parallel-plate capacitors. The cured film was sandwiched between two thin layers of gold deposited in a vacuum evaporator. The thickness of each gold coating was controlled to be roughly 100 nm, and the two layers of gold act as two electrodes of a capacitor. By changing the area and position of the top gold electrodes, we can monitor the dielectric performance at various positions of the cured film. A schematic of these mini capacitors to allow multi-measurements is shown in Figure 4.19. Each capacitance measurement was taken by averaging over 100 cycles, and several capacitance measurements were taken on each film. The typical dielectric performance of PFA / BT nanoparticle composite films with increasing ceramic loading between 100 Hz and 1 MHz is shown in Figure 4.20.

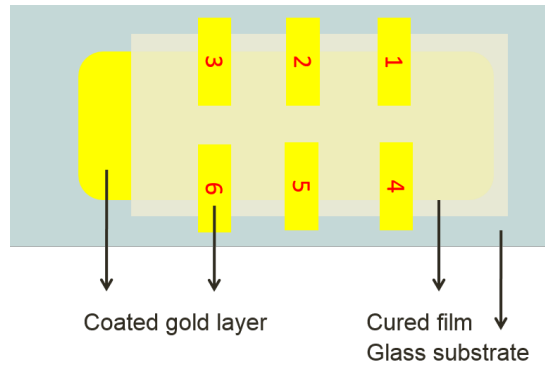
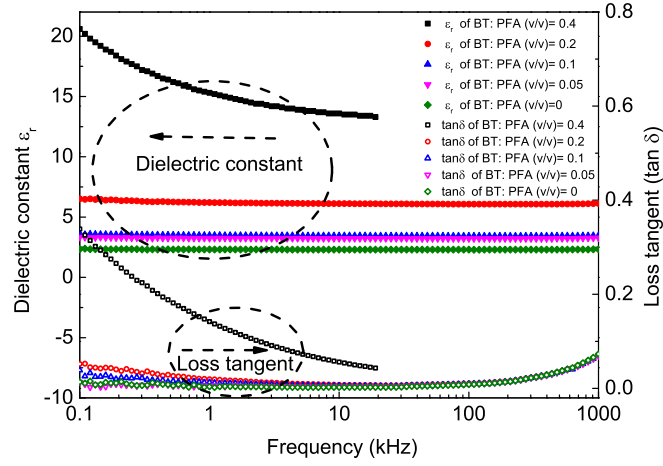
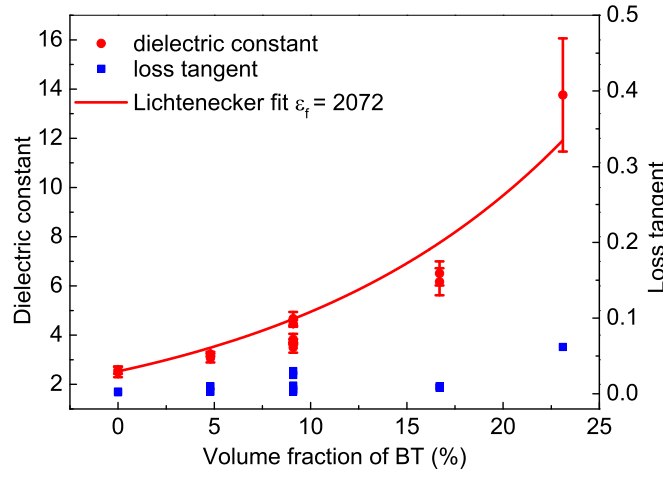


Figure 4.19: Illustration of the parallel capacitor structure

In Figure 4.20 (a) we can see relatively stable dielectric performance over the frequency range for films with lower BT loadings. As the BT:PFA volume ratio increased, the dielectric relaxation at the very low frequencies (below 100 Hz) became obvious. The measurement for the highest loading was stopped half way due to pin-hole effect in which films were porous and presented with many pin-holes as the BT loading increased and were prone to cause short-circuit between



(a)



(b)

Figure 4.20: (a) Dielectric measurements at low frequencies for PFA / BT composite films with varying volume ratios of barium titanate ;(b) dielectric constant and loss tangent of PFA / BT composite films at 10 kHz plotted against BT volume fraction and fitted using the Lichtenecker equation

the top and bottom electrodes at higher frequencies. For the rest BT loadings, stable dielectric constant measurements were seen. The loss tangent measurements reveal patterns of first decreasing at very low frequencies (below 100 Hz) and then stabilise and increase. The initial loss tangent drop was suspected to be caused by dielectric relaxation of BT, which is more distinguished for the highest loading. A similar relaxation effect for titanate-polymer composites between 10 Hz and 1 kHz was reported in [25]. The dielectric constant and loss tangent measurements at 10 kHz for composite films with different BT loadings are compared

in Figure 4.20 (b) where each dot represents one sample (or film) with standard deviation of 4-14 measurements taken on this sample plotted as the error bar. For some BT loadings, more than one sample were measured hence were seen as multiple data points. The scatter in measurements taken on a single film can be significant as the composite films get denser indicating that the distribution of BT on a single film is not completely uniform. Some variation in the dielectric measurements from film to film can also be observed, particularly for composite films with a BT:PFA volume ratio of 0.1, which might be related to particle agglomeration effects as discussed below. Possible factors that might contribute to the reproducibility of these measurements include composition variations during the spraying process related to suspension rheology and powder sedimentation, errors in composition calculations using estimated weight percentages for PFA water suspensions and non-uniform thicknesses of the films.

The Lichtenecker or logarithmic mixing law [26] shown in Equation 4.1 was used to fit the averaged data points (with no weighting applied) until a Chi-Square tolerance of 1E-9 was reached. ε_m was held constant at 2.5 as measured in experiment and ε_f was varied to achieve the best-fit.

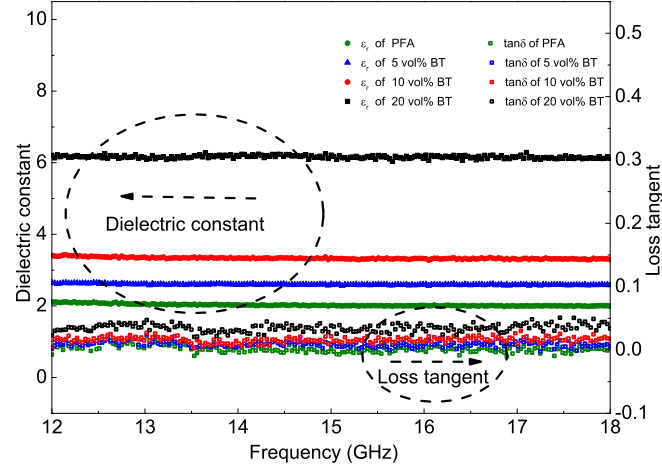
$$\log \varepsilon_{eff} = f \log \varepsilon_f + (1 - f) \log \varepsilon_m \quad (4.1)$$

where ε_{eff} , ε_f and ε_m represent the dielectric constant of the composite, the filler, and the matrix respectively and f is the volume fraction of the filler. The estimated dielectric constant for the BT nanoparticles based on the converged fitting was 2072. This value is close to the dielectric constant value normally quoted for bulk barium titanate in this frequency range ($\varepsilon_r \sim 2000$) [1, 27], but higher than some other reported estimates. For example, Cho et al. estimated 282 for 0.25 μm BT nanoparticles in epoxy/BT composites [11].

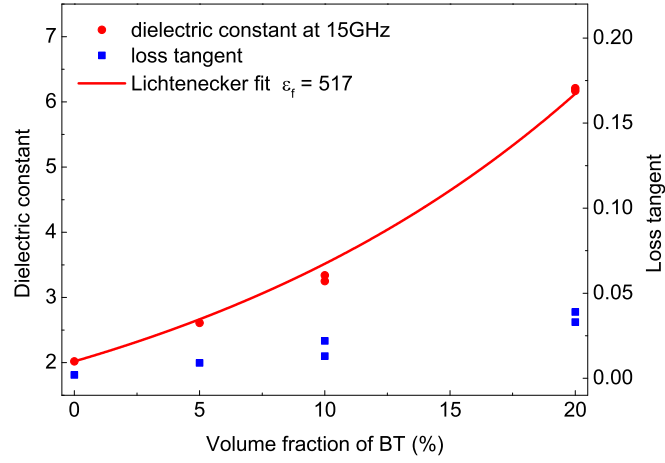
High frequency range

For the higher frequency waveguide measurements, 1-2 composite blocks for each composition were prepared as discussed above. When examined by optical microscopy, typical cross-sections showed a compact structure free of air gaps, but with residual layer boundaries visible after pressing in Figure 4.12. Waveguide measurements of these PFA / BT block samples with various loadings over the frequency range 12 to 18 GHz gave a stable dielectric performance with no significant dielectric relaxation. The dielectric properties at 15 GHz for composites with various loadings are compared in Figure 4.21, and best-fitting of the data again using the Lichtenecker mixing law gave an estimated dielectric constant of the BT nanoparticles of 517 which is a reasonable value compared to the reported dielectric constant of 280 for BT ceramics at 5.6 GHz [1]. This simple pressing process seems to offer a reliable way of producing samples from sprayed thin films for testing at high frequencies, and could be readily applied to building graded-index layered structures for thermoplastic polymer-based composites.

A comparison of the dielectric constants of thin sprayed composite films at 10 kHz and the same materials hot-pressed into the block format at 15 GHz is given in Figure 4.22. Consistent with previous reports of bulk BT behavior but not studied for composites films previously, there was a significant difference in the dielectric constant of the composites in the low frequency and high frequency measurements. The variations in measured dielectric constant from samples of nominally identical loading are most likely to be from variations in actual loading (i.e a systematic error from the fluctuations in the spray process as mentioned above) which are more severe in the low frequency measurements on single layer films than they are in the composite blocks made from many layers which averages out the sheet-to-sheet variations.



(a)



(b)

Figure 4.21: (a) Dielectric measurements at high frequencies for PFA / BT composite blocks with varying volume ratios of barium titanate; (b) dielectric constant and loss tangent of PFA / BT composite films at 15 GHz plotted against BT volume fraction and fitted using the Lichtenecker equation

4.4 Conclusion

SEM examines the microstructure of the sprayed films and shows that 1) pore-free films can be deposited if the spraying conditions are appropriately controlled, 2) after trying various spraying parameters, the most homogeneous distribution of BT nano-powders in the PFA matrix has been achieved across all compositions experimented in this work. Almost agglomerate-free film cross-sections were seen in SEM and TGA results showed good agreement with nominal values. A confocal microscope was used to measure the surface roughness of sprayed PFA films

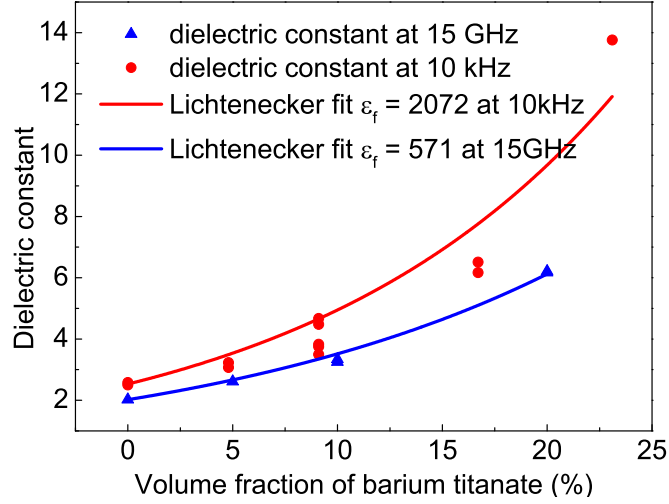


Figure 4.22: Comparison of low frequency and high frequency dielectric constants of sprayed PFA-BT composite films

to give an indication of the film surface quality prepared by spraying technique. An areal roughness, S_a , of $4.94 \mu\text{m}$ was obtained. TG/DTA measurement of PFA films confirmed the melting point of PFA to be around 306°C , an important temperature to be controlled when hot pressed PFA/BT composite films. TG/DTA measurements of PFA/BT composite films give consistent compositional results with the nominal values, which again suggested a uniform microstructure of these composite films.

Dielectric measurements of sprayed PFA / BT composite films at low frequencies (kHz) and high frequencies (GHz) were compared in this work. Measurements of the composite films at high frequencies (12-18 GHz) were achieved by a well-controlled hot pressing process to create block samples suitable for insertion into a waveguide. The Lichtenecker mixing rule was used to fit the data and to estimate the dielectric constant of BT nanoparticles in the different frequency ranges, and yielded 2072 and 572 at 10 kHz and 15 GHz respectively. These estimated dielectric constants at low frequencies agree well with published data for bulk BT ceramics, but are generally higher than those estimated from composite data using mixing rules. There was a reduction of about 30 % in the effective dielectric constant of the PFA / BT composites measured at high frequencies compared to

low frequency measurements. This should allow extrapolation in the future of results from convenient low frequency measurements to the high frequency range where many important applications of high k materials are being developed.

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Chapter 5

Dielectric properties of Epoxy based block materials at high frequencies (12-18 GHz)

5.1 Introduction

Polymer-ceramic composites have been studied extensively for microwave frequency applications. At the low frequency range (from KHz up to MHz), these composites are of interest for producing capacitors and energy storage devices where a high dielectric constant is required as well as good compatibility with the printed circuit boards [1, 2]. There is an increasing interest in higher frequency (up to GHz) applications of polymer-ceramic composites in recent years. The most common applications include antennas, radar, communication systems and beam steering [3, 4]. For such applications, frequency stable high dielectric constants and low dielectric losses are most important. Depending on the application, low processing temperatures, low cost, low loss, high breakdown field, and weak temperature and frequency dependence are also typical requirements. To meet these various demands, a variety of ceramic and polymer systems have

been developed and tested. Ferroelectrics such as barium titanate (BT), barium strontium titanate (BST), lead magnesium niobate (PMN) and lead zinc titanate (PZT) are some commonly used ceramics in these studies because of their high dielectric constant values [5]. Epoxy, polyvinylidene fluoride (PVDF) and its copolymers and polyimide (PI) are some common choices for polymer matrices [6, 7]. A dielectric constant of 13.1 has been reported by Cheng et al. for the same epoxy/barium titanate composite system as studied in this work at 1 GHz [8]. Reference data for these composites systems at relatively low frequencies can be found in [9]. Rather little data have been reported in the high frequency range we are interested in. Various mixing laws have been proposed to fit the data from measurements of dielectric performance [2, 10–14]. However, a systematic assessment of the reproducibility of this data is rarely given in these reports, nor is there much discussion on the validity of the mixing laws for different kinds of composite materials.

In this chapter, results on the dielectric properties of epoxy/barium titanate composites at 12-18 GHz measured by the waveguide method are given. Barium titanate (BT) powders is the best studied ferroelectric and possesses a characteristic high dielectric constant that depends on the particle size, temperature and frequency. An epoxy matrix was chosen because of the relatively high dielectric constant of 3 as well as the ease of processability. We are interested in the fabrication of 3D composite structures with precisely defined high frequency properties at specific locations, and so need to be able to accurately predict the relationship between composite morphology and composition and dielectric performance. The data consistency was investigated by comparing the properties of multiple samples with the same composition and by carefully examining the influence of microstructure. Various mixing rules were compared and fitted to the data, and the principles behind these different mixing rules were investigated to better understand their applicabilities.

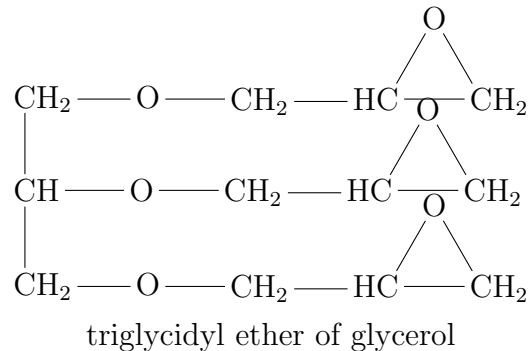
In addition to BT, BST and CT ceramics were also considered in this work as lower-loss alternatives to produce composites with lower dielectric losses while maintaining a reasonably high dielectric constant. A mature and repeatable processing route to prepare highly uniform epoxy/BST composites from badly agglomerated BST powders is proposed in this chapter. Accurate loss measurements using a split-post technique, and reliable loss tangent data obtained for the epoxy composite materials manufactured in this work.

5.2 Experimental

5.2.1 Materials

Epoxy resin

A four-component Agar 100 Resin kit was used as the epoxy supply. It has the same formulation as Epon 812 (or triglycidyl ether of glycerol whose chemical structure is shown below [15]) but a lower viscosity which is beneficial for preparing high volume content ceramic filled composites. The four components include epoxy resin, hardener DDSA, hardener MNA and accelerator BDMA, which when mixing in a specific ratio can produce epoxy resins with various hardness values. Throughout this work, a medium hardness was chosen for easy material machining and microtome sample preparation. The pre-warmed components were mixed well and cured at 60 °C for at least 24h.



Ceramics

Micron-sized barium titanate BaTiO_3 (BT) particles ($< 3\mu\text{m}$) supplied by Sigma Aldrich were used as the prime source of ceramic fillers. Two batches of BaTiO_3 powders were ordered from Sigma Aldrich which proved to possess slightly different particle surface chemical properties. As stated on the specification sheet, batch No.1 has Loss on Ignition (1000 °C, 1h) of 0.5 % while batch No.2 has that of < 0.1 %. This slight difference resulted in some particle agglomeration for batch No.2 when blended with epoxy resin while batch No.1 was agglomeration-free, presumably due to less surfactant left on the BT particles in batch No.2 than batch No.1. $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) powder with a manufacturer-indicated Sr content x value of 0.3 supplied by Trans-Tech was also investigated for its potential as high permittivity alternative to BaTiO_3 at high frequencies.

Barium Strontium Titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, is a solid solution of BaTiO_3 and SrTiO_3 , and denoted as BST. As a ferroelectric, it shows attractive properties like high dielectric constant, good thermal stability, what is more, unlike many other ferroelectrics it shows excellent high frequency characteristics [16]. It is investigated a great deal as a suitable room temperature ferroelectric for applications in dynamic random access memories (DRAMs), bypass capacitor, IR detector and tunable microwave devices [16–18]. The partial substitution of Sr for Ba adjusts the Curie temperature, as seen in Figure 5.1, with loss tangent volumes ranging from 0.001 to 0.1 as the x value increases from 0 to 1. Although the tetragonal phase is desired for high dielectric constant applications at room temperature, the loss factor is also higher for the ferroelectric phases. Therefore in some cases where a low loss is paramount, a paraelectric phase at room temperature is preferred [16].

The main fabrication methods for BST films are sol-gel, and pulsed laser deposition (PLD), and for bulk materials standard solid-state reaction processes. The dielectric constant of BST is dependant on factors such as the fabrication

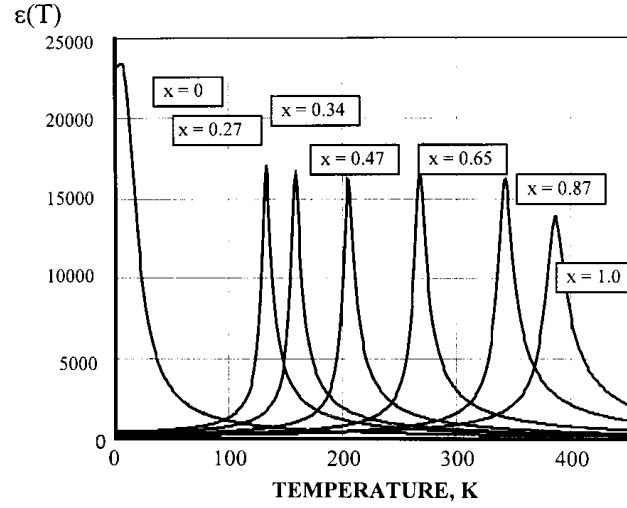


Figure 5.1: Dielectric constant of $(\text{Ba}_x, \text{Sr}_{1-x})\text{TiO}_3$ single crystals as a function of temperature for different contents of barium [19]

Table 5.1: Dielectric measurements at high frequencies reported in the literature for BST with various strontium contents x

Strontium content x	Frequency	Dielectric constant ϵ_r	Loss factor $\tan\delta$
0.4 [21]	8 GHz	1000	0.04
0.4 [22]	10 GHz	260	-
0.4 [23]	10 GHz	730	0.04
0.25 [24]	1 GHz	1746	0.12
0.5 [24]	1 GHz	910	0.008
0.75 [24]	1 GHz	320	0.002
0.5 [25]	1-16 GHz	635	-
0.55 [26]	10 GHz	1205	0.0138
0.5 [26]	10 GHz	1099	0.018
0.4 [26]	10 GHz	1002	0.0091

process, composition, temperature and frequency. Doping (in particular of Mg and Mn) has been investigated and reported to have profound effect on the dielectric performance of BST. A dielectric constant of 1200 and loss factor of 0.005 at 12.6 GHz had been reported for 2% Mn:BSTO thin films [20]. Dielectric constant data of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ was gathered from the literature and is listed in the Table 5.1.

Other perovskites such as calcium titanate (CaTiO_3) powders from Sigma Aldrich were explored in this work as a low-loss material. The SEM images of

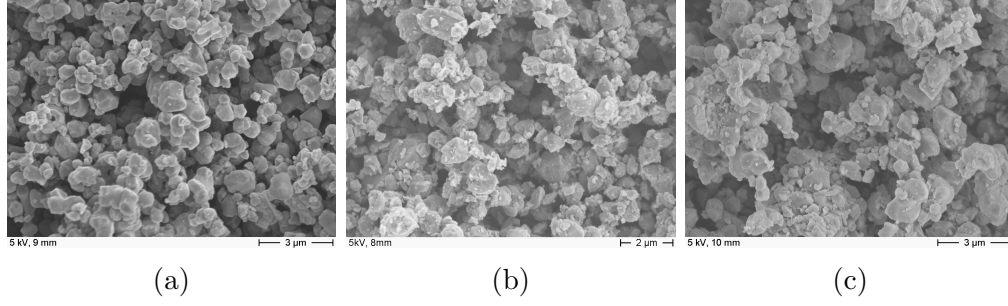


Figure 5.2: SEM images of as-received BT(a), BST (b) and CT (c) powders

the as-received ceramic powders are shown in Figure 5.2, from which we can see that BT powders appear to have more uniform particle size distribution than BST and CT powders. All three powders show faceted particle geometries but some pallets and flakes particle geometry are observed only in BST and CT powders.

Particle sizes

The as-received BT and BST particle sizes were measured by Mastersizer 2000 and the results shown in Figure 5.3. Powders were dispersed in water with the ultrasonic probe running while taking measurements to facilitate dispersion, but agglomerates can still be observed in these results. The mean particle sizes $d_{(0.5)}$ are $1.92 \mu\text{m}$ and $1.37 \mu\text{m}$ for BT and BST respectively.

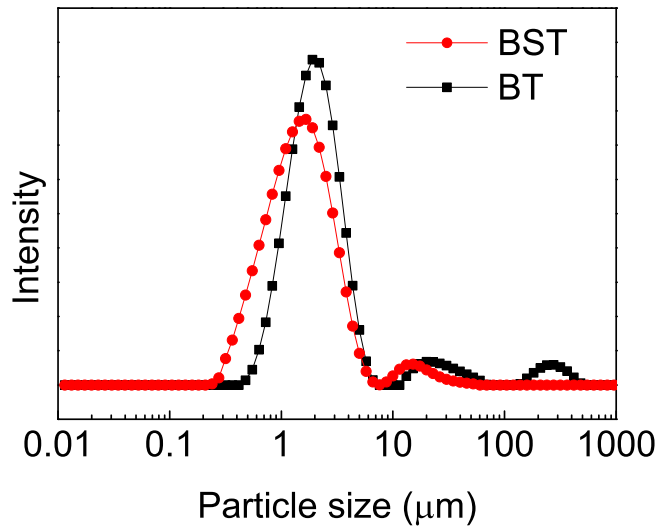


Figure 5.3: Particle size measurements for as-received BT and BST powders with evidence of agglomeration shown as small additional peaks

X-ray diffraction

BST powders were characterized by x-ray diffraction to determine its crystal structure and to calculate precisely its lattice parameter. Because the lattice parameters are dependent on the Ba to Sr ratio (decreasing with higher Sr content [27]), this measurement can be used to estimate the x value in the $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ formula. Powders were press-fitted into the XRD powder diffraction sample holder with the sample surface flush with the surface to get accurate 2θ values. All the peaks were identified and labelled in Figure 5.4. No change was observed in XRD scan for BST powders after heat-treatment at 1000 °C for a few hours indicating an absence of structural or compositional changes. Peaks were refined with the X'pert Highscore software profile fitting option to resolve any possible peak splitting. No peak splitting was observed in the XRD data from the BST powder and a cubic phase was concluded. Precise lattice parameter calculation was conducted using every peak with an identified set of Miller indices and the lattice parameter a was calculated from equation 5.1 and the Bragg equation 5.2.

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (5.1)$$

$$\lambda = 2d\sin\theta \quad (5.2)$$

Errors can be corrected by utilising extrapolation functions of either the Bradley-Jay ($\cos^2\theta$) or the Nelson-Riley function ($\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}$) to achieve high precision lattice parameters [28]. The extrapolation process is illustrated in Figure 5.5 from which it can be seen that the Nelson-Riley function gives a better convergence for a values with an extrapolated values of $a = 3.973 \text{ \AA}$. The calculated a value was cross-referenced with relevant XRD database (PDF number 01-089-0274, 01-089-8211, 00-044-0093) and a good match was found in the reported XRD measurements of $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ which was interpreted as a tetragonal phase with very similar c and a values ($a=3.9724 \text{ \AA}$, $c=3.9703 \text{ \AA}$) [29]. The x value of

0.33 is close to the initial stoichiometric ratio of 0.3 for starting raw materials as indicated by the supplier. No peak-splitting was spotted in the XRD scan at any of the characteristic high angles where the tetragonal peak-splitting is likely to be easily detected. Given the exceptionally small tetragonality (i.e. c/a ratio very close to 1), the x-ray diffractometer used probably would not be able to detect any peak-splitting even if there is any. Therefore, a tetragonal phase can not be deduced based on our XRD data. More accurate measurements would be possible with an X-ray synchrotron with higher angular resolution.

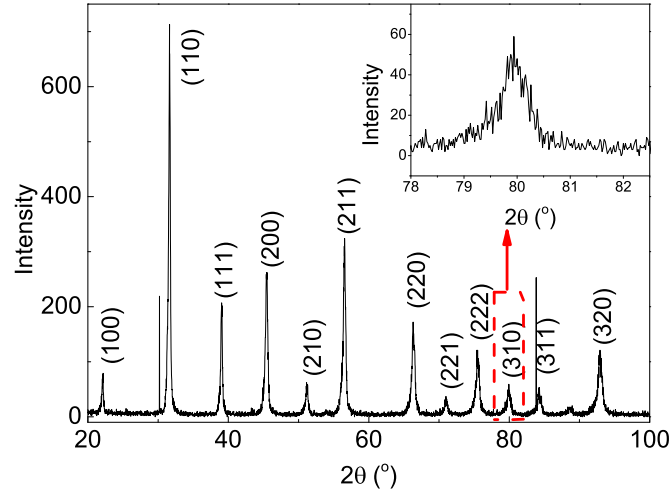


Figure 5.4: XRD scan for BST powders from 20° to 110° with a blow-up of a high angle peak (310) where tetragonal peak-splitting is most likely to be detected

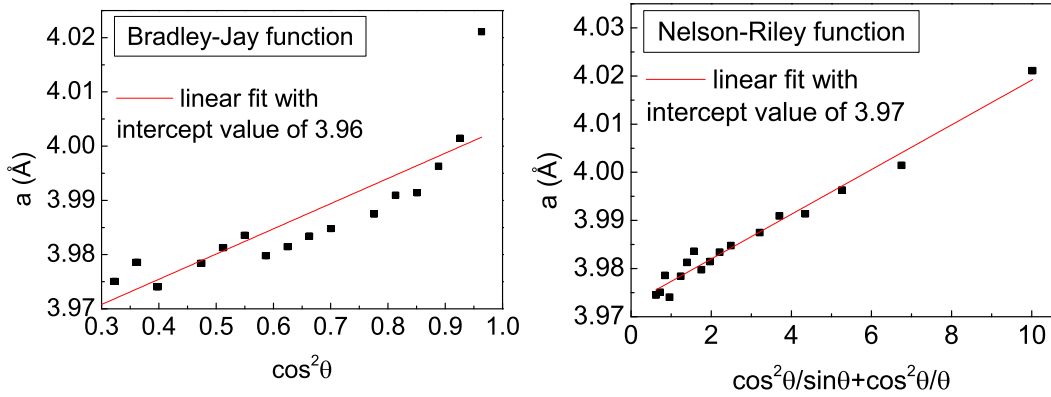


Figure 5.5: Linear fittings of $\cos^2\theta - a$ and $(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}) - a$ plots showing that Nelson-Riley function gives a better converged a value – 3.97 Å

WDS

Wavelength diffractive spectroscopy was used to quantify the stoichiometry of BST powders. As-received and heat-treated (at 1000 °C) BST powders were embedded in resin and ground and polished down to 1 μm grade for WDS examination. Excluding one or two out of range data points possibly resulted from impurities or contamination, 16 data points from each sample were taken and averaged for the atomic ratio of Ba/Sr. The standard deviation in the measurements were calculated and plotted in Figure 5.6. The fact that the standard deviations for both sets of data were a bit high suggested that the polish might not be good enough and sample preparation imperfect. The averaged atomic ratio of Ba/Sr around 2 corresponds to an x value of 0.33 in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, which agrees well with the XRD data above. Combining the XRD and WDS results, we can conclude that the BST powders we used in this work have the chemical formula of $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$.

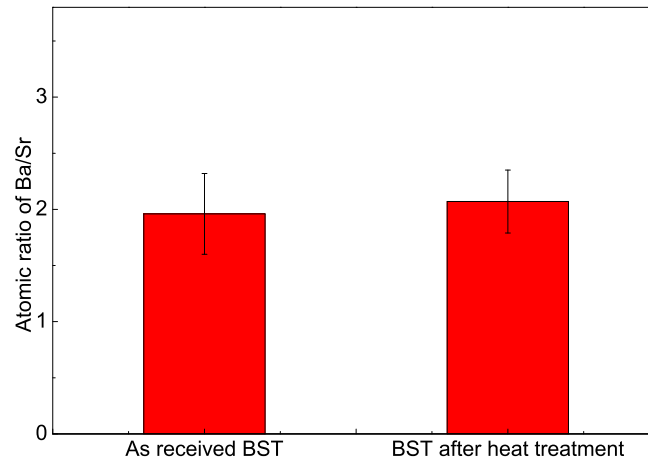
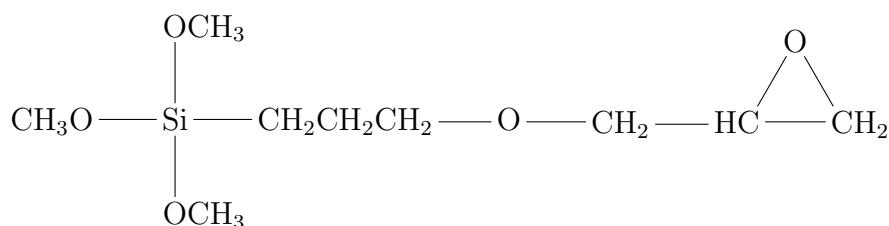


Figure 5.6: Atomic ratio calculation of Ba/Sr in $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ formula from WDS for as-received and heat-treated BST powders respectively with an average value of 1.97 and 2.07 and standard deviation of 0.33 and 0.28 accordingly

Silane coupling agents

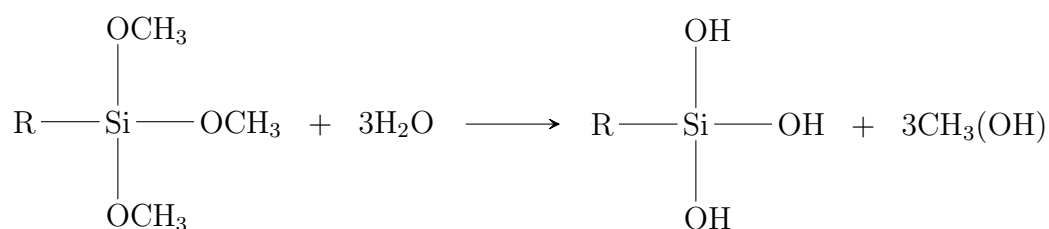
Inorganic materials such as BaTiO_3 with hydroxyl-containing surfaces are hydrophilic in nature and are difficult to disperse in non-aqueous organics such as epoxy resins [30]. The dissimilarity in the material chemistry not only results in agglomerates of ceramic particles but also poor composite mechanical properties. Silane coupling agents are widely used to modify the surface chemistry of materials and therefore to enhance bonding between the organic and inorganic parts (at least one of which has siliceous surface properties) by forming stable covalent bonds between the two. Silane coupling agents can be described by the general formula of $\text{R}-(\text{CH}_2)_n\text{-Si-X}_3$, where X and R are the two functional groups that represent a hydrolyzable group (typically alkoxy group) and an organofunctional group respectively [31]. While the hydrolyzable group X is responsible for forming siloxane bonds with the inorganic surfaces, the right organofunctional group R enables stronger affiliation with the functional group of the organic matrix (epoxy resin in our case) in order to facilitate the formation of uniform polymer-ceramic composite system. The choice of R depends on the functional groups of the organic material. For epoxy resin, amine, anhydride and epoxy groups are recommended for silane coupling agents [31]. From the existing literature on epoxy composite systems, (3-Glycidoxypropyl)trimethoxysilane $\text{C}_9\text{H}_{20}\text{O}_5\text{Si}$ (GPTMS), whose chemical structure is shown below, is reported to be effective in dispersing ceramic fillers [30, 32–36]. In this work, GPTMS (MW 236.34 g/mol, by Sigma Aldrich) is used for dispersing barium titanate and barium strontium titanate powders in epoxy matrices.



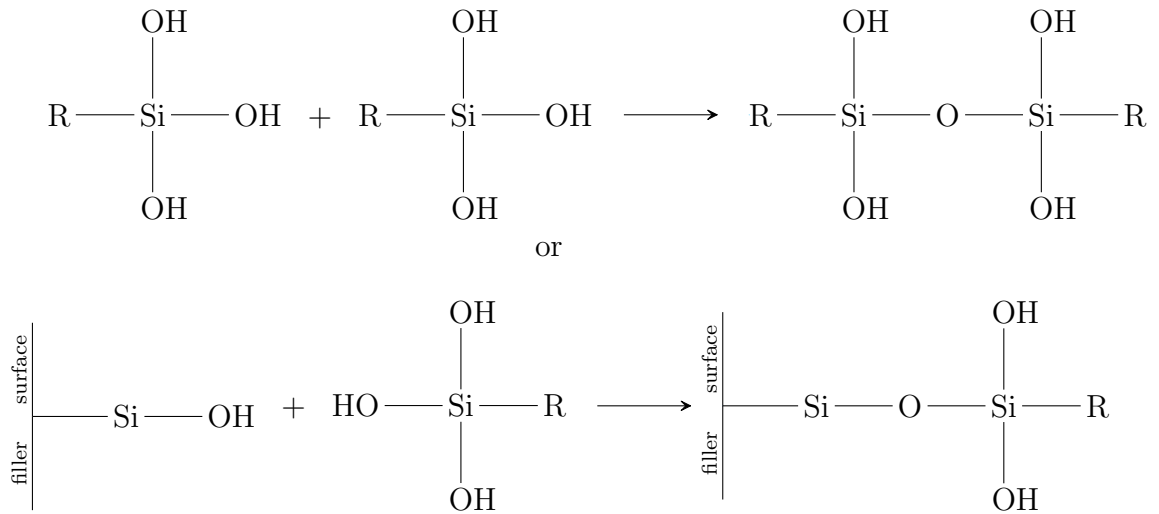
(3-Glycidyloxypropyl)trimethoxysilane

The way silane coupling agents work involves two steps; hydrolysis and condensation. The alkoxy groups are initially hydrolysed to form silanol bonds (Si-OH). The source of water could be either from an aqueous environment or from the water absorbed on the filler surface. Once the silanol bonds are formed, they will condense with other silanol bonds into siloxane bonds (Si-O-Si) through loss of water. The condensation process could happen either between silanol groups on alkoxy silanes forming oligomers or between silanol groups on alkoxy silanes and on filler surfaces. Elevated temperatures (50 - 120 °C) may be required for the condensation process. The hydrolysis and condensation processes for GPTMS and NPATMS were experimentally observed by adding a few drops of silane coupling agents into water. Because of the poor solubility of alkoxy silanes in water, phase separation was seen in the beginning. With the hydrolysis taking place over time (ca. 15min for GPTMS), the silane water solution became clear showing it had become one phase. The clear solution was then put into an oven at 110 °C for about 15 min to encourage the condensation to occur, after which the solution became cloudy as silanols condensed to form siloxanes. The chemical reactions were illustrated below:

Hydrolysis:



Condensation:



Methods to apply silane coupling agents have been summarised in the brochure provided by Gelest Inc. [31]. The most effective method for powders surface treatment involves a spray-dry equipment that allows the silane agents to condense onto the powder surface while the particles are separated. Given the restriction of facilities, alternative non-spray-on methods were sought in this work. Combining the summary by Gelest Inc. and methods for epoxy-ceramic composite silane agent treatments reported in the literature, the following three application methods were considered, deposition from aqueous alcohol [30, 32, 33], from aqueous solution [34] and from anhydrous liquids [35, 36], with various processing conditions and parameters given in the different reports. Deposition from aqueous alcohol features a 95 % ethanol and 5 % water solution whose pH value is adjusted to 4.5 - 5.5 with acetic acid, to which 2 % of the silane agent is added. Ceramic powders are then stirred in the prepared solution for some time before being dried and cured at high temperatures (~ 110 °C). For aqueous solution deposition, approximately 0.5 - 2 % of the silane agent is dissolved in water and then the solution is adjusted to pH 5.5 with acetic acid. The aqueous solution can either be sprayed onto ceramic powders or used as a stirring medium. After the silane agents are deposited, the powders are washed by water to remove residual

silanes, dried and cured for 20-30 min at $\sim 110^\circ\text{C}$. Anhydrous liquid deposition adopts toluene, tetrahydrofuran or hydrocarbon solutions as base solvents. After addition of 5 % of silane, ceramic powders are treated in the solutions for 12 - 24 hours. Powders are washed with clean solvent for a couple of times to remove organic residues and the solvent is then removed by air drying or vacuum drying with no further curing required.

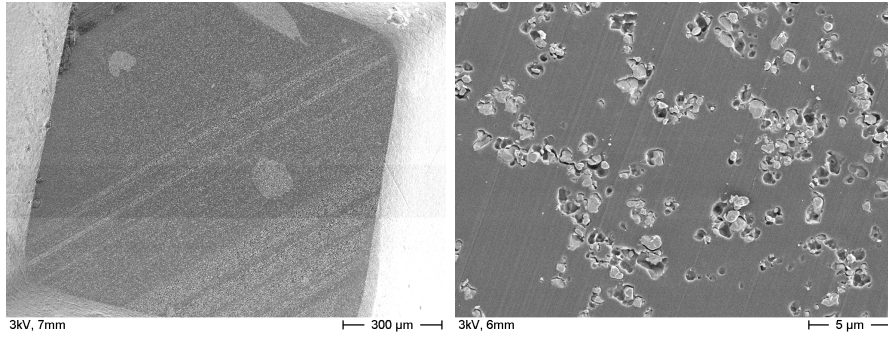
5.2.2 Sample preparation

Particle surface treatment

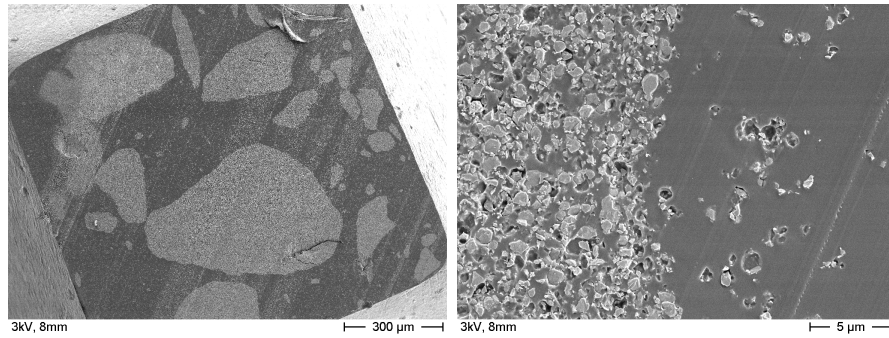
Minor agglomeration was found in epoxy composites of as-received second batch BT powders, while significant agglomeration observed in the epoxy composites of as-received BST powders, shown in the SEM images of their cross-sections in Figure 5.7. This encouraged me to explore possible dispersion agents. Silane coupling agents were first tested on BT powders (batch No.2) as there are more reports in the literature regarding silane treatment on BT powders [32, 33, 35, 37]. The successful processing route was then repeated to work on BST powder, because of the similarity in the property of the two powders.

Preliminary tests were conducted to investigate the effect GPTMS has on dispersing BaTiO_3 powders in aqueous alcohol, aqueous solutions and anhydrous liquids (toluene in our case). It was found that for the first two conditions where water was used, the treated ceramic powders must be dried completely before compositing it with the epoxy solution which is non-aqueous. In-situ drying would inevitably cause particle re-agglomeration and reverse previous efforts to separate the particles. Consequently I had to proceed to undertake all powder surface treatments in toluene solutions.

Weighed ceramic powders were added into a sufficient volume of a solution of 5 vol% of GPTMS in toluene. The beaker containing the suspension was placed in an ice bath and ultrasonicated by a high power ultrasonic processor at 60 %



(a) epoxy-10vol%BT microtome sample



(b) epoxy-10vol%BST microtome sample

Figure 5.7: Varied degrees of agglomeration seen in SEM images of epoxy composites with as-received BT and BST powders at high and low magnifications

of its maximum amplitude (750 Watt) with settings of 55 seconds off pulse after every 5 seconds of running to control excessive heat from the ultrasonicator at such high amplitude for a continuous 12 h. Plastic films were used to cover the beaker to prevent toluene evaporation under the excessive heat generated by the ultrasonic probe. As described earlier, the silane deposition in anhydrous solution takes 12-24 h to be effective. The ultrasonication process lasted for about 12 h for the Si-O-Si bond to form on the ceramic particle surfaces. The toluene solvent was then removed from the system by putting the solution in vacuum or/and at elevated temperature to expedite the process. The evaporation needed to be fast and a minimal amount of toluene residue can be left to avoid re-agglomeration. It is worth mentioning that the toluene residue, although in a small amount, still had several effects (proportional to the amount) on the composite properties later when mixed with epoxy: 1) toluene residue hindered the cross-linking process of

the epoxy [38] and hence extended the composite curing times as well as reducing the composite hardnesses; 2) toluene residue diluted the theoretical composition resulting in an actual volume fraction of ceramic powders smaller than theoretical calculation. To get rid of its influence and remove the toluene completely, the suspension after ultrasonication was centrifuged (10 min each time @ 3000 rpm) and washed twice with acetone. Because of the high vapour pressure of acetone, it evaporated rapidly off the system and left minimal traces in powders so that the powder still appeared to be wet instead of completely dried. The freshly prepared ceramic powders were used to prepare epoxy/ceramic composites immediately.

Another surface treatment considered for BST powders is heat treatment. BST powders were placed in an oven at 1000 °C in air for a few hours to eliminate absorbed CO₂, H₂O and potential impurities. Heat treatment of BST ceramics has been reported in the literature before to have the effect of enhancing the dielectric constant, but without a clear understanding of why this was beneficial [39]. It was speculated that the cause could either be macroscopic, i.e. thermal stress or grain growth induced by heat treatment or microscopic, i.e. phase or compositional changes after heat treatment.

The complete processing chain for epoxy/BST composites is illustrated in Figure 5.8. SEM images of the cross-sections of epoxy/BST composites prepared in this way (Figure 5.9) prove that this processing route is effective in breaking down BST agglomerates and dispersing the BST powder uniformly in epoxy resin. The dispersion improvement is remarkable when compared with Figure 5.7.

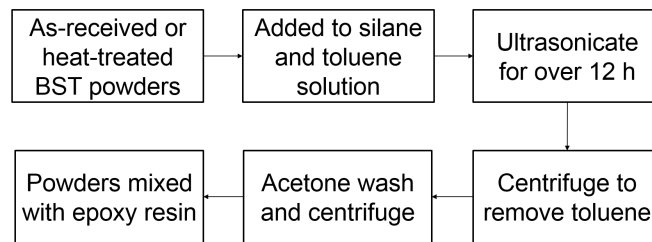
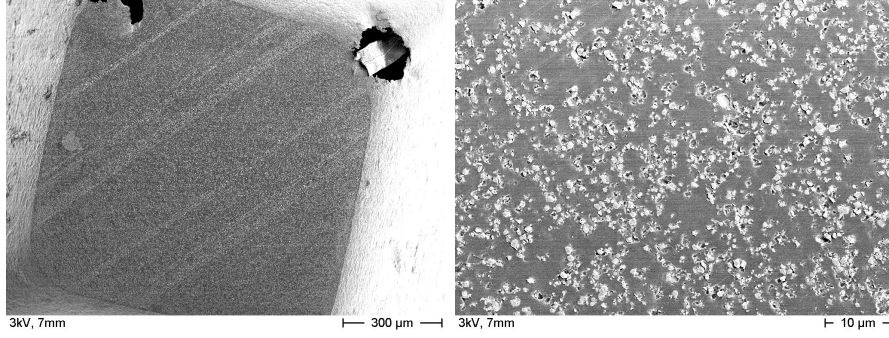
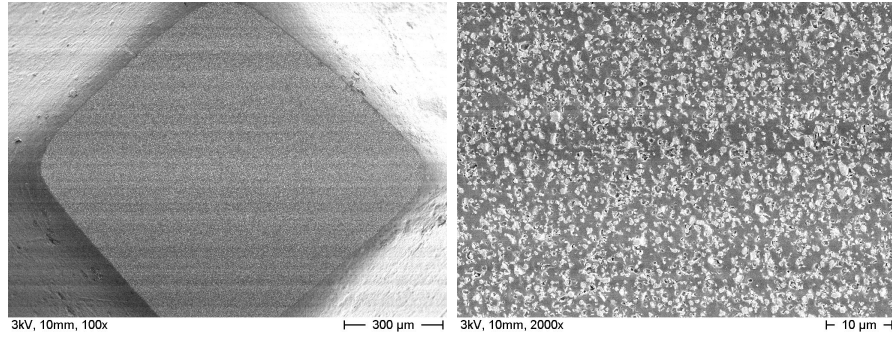


Figure 5.8: Process flow diagram for preparing uniform epoxy/BST composites



(a) epoxy-5vol%BST treated by GPTMS microtome sample



(b) epoxy-30vol%BST treated by GPTMS microtome sample

Figure 5.9: Almost agglomerate-free cross-sections of epoxy-5vol%BST and epoxy-30vol%BST composites after surface treatment with silane GPTMS

Casting

Epoxy base material was prepared by mixing pre-warmed (at 60 °C) resin, hardeners and accelerator in ratios as stated in the manufacturer instructions. Pipettes were used throughout the process to ensure accurate measuring, particularly for measuring the volume of epoxy to be compounded with ceramic powders. Ceramic powders were weighed and added into the epoxy by volume fraction. Direct mixing suffices for most epoxy/BT composite preparation. To eliminate the small fraction of agglomerates in epoxy/BT composites made from BT batch No.2, an ice-water bath sonication for about 1 hour was introduced to facilitate better dispersion. BST powders require more sophisticated particle surface treatment before mixing with epoxy because of the bad agglomeration in these BST powders. The epoxy composite pastes were hand-stirred vigorously for approximately 30 min until well-dispersed mixtures were achieved. Composites with ceramic load-

ings of less than 30 vol% were put into a vacuum oven at room temperature that goes down to -0.1 MPa to remove any trapped air bubbles. One or two drops of acetone solvent were sprayed onto the surface of the composite paste to facilitate air bubbles popping by temporally thinning the epoxy and reducing its surface tension. The acetone evaporated rapidly so no residues were left in the composites. Due to the viscosity increase with the volume fraction of barium titanate, only in mixtures with loadings up to 30 vol% are air bubbles able to reach the surface and hence could be degassed efficiently in the vacuum oven. The degassed composites were poured into PTFE moulds and put into a furnace at 60 °C to cure for at least 24 hours. For each composition, up to identical 5 samples in dimensions of 15.8 mm x 7.9 mm were prepared for waveguidement measurements.

In this work, epoxy/BT composites with filler loadings of up to 43 vol% were prepared, above which the mixture became too viscous to stir. The degassing process was conducted only for filler loadings below 30 vol%. To investigate the highest dielectric constant we can achieve in a controllable fashion by substituting BT with BST powders, epoxy-30vol%BST composites (which is about the highest content of BST in the epoxy that can still be degassed) with various BST surface conditions were prepared, measured, and compared with the same volume fraction BT composites. Epoxy-30 and 40 vol%CT composites were also prepared to explore the opportunities to lower the losses at high frequencies.

5.3 Results and discussion

FTIR

The hydrolysis and condensation process for silane coupling agent GPTMS were examined by FT-IR as shown in Figure 5.10 where the infrared absorption of as-received GPTMS, GPTMS after 15 min of hydrolysis and GPTMS after 15

min of condensation at 110 °C were compared. The characteristic peaks at $\sim$

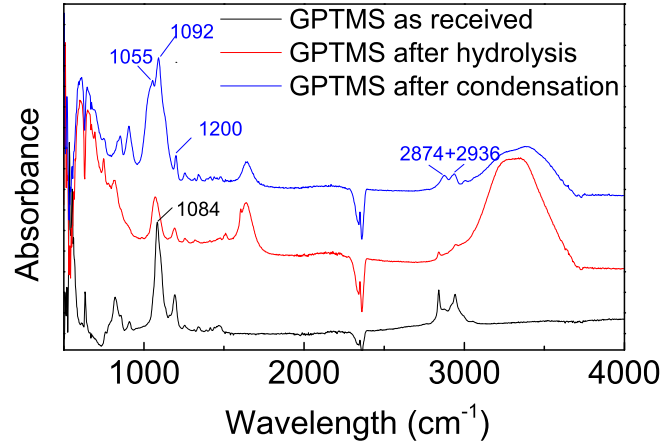


Figure 5.10: Comparison of FTIR results of as-received GPTMS, GPTMS after 15 min of hydrolysis and GPTMS condensed for 15 min at 110 °C after the hydrolysis

1100 cm^{-1} were assigned to Si-O groups [40]. Specifically, the peak at 1085 was assigned to the Si-O-C bond and was observed in as-received GPTMS [41]. The peak was broadened and shifted a little to the left after hydrolysis because of overlap with the peak at $\sim 1050\text{ cm}^{-1}$ which was assigned to MeOH [42]. The peak splitting became obvious after the appearance of the absorption peak of the Si-O-Si group at $\sim 1080\text{ cm}^{-1}$ [35] during condensation. In addition to the peak of $\sim 1080\text{ cm}^{-1}$, it has been pointed out in [43] that the absorption peak at 1200 cm^{-1} is also characteristic of the Si-O-Si bond. The absorption peaks observed at ~ 2850 and $\sim 2940\text{ cm}^{-1}$ accounted for the symmetric and asymmetric stretching vibration of $-\text{CH}_2-$ respectively [35, 40].

Successful Si-O-Si bond formation on ceramic particle surfaces was proved by comparing FTIR results of as-received ceramic powders and powders after the GPTMS surface treatment. Figures 5.11 and 5.12 are FTIR results after GPTMS surface treatments on BT and BST respectively as described above. To eliminate interference from toluene and other organic residues, FTIR was also taken on powders washed twice by ethanol. The detection of the absorption peak at $\sim 1100\text{ cm}^{-1}$ in BT and BST powders after the GPTMS surface treatment (before and

after washing with ethanol) is a strong proof of the successful formation of Si-O-Si bonds on the surface of the ceramic powders. The ethanol wash does help clean organic residues from the powders, as shown by the observed disappearance of peaks at ~ 2850 and ~ 2940 cm^{-1} after the ethanol wash, as well as the weakened peaks at ~ 1100 cm^{-1} and ~ 1050 cm^{-1} . Comparing Figure 5.11 and 5.12, it seems the GPTMS treatment had a stronger effect on BST powders than BT powders, as more intense peaks for the Si-O-Si group were seen on BST powders.

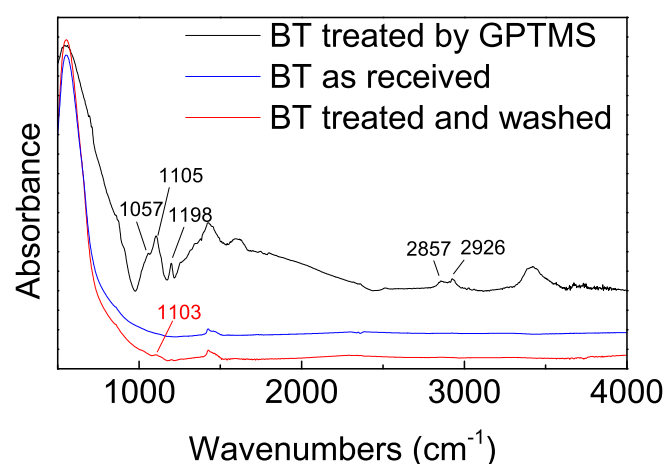


Figure 5.11: Comparison of FTIR results of as-received BT powders, BT powders dried directly after GPTMS surface treatment, and BT powders washed by EtOH twice after GPTMS surface treatment

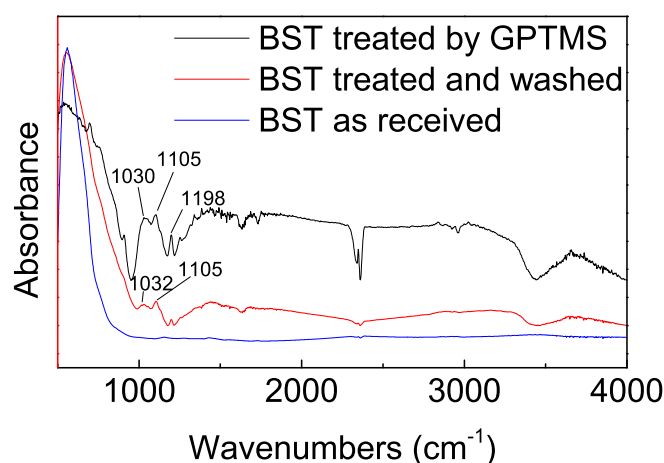


Figure 5.12: Comparison of FTIR results of as-received BST powders, BST powders dried directly after GPTMS surface treatment, and BST powders that was washed by EtOH twice after GPTMS surface treatment

5.3.1 Permittivity measurements

Instrumental errors

Given that the permittivity measurements described in this work were newly developed in our group, a few measures were taken on my samples to authenticate the validity and accuracy of these measurements before systematic measurements were taken and further analysis conducted. The first step of the process was to determine the instrument error in the VNA and waveguide system and assess the stability of measurements. A epoxy-15vol%BT waveguide sample was used to study the instrumental errors. The sample was inserted into the waveguide, measured and taken out repeatedly for 10 measurements. The dielectric constant and loss tangent data for these 10 measurements are shown in Figure 5.13. The average value is 5.86 with a standard deviation of 0.03 which indicates an instrument error of within 5% that can be considered negligible in this case.

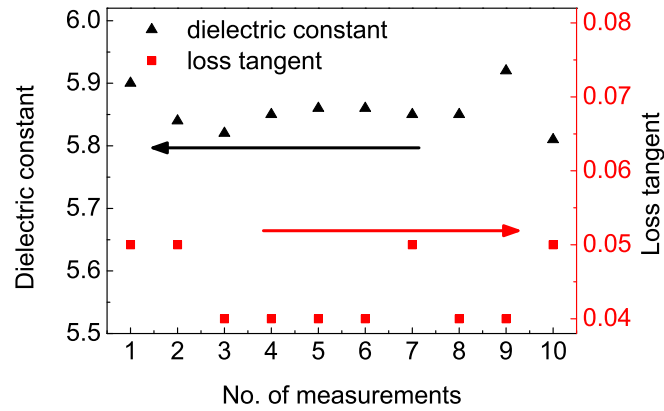


Figure 5.13: Ten repeated measurements of one epoxy-15vol%BT sample to examine the instrumental error

Reference measurements and effect of degassing

A series of epoxy/BT composite samples with BT loadings up to 40 vol% were initially prepared and measured by the VNA in our group in Oxford and later the same samples were measured by the VNA in one of our collaborators - Exeter University where they had more experience in reliable waveguide measurements.

The results are compared in Figure 5.14. A good agreement was found between the Oxford data (the black dots) and the Exeter data (the blue dots), proving a reliable waveguide method to measure permittivity and permeability values has been established in our group.

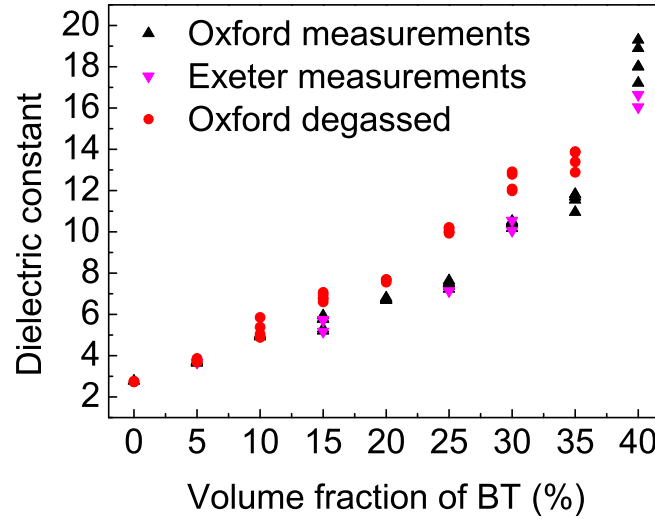


Figure 5.14: Comparison of waveguide measurements made in Oxford and in Exeter of epoxy-BT composites with various BT loadings to ascertain the legitimacy of Oxford measurements. A vacuum degassing process was introduced to the sample preparation to achieve higher and stable results

When composite samples were sectioned with a saw, the revealed cross-sections were examined under an optical microscope (Figure 5.15). A varying concentration of air bubbles were visible in samples of all compositions, and were believed to be introduced into the composites during mixing. The adverse effects of the entrapped air include: 1) lowered the effective permittivity values of the composites; 2) non-uniform electromagnetic properties of composites resulted from non-uniform distribution of air bubbles. To eliminate the influence of air bubbles, a vacuum degassing process of less than 30 min was introduced after the composite pastes were well-mixed and before curing. The degassed samples were measured by the waveguide method showing as expected higher permittivity values compared to undegassed samples (Figure 5.14). The optical microscope images of some degassed samples are shown in Figure 5.16. Comparing to Figure 5.15, it

can be seen that the process was very effective in removing all the air bubbles.

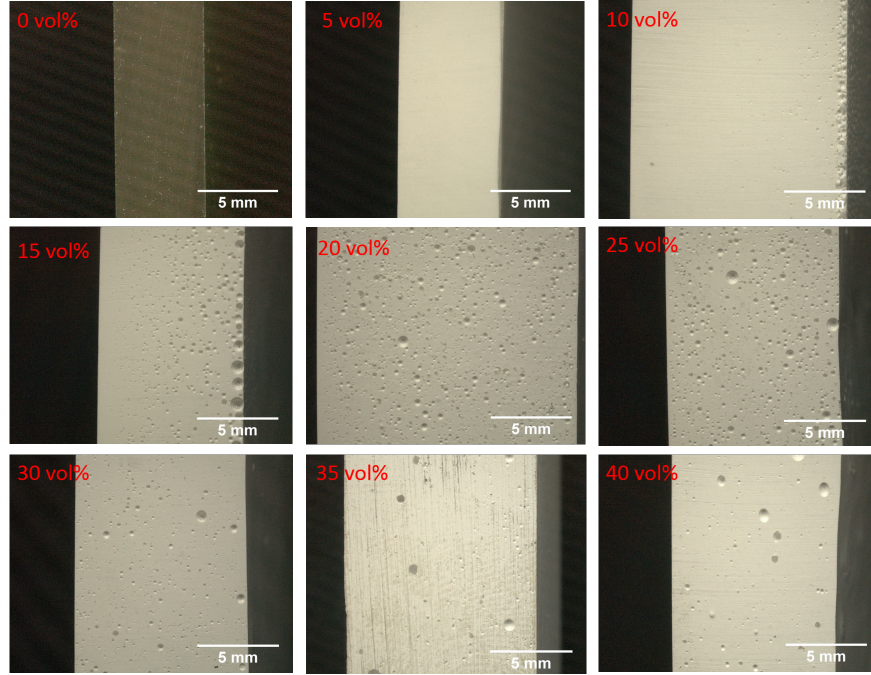


Figure 5.15: Optical microscope images of undegassed epoxy/BT composite samples across different compositions with clear evidence of entrapped air

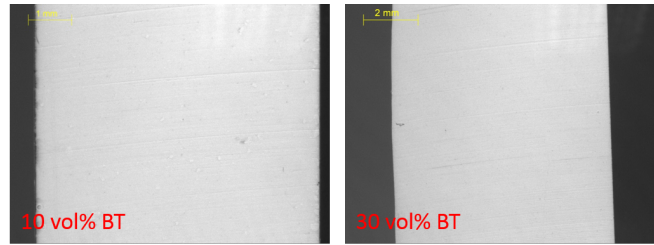


Figure 5.16: Optical microscope images of degassed epoxy-10vol%BT and epoxy-30vol%BT composite samples with no sign of air bubbles

Epoxy/BT composites

Once the reliability of the waveguide measurements in our group was established, a series of epoxy/BT composites with BT loadings from 0 to 43 vol% were prepared to explore the capability of producing composites with controllable dielectric properties. The typical dielectric performance of epoxy/BT samples at various compositions between 12 - 18 GHz are shown in Figure 5.17. As expected, the

dielectric constant, ϵ_r , values are non-dispersive and constant over this frequency range. It can be seen though that epoxy/BT composites with higher BT loadings exhibit noisier results. This phenomenon is related to the shift of propagating wavelength inside samples as their permittivity (or reflective index) increases,

$$f = \frac{c}{n\lambda} \quad (5.3)$$

where f is the frequency of the propagating wave, n represents the refractive index of the media, i.e. the sample in our case, λ is the wavelength inside the media, and c is the wave propagation velocity in vacuum which is about 3×10^8 m/s. An increase of sample refractive index causes a corresponding reduction in the wavelength of the propagating wave. If at a certain refractive index value, the half-wavelength $\lambda/2$ was reduced to the value of the waveguide cavity width d (i.e. the sample thickness) or below, the cavity's fundamental frequency, also referred as the lowest resonant frequency, is reached and a resonance condition will be established. For a sample thickness of 2 mm, the half-wavelength limit would be 4 mm, which corresponds to a refractive index of about 4.2 or a relative permittivity of 17.6 (when permeability is 1) at 18 GHz. Therefore, when the sample dielectric constant increase as the loading of BT increases, the signal gets noisier as it approaches the cavity's fundamental frequency. To counteract the impact of the increase of the permittivity values, thinner samples (usually 1 mm) were prepared for composites with high BT loadings (not suitable for low BT loadings as a strong enough reflection signal needs to be detected for the calculation of permittivity). Based on practical experience, samples with BT loadings of 30 vol% and above are best measured with thinner samples with thickness of 1mm.

Up to five epoxy/BT composite samples for each composition from 0 to 43 vol% were prepared and measured by the waveguide method. Their dielectric con-

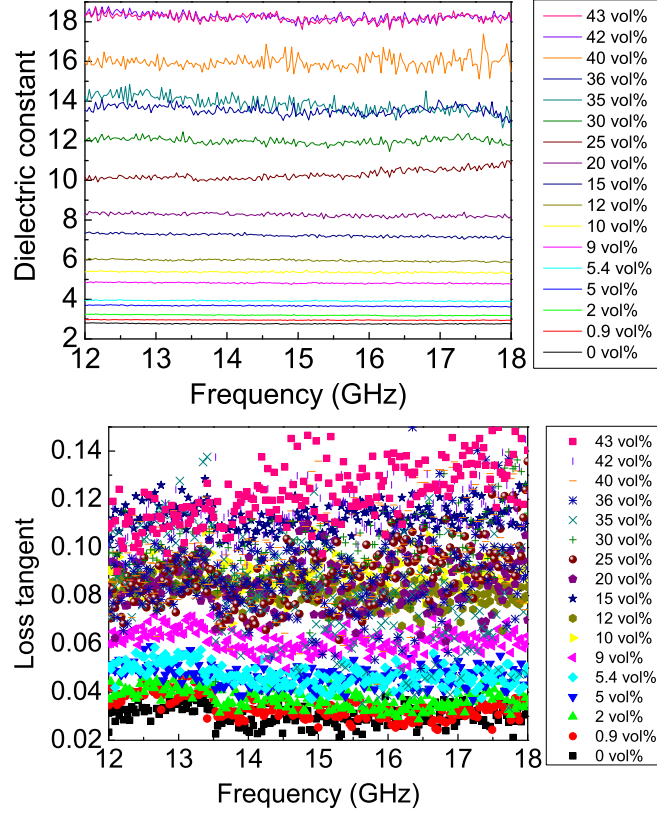


Figure 5.17: Dielectric constant (top) and loss tangent (bottom) at scanning frequency 12 to 18 GHz for epoxy/BT composites with BT volume fractions from 0 to 43 %

stants at 15 GHz are plotted in Figure 5.18. The dielectric constant of epoxy/BT composites steadily increases from around 3 to over 18 as more BT is added as expected. Loss tangent values from around 0.03 to 0.12 are obtained in the waveguide measurements for these epoxy/BT composites. Note that when comparing to the PFA/BT high frequency data achieved in Chapter 4 by the same waveguide measurement, the loss tangent value of a PFA/BT composite giving a dielectric constant of 6 is around 0.03 while the epoxy/BT composite giving the same dielectric constant has a loss tangent value of around 0.08. A strong evidence of the importance of using low loss polymer matrices in controlling the dielectric loss in composites. It is also obvious that the dielectric constant values for the epoxy/BT composites with loadings higher than 30 vol% are more scattered, which can be explained by the fact that only composites with BT loadings up to 30 vol% were

vacuum degassed (hence strictly two-component systems without air bubbles). For composites with loadings higher than 30 vol%, their dielectric properties fluctuate in accordance with the amount of air bubbles in the system and the homogeneity of the air bubbles distribution, and hence are more scattered. As a result, only data for composites within the composition range 0 to 30 vol% (data included in the red circle) are used for mixing rule fitting, as discussed below. For composites with BT loadings less than 30 vol%, good data consistency was seen for measurements from different samples with the same composition, which could be evidence of uniform distribution of BT particles inside the epoxy resin. To examine the microstructure of the epoxy/BT composites, SEM images of the cross-sections of epoxy/BT composites with a range of compositions were taken, and shown in Figure 5.19, all of which reveal a homogeneous microstructure in the epoxy/BT composites.

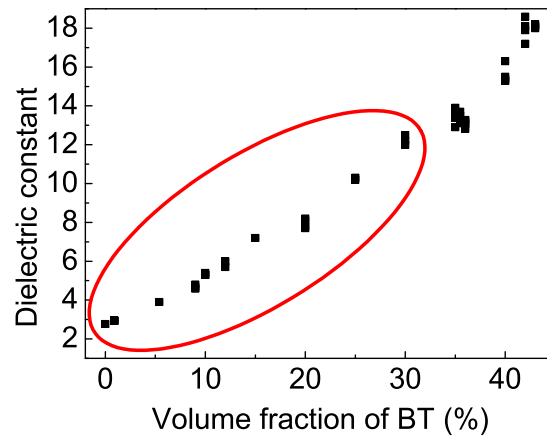


Figure 5.18: dielectric constant of all epoxy/BT composites at 15 GHz plotted against BT loadings from 0 to 43 vol%

Epoxy/BST composites

Epoxy-30vol%BST composites containing BST powders processed in a variety of ways were prepared and tested in this work:

- a. as-received BST powders
- b. BST powders treated with GPTMS

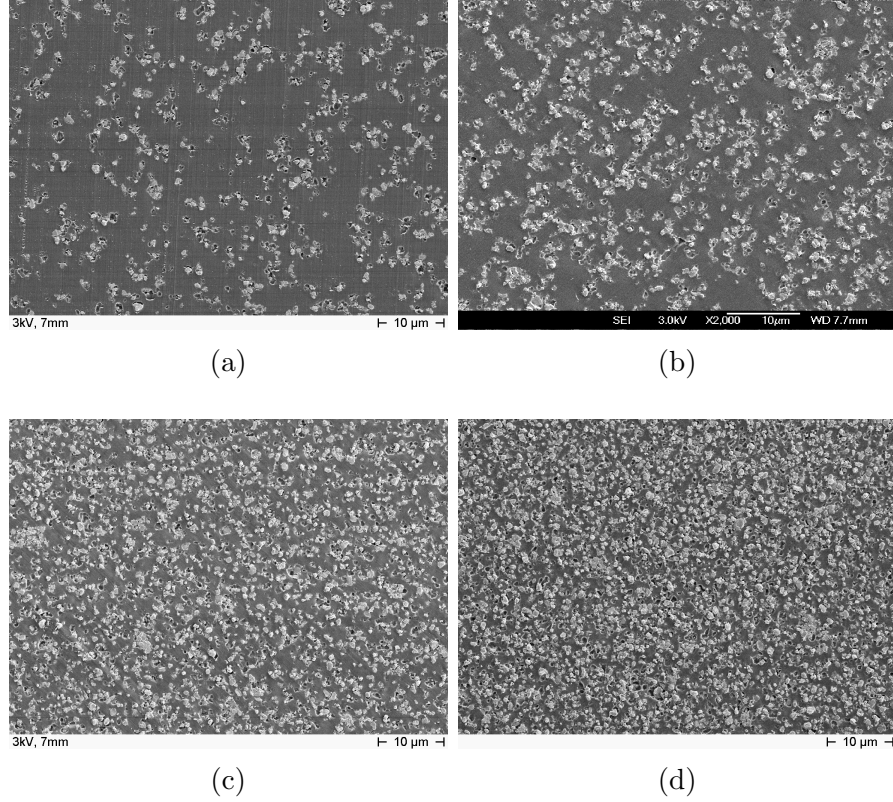


Figure 5.19: SEM images of (a) epoxy-5vol% BT (b) epoxy-15vol% BT (c) epoxy-25vol % BT (d) epoxy-35.5vol% BT samples

- c. BST powders that have been heat-treated
- d. BST powders that have been heat-treated and then GPTMS treated
- e. BST powders that have been heat-treated, GPTMS treated and washed in acetone

The waveguide and density measurements of these samples are shown in Figure 5.20. We can see that composites made from GPTMS-treated BST powders (B) show slightly lower dielectric constants than untreated BST (A) which is probably caused by the sedimentation effect in the untreated BST composites and samples being made from the bottom of cured composites. The density measurements substantiate this hypothesis, showing a higher density for composites made from untreated BST powders than GPTMS-treated ones. The density of pure epoxy was measured to be 1.19 g/cm^3 and the density of BST powders

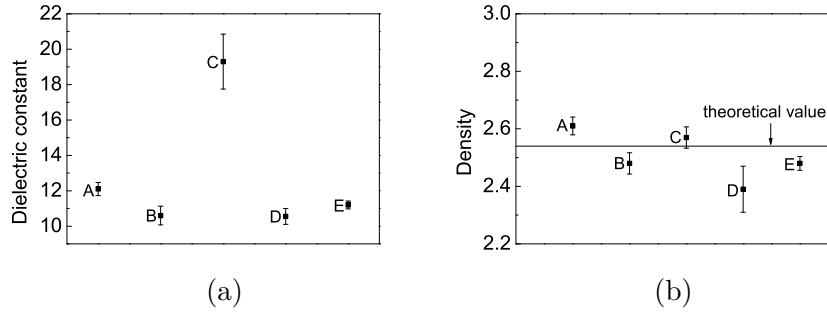


Figure 5.20: Dielectric constant and density measurements for epoxy-30vol%BST composites in five groups: A. composites made from untreated BST powders; B. composites made from GPTMS-treated BST powders; C. composites made from heat-treated BST powders; D. composites made from heat-treated and GPTMS-treated BST powders; and E. composites made from heat-treated, GPTMS-treated and acetone washed BST powders

was indicated in the manufacturer's sheet as 5.7 g/cm^3 , therefore we can calculate the theoretical density value for the epoxy-30vol%BST composite to be 2.54 g/cm^3 which is marked using a horizontal line in Figure 5.20 (b). The composites made from acetone-washed BST powders after particle treatment (E) although has about the density as the ones not washed by acetone (B and D) present a small increase of dielectric constant and narrower standard deviation, which is most likely caused by acetone's function of removing toluene residues and the resulted in more homogeneous and compact composites.

Comparing measurement data between composites made from heat-treated BST powders (C) and untreated BST powders (A), we see a substantial increase in the dielectric constant after the heat treatment while maintaining the same level of density. The unchanged density excludes the possibility of dielectric constant enhancement from compositional variation due to BST agglomeration and sedimentation after heat-treatment. Therefore such enhancement is deduced to be inherent to BST itself. The reason behind the dielectric property change in BST powders after the heat treatment remains unclear. As discussed earlier, heat-treated BST powders were examined by XRD and WDS with no significant changes observed, so it is not very likely the dielectric constant increase is from

structural or compositional changes. No obvious particle growth after the heat treatment can be seen under SEM examination. It could be the removal of impurities or induced thermal stress in these BST powders after heat treatment that caused the dielectric constant change.

Because of the severe agglomeration of BST powders, a big standard deviation is seen in the dielectric measurements of heat treated samples (C). Such scattered dielectric properties would fail to meet our goal of precise control of the dielectric constant in metamaterials, despite the much higher dielectric constant it provides. To secure more stable dielectric properties, the heat treated BST powders were then modified by GPTMS and the dielectric constant increase was no longer observed (D and E). It is not clear why the application of coupling silane on the surface of BST powders would reverse the permittivity increase introduced by the heat treatment.

It is worth noting that particle sedimentation due to agglomerates was much worse for low BST volume fractions for rheological reasons that composites with low BST loadings are less viscous and particles are easier to settle down. The cured composite block became delaminated into two layers. Until a better way to de-agglomerate the heat treated BST powders without reversing the dielectric constant increase induced by heat treatment is found, the BST powders is not an attractive alternative to BT powders in our work.

Loss measurements

Loss was gradually recognised during my project to be a critical factor that limits the performance of dielectric metamaterial devices. As discussed in Chapter 3, although the waveguide measurement gives loss tangent information, it is not suitable for very low loss materials. To obtain accurate loss measurements for low loss materials, and to establish the measurement capability in our group, a resonator technique was explored in this work. Loss reference data for the composites used

in this work was obtained for split-post resonator measurements. Efforts were also made to search for low loss dielectric materials without compromising too much on the dielectric constant.

A picture of split-post resonator for 15 GHz operation and samples ready for test is shown in Figure 5.21. No special sample preparation was needed for the split-post measurement except for making sure the sample disc is thin enough (depending on its dielectric constant) to generate a nice, sharp resonant peak on the VNA. For 10 GHz measurements samples were usually around 1mm thick and for 15 GHz measurements samples were ground down to 0.4 - 0.6 mm thick. All

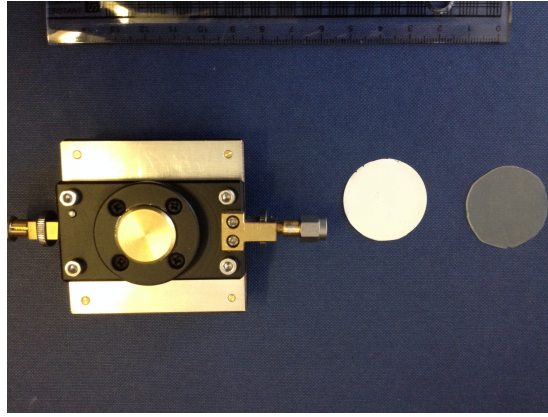


Figure 5.21: Split-post and samples ready for measurements at 15 GHz

split-post measurements (dielectric constant ϵ_r and loss tangent $\tan\delta$) taken in this work are listed in Table 5.2 with resonant frequencies between 10 - 15 GHz. To corroborate the accuracy of the split-post measurements, test measurements were performed on two commonly used and commercially available low-loss polymers; PTFE and ABS. The split-post measurements for both polymers agree very well with the reported loss tangent values in the literature, therefore the validity of our split-post measurements was proved. When comparing the split-post and waveguide measurements, we found that although not able to correctly measure the loss tangent for very low loss materials (e.g. PTFE), waveguide measurement gives loss tangent values of same order of magnitude for comparatively high loss materials (e.g. all epoxy and epoxy composites). Epoxy/BST composites have

Table 5.2: Split-post measurements at resonant frequencies between 10 and 15 GHz and waveguide measurements for the same materials at 15 GHz as comparison

Materials	Split-post measurement $\varepsilon_r/\tan\delta$	Waveguide measurement $\varepsilon_r/\tan\delta$
PTFE	2.04/0.0005	2.04/0.004
ABS	2.7/0.006	-
Epoxy	3/0.04	2.89/0.045
Epoxy-10vol%BT	5.03/0.053	5.35/0.09
Epoxy-20vol%BT	7.95/0.06	8.1/0.06
Epoxy-30vol%BT	12.46/0.13	12.2/0.07
Epoxy-40vol%BT	-	16.45/0.1
Epoxy-20vol%BST	7.67/0.05	7.55/0.07
Epoxy-30vol%BST	11.73/0.04	11.2/0.06
Epoxy-40vol%CT	12.3/0.03	11.75/0.035

smaller loss tangents than epoxy/BT composites, and epoxy/CT composites have the lowest loss of the three, but due to the high loss in epoxy resins all these epoxy composites show loss tangent values above 0.03. If there is a need to significantly reduce the loss in these composite materials, alternative polymers should be considered, bearing in mind the probable consequence of a different manufacturing route than casting would be called for when changing the polymer.

5.3.2 Mixing rules

The dielectric constant data for epoxy/BT composites with BT loadings from 0 to 30 vol% were fitted using various mixing rules as shown in Figure 5.22. The mixing rules most commonly seen and used in the literature for similar problems were considered in this work (for the sake of clarity, in all equations ε_m denotes the dielectric constant of the polymer, ε_f denotes the dielectric constant of the ceramic filler and f denotes the volume fraction, and ε_{eff} is the effective dielectric constant of the composite):

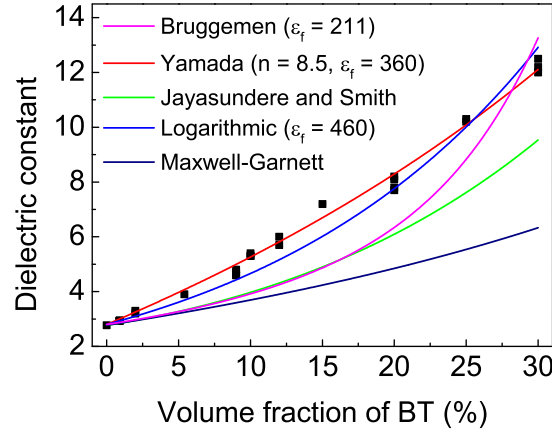


Figure 5.22: Epoxy/BT composites with BT loadings from 0 to 30 vol% dielectric constant data fitted with various mixing rules

1. Maxwell-Garnett equation [Ari]:

$$\varepsilon_{eff} = \varepsilon_m + 3f\varepsilon_m \frac{(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m - f(\varepsilon_f - \varepsilon_m)} \quad (5.4)$$

2. Bruggeman equation [Ari]:

$$(1 - f) \frac{\varepsilon_m - \varepsilon_{eff}}{\varepsilon_m + 2\varepsilon_{eff}} + f \frac{\varepsilon_f - \varepsilon_{eff}}{\varepsilon_f + 2\varepsilon_{eff}} = 0 \quad (5.5)$$

3. Logarithmic (or Lichtenecker) [Ari]:

$$\log \varepsilon_{eff} = f \log \varepsilon_f + (1 - f) \log \varepsilon_m \quad (5.6)$$

4. Yamada equation [14]:

$$\varepsilon_{eff} = \varepsilon_m \left[1 + \frac{f(\varepsilon_f - \varepsilon_m)}{\varepsilon_m + n(1 - f)(\varepsilon_f - \varepsilon_m)} \right] \quad (5.7)$$

5. EMT equation [12]:

$$\varepsilon_{eff} = \varepsilon_m \left[1 + \frac{nf(\varepsilon_f - \varepsilon_m)}{n\varepsilon_m + (1 - f)(\varepsilon_f - \varepsilon_m)} \right] \quad (5.8)$$

6. Jayasundere and Smith (JS) equation [13]:

$$\varepsilon_{eff} = \frac{\varepsilon_m(1-f) + \varepsilon_f f \left[\frac{3\varepsilon_m}{(\varepsilon_f + 2\varepsilon_m)} \right] \left[1 + \frac{3f(\varepsilon_f - \varepsilon_m)}{(\varepsilon_f + 2\varepsilon_m)} \right]}{(1-f) + f \frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \left[1 + \frac{3f(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \right]} \quad (5.9)$$

A closer look at Yamada and EMT equations shows that they actually share the same format with a reciprocal parameter n which was introduced to account for particle morphology. These five equations (excluding EMT) were used to fit my dielectric constant data, with ε_m being held constant at the measured value of 2.8 and ε_f varied to achieve the best-fit. From the graph we can see that the Maxwell-Garnett and Jayasundere and Smith equations do not fit the data at all, but the Bruggeman and Logarithmic equations do give converged fittings (a Chi-Sqr tolerance value of 1E-9 was reached) with ε_f estimates of 211 and 460 respectively, and the Yamada gives the best fit of all with an n value fixed at 8.5 yielding an ε_f value of 360. These predicted dielectric constants for the 3 μm BaTiO₃ powders used in this work are reasonable when compared with the estimated value of 572 for 300 nm BaTiO₃ powders in the previous chapter and the data reported in [10, 44].

The physical basis behind these mixing rules will be briefly discussed below and their respective applicability explored. Let us start with the Maxwell-Garnett equation which the basic mixing rule to which all the rest of the mixing rules (with the exception of logarithmic which is a power law) are related. In the Maxwell-Garnett equation, a model of one spherical inclusion ε_f embedded in the host material ε_m was constructed. When an external field $\mathbf{E}$ was applied, the averaged dielectric constant ε_{eff} of the system can be defined by:

$$\langle \mathbf{D} \rangle = \varepsilon_{eff} \langle \mathbf{E} \rangle \quad (5.10)$$

$$\langle \mathbf{D} \rangle = f\varepsilon_f \mathbf{E}_f + (1-f)\varepsilon_m \mathbf{E}_m \quad (5.11)$$

$$\langle \mathbf{E} \rangle = f\mathbf{E}_f + (1 - f)\mathbf{E}_m \quad (5.12)$$

Putting equation 5.11 and equation 5.12 back into equation 5.10, we get

$$\varepsilon_{eff} = \frac{f\varepsilon_f A + \varepsilon_m(1 - f)}{fA + (1 - f)} \quad (5.13)$$

Where A denotes the field ratio between internal and external field $\mathbf{E}_i = A\mathbf{E}_m$.

$$A = \frac{\varepsilon_m}{\varepsilon_m + n(\varepsilon_f - \varepsilon_m)} \quad (5.14)$$

For a sphere, $n = 1/3$ and A is known to be [45]

$$A = \frac{3\varepsilon_m}{(\varepsilon_f + 2\varepsilon_m)} \quad (5.15)$$

Replacing the A in equation 5.13 with 5.15, we get the Maxwell-Garnett equation

$$\varepsilon_{eff} = \varepsilon_m + 3f\varepsilon_m \frac{(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m - f(\varepsilon_f - \varepsilon_m)} \quad (5.16)$$

The Maxwell-Garnett and Bruggeman models represent two types of mixing rules based on different physical origins as described in [Ari] and [11]. The Maxwell-Garnett theory assumes a separated-grain structure (Figure 5.23(a)) where grains with ε_f are embedded in a continuous media ε_m , however the Bruggeman theory proposed an aggregated-structure (Figure 5.23(b)) that treats both phases equally. Bruggemen's very definition decides there is no discrimination between matrix and filler, and the equation is intrinsically symmetric (that is, if you interchange ε_f with ε_m , f with $1 - f$, you will still get the same ε_{eff} , a rule that does not hold for Maxwell-Garnett). The difference between Maxwell-Garnett and Bruggemen models has been described as; a composite system in which one phase (filler) is surrounded by another (matrix) is in theory better described by the Maxwell-Garnett equation, whereas the Bruggeman is more ap-

appropriate for two phases mixed in a random basis [46]. It is worth mentioning that the Maxwell-Garnett and Bruggemen equations yield the same ε_{eff} at very low filling factor ($f \ll 1$). In our case, a proven homogeneous distribution of BT powders inside epoxy matrix seems to be more relevant to the model that the Maxwell-Garnett equation assumes.

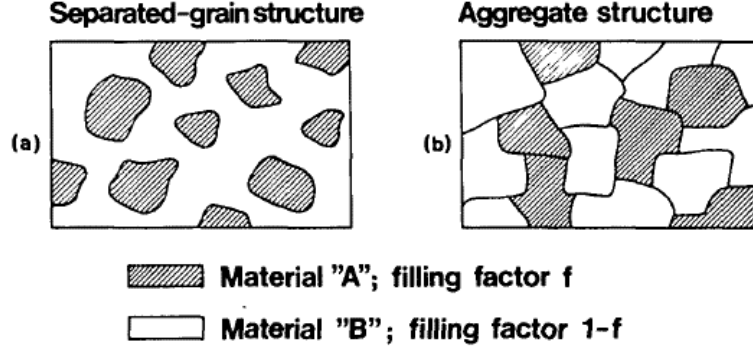


Figure 5.23: Schematics of the two-phase separated-structure (a) assumed for the Maxwell-Garnett model and aggregated-structure (b) assumed for the Bruggemen model [11]

Then why did the Maxwell-Garnett equation fail to produce a good fit to our data? If we compare the Maxwell-Garnett equation with the Yamada or EMT equations, we can see that they are effectively Maxwell-Garnett-type mixing law. More specifically, the Yamada or EMT equations are more generic forms of Maxwell-Garnett equations, with a parameter n that relates to the field ratio between internal and external fields. It was set to $1/3$ in the Maxwell-Garnett equation, under the assumption of spherical inclusions. The Yamada and EMT mixing rules have been widely used for fitting polymer-ceramic composites experiment data because they give better results than other mixing formulae [47, 48]. The physical meaning of the parameter n is described as a factor that is dependant on the morphology of the dielectric particles. When used as an empirical formula, the fitted curves give an n value in the range between $1/8$ - $1/10$ (or 8 - 10 in the Yamada equation) in most cases. Table 5.3 gives a list of n values with references. Some authors have conducted numerical analysis of the effect of

Table 5.3: List of morphology factor n values found in the literature

Composites	Morphology factor n (all converted to EMT format)	Reference
PVDF/CCTO	0.11	P.Thomas et al. [47]
Epoxy/PMN-PT	0.13	Y.Rao et al. [12]
PVDF/NBCTO	0.11	Su et al. [48]
PVDF/PZT	0.12	Yamada [14]
Epoxy/BT	0.19	Cho et al. [10]

Table 5.4: polarizability factor α_n for various particle shapes

Shapes	$\alpha_n (\varepsilon_r=\infty)$
Tetrahedron	5.0285
Cube	3.6442
Octahedron	3.5507
Dodecahedron	3.1779
Icosahedron	3.1304
Sphere	3

particle shape on dielectric polarization [49, 50], calculating the polarizability, α_n , for arbitrary shapes. The values for the extreme case $\varepsilon_r=\infty$ ($\varepsilon_r = \varepsilon_f/\varepsilon_m$ which features a huge difference between ε_f and ε_m values) are listed in table 5.4.

$$\alpha = \frac{(\varepsilon_f - \varepsilon_m)}{\varepsilon_m + n(\varepsilon_f - \varepsilon_m)} \quad (5.17)$$

For a spherical inclusion, $n = 1/3$ in equation 5.17 but depends on the shape of particles. When the particle shape changes, equation 5.17 will no longer be valid, and if we assume the same format holds for all shapes, when $\varepsilon_r=\infty$ simple algebra will give us $n = 1/\alpha_n$. Thus for these various shapes of particles, the n value should fall in the range 1/5 - 1/3.

Jayasundere and Smith modified the original Maxwell-Garnett equation to include the interaction between scatterers by considering a dipole model, see equation 5.18.

$$\varepsilon_{eff} = \frac{\varepsilon_m(1 - f) + \varepsilon_f f * A * B}{(1 - f) + f * A * B} \quad (5.18)$$

$$A = \frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \quad (5.19)$$

$$B = 1 + \frac{3f(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \quad (5.20)$$

The field ratio A was replaced by $A * B$ where B is dependent on the filler volume fraction which means that the field distribution changes as the dielectric loading goes up. In theory, because B is larger than 1, $A * B$ will always be larger than A , so that the field ratio is increased when multiple interactions are allowed, corresponding to a decrease in n value. However, this decrease is still not substantial enough to account for the experiment data, suggesting a need to introduce structural multipole effects [51–53] to model real physical situation where the particles are small and tend to cluster together. In theory, the multipole effect varies with filler loading so n would not remain constant but we believe that for relatively small particles (in my case $\sim 1 \mu\text{m}$) and relatively well separated as shown in Fig. 5.19, an averaged n value should be able to give a curve that will reasonably reflect the correlation between filler loading and composite dielectric properties. This explains why the rather simple Yamada or EMT equations can be used to give good fit to our experiment data. This n has to be lower than $1/3$, but the exact value still depends on particle size.

5.4 Conclusion

In this chapter, epoxy based composites were manufactured by casting and their dielectric properties characterised at frequencies between 12 and 18 GHz. Systematic results have been achieved on epoxy/BT composites, where BT loading from 0 to 30 vol% providing dielectric constant values from 3 to 12 can be manufactured in a controllable and predictable way. Homogeneous microstructures were verified for all epoxy/BT composites by SEM images. The dielectric data were fitted using various mixing rules, among which the Yamada equation gives

the best fit with a dielectric constant estimate of 360 for BT powders with a morphology factor n of 8.5. The morphology factor n is believed to be dependant on particle size and shape and should have a value higher than 3.

Epoxy-30vol%BST composites were prepared to investigate the potential of substituting BT with BST to achieve higher dielectric constant values and lower loss. However, the supplied BST powders were found to be severely agglomerated which was suspected to be the outcome of particular surface treatment taken during the manufacturing process by the supplier. Due to serious agglomeration in these BST powders, particle surface treatments were studied to facilitate particle dispersion in epoxy resin. A successful silane treatment process was developed in this work and was proved to be effective in breaking up BST agglomerates and producing homogeneous epoxy/BST composites. These epoxy/BST composites did not, however show higher dielectric constants than equivalent epoxy/BT composites unless the BST powders were heat treated. Without the silane treatment, highly agglomerated BST powders would be no practical use in making epoxy/BST compounds as the particle clusters settle down in epoxy (especially for low BST loading concentrations) and it will not be possible to produce composites with consistent dielectric properties.

High volume fraction epoxy/CT composites were also prepared and tested in this work to find out the effect of using a low loss ceramic filler. It was found that with CT ceramic filler, the composites loss can be reduced to less than 0.03, the lowest values measured in this work. In light of the relative high loss of the epoxy matrix, it is not likely that this strategy will reduce composites loss any further. If a low loss composite is required, a different type of polymer with lower loss should be considered, where the simple casting processing route might no longer be suitable.

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Chapter 6

Advanced applications

6.1 Anisotropic Dielectrics

6.1.1 Introduction

Anisotropy refers to structures with properties that are directionally dependant. In this work, I consider a laminated structure that is made of alternating layers with two different dielectric properties (as illustrated in Figure 6.1) and investigate how such a structure responds to an electric field applied along different directions (x and z directions). The flexibility that 3D printing has in controlling the geometry and structure of a sample enables us to manufacture such laminated structures quickly and accurately. To measure the dielectric performance of these two scenarios, waveguide samples with the parallel and perpendicular structures shown in Figure 6.2 were prepared by 3D printing and the effective relative permittivity values measured by the waveguide method. Existing theories were reviewed to predict the outcome of these measurements. Models were constructed in COMSOL Multiphysics to simulate these two cases and the experimental data achieved was compared to the simulation results.

In the theory of mixing, efforts have been made to search for the absolute bounds of effective permittivities of a two-phase mixture, the bounds that the

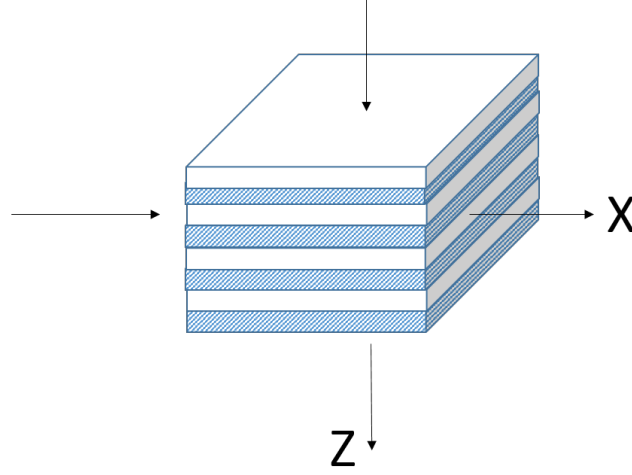


Figure 6.1: Laminated block formed by layers of two different dielectrics. When the electric field is applied in X and Z directions, the macroscopic dielectric properties will be different

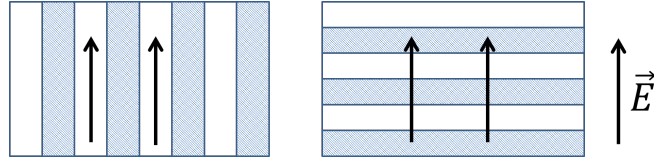


Figure 6.2: Parallel (left) and perpendicular (right) structures in a waveguide representing the aforementioned two electric field orientations

effective permittivity of a mixture of selected materials will always fall within no matter what alignment and geometry of materials used to construct the mixture [1, 2]. Among these bounds, the Wiener bounds refer to a model very similar to my case. Wiener bounds define that the maximum effective permittivity for a given volume fraction of inclusions is when the inclusion is aligned along the flux direction and the minimum is when the inclusion is perpendicular to the flux, as depicted in Figure 6.2. The maximum and minimum effective permittivities are predicted to be:

$$\varepsilon_{eff,max} = f\varepsilon_f + (1 - f)\varepsilon_m \quad (6.1)$$

$$\varepsilon_{eff,min} = \frac{\varepsilon_f \varepsilon_m}{f\varepsilon_m + (1 - f)\varepsilon_f} \quad (6.2)$$

where ε_f and ε_m represents the dielectric constant of the inclusion and matrix material respectively and f is the volume fraction of the inclusion.

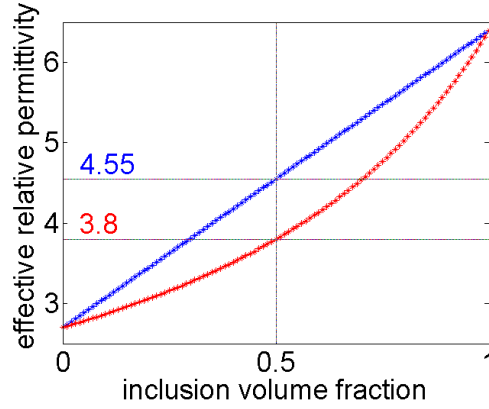


Figure 6.3: Wiener bounds for a two-phase mixture with $\varepsilon_m = 2.7$ (ABS) and $\varepsilon_f = 6.4$ (ABS/BT composite) respectively. The calculated maximum and minimum effective dielectric constants for a 50/50 mixture of these two materials are 4.55 and 3.8 as marked on the graph

Equations 6.1 and 6.2 were used to predict the effective relative permittivities of parallel and perpendicular samples prepared as shown in Figures 6.1 and 6.2. The two phases used in this work were pure ABS with a measured dielectric constant of 2.7 and the ABS/BT composite with a measured dielectric constant of 6.4. A BT volume fraction of 50% was chosen that gives equal contribution from both phases. The plot of Wiener bounds for the ABS and ABS/BT two phase mixtures is shown in Figure 6.3, with the predicted maximum and minimum effective dielectric constant at 50 vol% marked on the graph. According to Wiener bounds, the maximum effective relative permittivity (corresponding to the parallel structure) is estimated to be 4.6 and the minimum effective relative permittivity (corresponding to the perpendicular structure) is estimated to be 3.8. According to this prediction, an anisotropic effect will be observed in dielectric samples with same composition but showing different dielectric constants as a result of different alignment of the layered structure.

In this work, dielectric slabs containing 12 parallel stripes and 6 perpendicular stripes (so that they have the same spacing) were manufactured and tested. Corresponding simulations were constructed and compared to the experiment.

6.1.2 Simulation

Models simulating the properties of waveguide samples with anisotropic dielectrics inserted were constructed in COMSOL Multiphysics using the RF module. Waveguides with standard dimensions of 7.9 mm x 15.8 mm for TE₁₀ mode propagation at 12 - 18 GHz were built. The waveguide length was set to be 40 mm. A 2 mm dielectric slab with periodic parallel or perpendicular structures was inserted in the middle of the waveguide (see Figure 6.4). The highlighted stripes are the ABS phase and the unhighlighted ones the ABS/BT phase. The electromagnetic properties of the materials used were set to be; for ABS $\varepsilon_r = 2.7 - 0.0162j$, $\mu_r = 1$, and for the ABS/BT composite $\varepsilon_r = 6.4 - 0.192j$, $\mu_r = 1$ according to experimental waveguide measurements. By activating port sweep in COMSOL, full S-parameter matrices can be computed and exported in the Touchstone file format. COMSOL is a finite element analysis software that by subdividing structures into smaller parts, the so called finite elements, approximate a more complex equation over the whole structures. A free tetrahedral mesh was used to mesh the entire geometry with a maximum element size equals to $3e8/(18e9*n*5)$ for two different materials, where n is the refractive index of the material to be meshed. The calculated maximum element sizes are 1.32 and 2.03 mm. This is because to resolve a wave properly, the maximum element size needs to be less than 0.2 of the local wavelength [3]. The minimum element size was left open for the computer to automatic calculate suitable lower limits so that the resulted tetrahedral mesh elements were less than the size of smaller components such as the stripe thickness. S-parameter and wave propagation results were collected from sweeps from 12 to 18 GHz at a step of 30 MHz, identical to my experimental waveguide measurements.

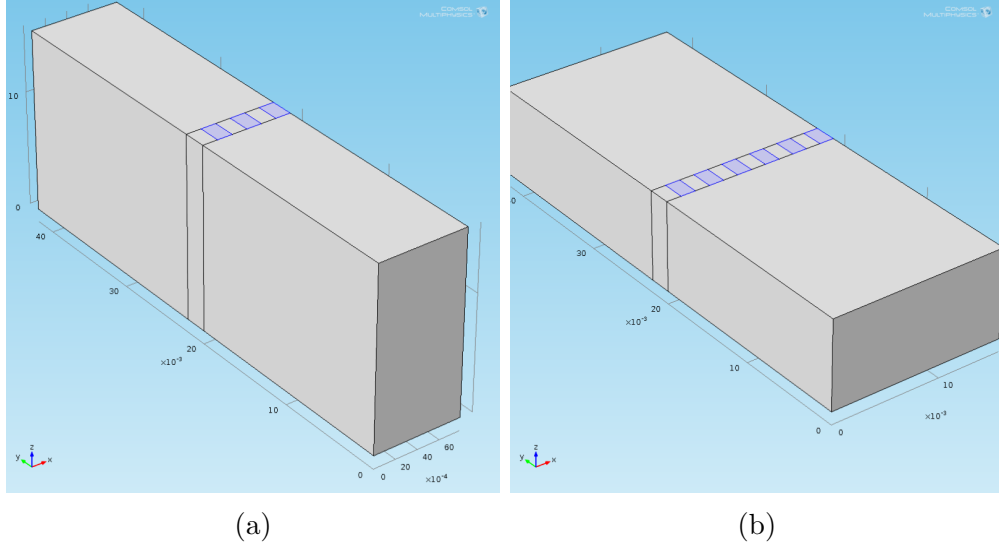


Figure 6.4: Comsol model of waveguides sandwiching (a) 6 perpendicular stripes sample and (b) 12 parallel stripes sample; In the layered sample structure, the ABS phases are highlighted to distinguish from the ABS/BT phase.

6.1.3 Experimental

Four dielectric blocks of pure ABS, pure ABS/BT composite, and mixtures with either parallel or perpendicular stripe structures for waveguide measurements were prepared by 3D printing using commercial ABS filament and in-house ABS/BT composite filament made with the help of Dmitry Isokov. The ABS/BT composite filament was manufactured within the group by extruding pre-mixed ABS and BT powders obtained from sol-gel method. The printed samples with periodic structures shown in Figure 6.5 possessed good interface property. The microstructure near the ABS and ABS/BT composite interface was examined by microtomy and SEM as described in previous chapters. The SEM images are presented in Figure 6.6, in which the ABS and ABS/BT interface could be distinctively observed. At higher magnification, well-dispersed BT particles can be recognised in the ABS matrix.

The dielectric properties of the printed samples were measured by the waveguide technique at 12 - 18 GHz. The NRW method [4] was used to extract the dielectric properties from S-parameters as described previously. The measure-

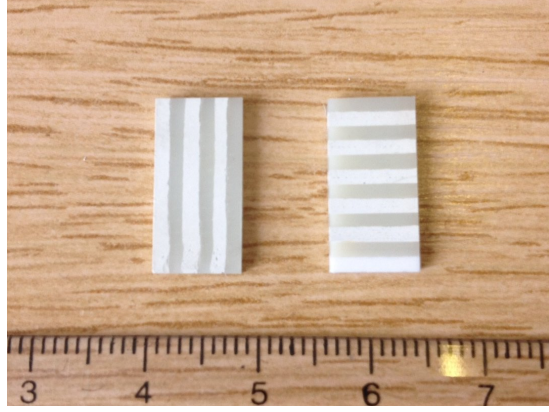


Figure 6.5: Picture of printed waveguide samples with perpendicular (left) and parallel (right) periodic structures. Samples were hand-polished to fit tightly into the waveguide after printing

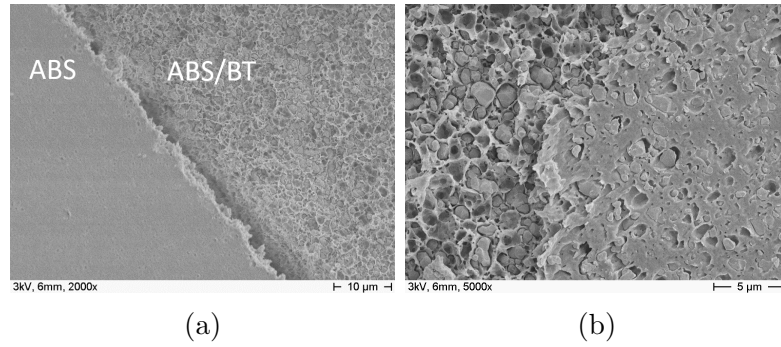


Figure 6.6: SEM images of printed mixture sample (a) the ABS and ABS/BT interface after microtomy at low magnification (b) a relatively homogeneous distribution of BT particles in the ABS/BT composite phase at higher magnification

ment data was then compared to the simulation data.

6.1.4 Results and discussion

Pure ABS and pure ABS/BT samples

The measured dielectric properties of the pure ABS and pure ABS/BT composite samples shown in Figure 6.7 were used as reference data in this work. The dielectric constant, ϵ_r , and loss tangent, $\tan\delta$, values were extracted from the waveguide measurements using the NRW method. The measured dielectric constant of the pure ABS was 2.64 and the loss tangent was 0.008. The measured dielectric constant of pure ABS/BT composite was 6.05 and the loss tangent was

0.034 at 15 GHz, consistent with the dielectric values we assumed in the simulation. Some fluctuation of the dielectric constant of ABS/BT filament around the measured value was expected due to imperfect mixture in the manufacturing technique. It is also observed that despite of the low-loss nature of ABS matrix, the addition of BT powders increased the loss value for the ABS/BT composite quite significantly.

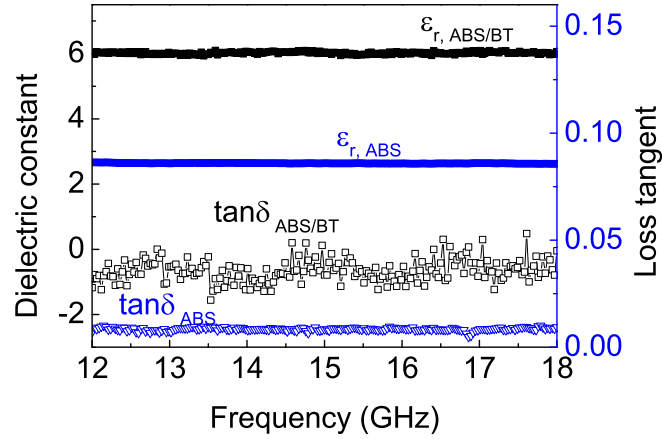


Figure 6.7: Waveguide measurements of pure ABS and pure ABS/BT composite samples at 12 - 18 GHz. The reference data are consistent with the values assumed in simulation

Periodic structures

The simulation results at 12 GHz for the mixture samples with 6 layer perpendicular structure and with 12 layer parallel structure at 12 GHz are presented in Figure 6.8 and Figure 6.9 respectively with views from three different perspectives. From the electric field normal ($\frac{V}{m}$) distribution we can see that only part of the wave is transmitted through the dielectric slab, while part of the wave is reflected back. Before the dielectric sample, we can see standing waves due to the superposition of transmitted and reflected waves. At the peak of the electric field amplitude, the electric field normal was around $7700 \times 10^3 \frac{V}{m}$. However after the dielectric samples, the amplitude dropped to around $3000 \times 10^3 \frac{V}{m}$. It is notable that for the perpendicular periodic structure, wave propagation in the

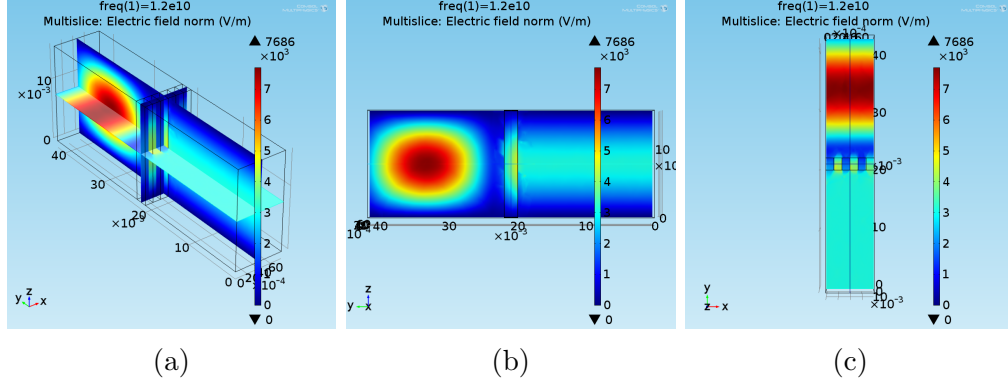


Figure 6.8: Simulation result (electric field normal) for 6 layer perpendicular structure at 12 GHz; the wave propagates opposite to y direction. The entire waveguide structure is 42 mm long with a 2 mm thick sample inserted in the middle. The wavelength in air equals to 25 mm.

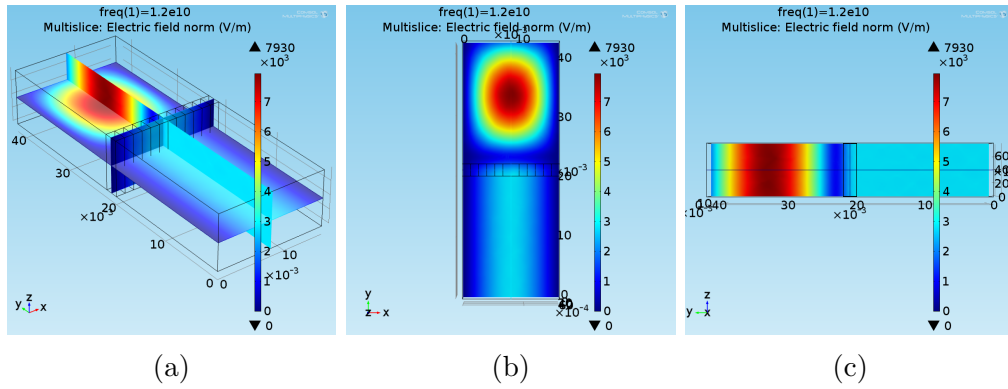


Figure 6.9: Simulation result (electric field normal) for 12 layer parallel structure at 12 GHz; the wave propagates opposite to y direction. The entire waveguide structure is 42 mm long with a 2 mm thick sample inserted in the middle. The wavelength in air equals to 25 mm.

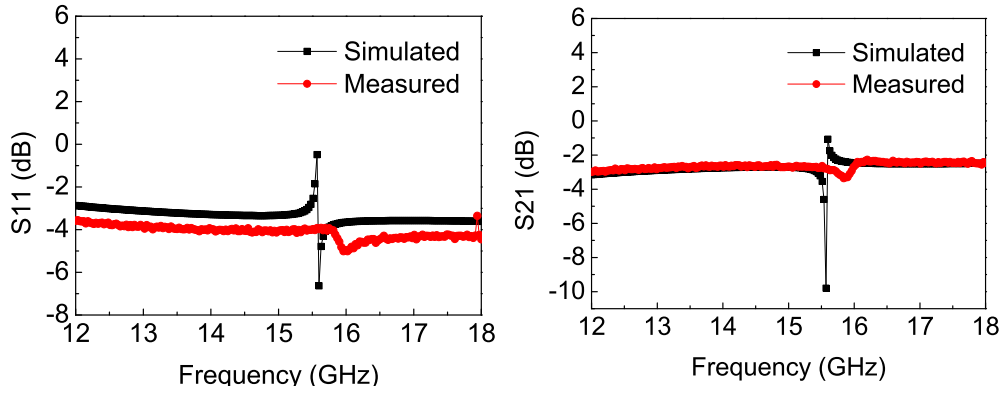


Figure 6.10: Comparison of simulated and measured S11 and S21 parameters in dB for the 6 layer perpendicular structure

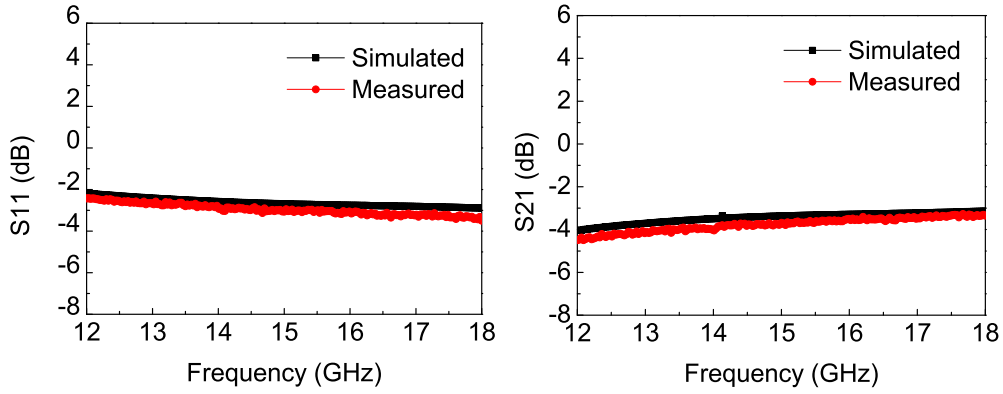


Figure 6.11: Comparison of simulated and measured S11 and S21 in dB for the 12 layer parallel structure

sample along the x direction (Figure 6.7 view (c)) was not continuous, and the transmission was mainly through the ABS/BT stripes. This phenomenon was caused by the higher dielectric constant of the ABS/BT stripes than the pure ABS stripes.

The S-parameter results from the simulation are plotted in dB scale and compared with the waveguide measurements in Figure 6.10 (the perpendicular alignment) and Figure 6.11 (the parallel alignment). Discontinuous curves with little variation were found in the simulated and measured S11 and S21 values for the perpendicular structure over the frequency range 12 - 18 GHz. The simulated S11 varied slightly from -2.9 dB to -3.6 dB and the measured S11 from -3.6 dB to -4.5 dB, while the simulated S21 varied from - 3.2 dB to -2.5 dB and the mea-

sured S21 from -3 dB to -2.5 dB. A resonant peak is observed in the S-parameter for the perpendicular structure at a frequency around 15.5 GHz. The cause of this resonance peak is unclear and is believed to be associated with the periodic laminated structure. The reason that the resonant peak was only observed in the perpendicular structure but not in the parallel structure is suspected to be related to the TE polarised waves propagating in waveguide. For the parallel alignment, smooth curves with little variation were found in the simulated and measured S11 and S21 values for the perpendicular structure over the frequency range 12 - 18 GHz. The simulated S11 varied slightly from -2.2 dB to -2.9 dB and the measured S11 varied from -2.4 dB to -3.5 dB, while the simulated S21 varied from -4 dB to -3.1 dB and the measured S21 from -4.5 dB to -3.3 dB. Overall, the measured and simulated S-parameters showed good agreement.

The NRW method was used to extract the dielectric constants from the simulated and measured S-parameters. The results are shown in Figure 6.12. The

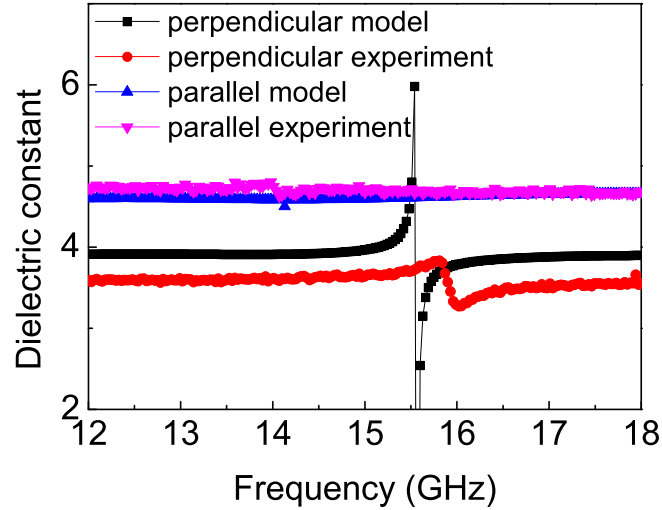


Figure 6.12: Simulated and measured dielectric constant for perpendicular and parallel structure samples were extracted using the NRW method

anisotropy effect was demonstrated as the perpendicular and parallel structure samples with same composition showed different dielectric constants. It is notable that for the parallel structure sample, the simulated dielectric constant is very closed to the measured values with $\epsilon_{r,model\perp} = 4.6$ and $\epsilon_{r,ex\perp} = 4.8$ at 15 GHz.

Both are also in excellent agreement with the predicted value by Wiener bounds $\varepsilon_{r,wbmax} = 4.6$. However, a bigger discrepancy is found between the simulated and measured dielectric constants for the perpendicular structure, with $\varepsilon_{r,model\parallel} = 4$ and $\varepsilon_{r,ex\parallel} = 3.6$ at 15 GHz, but still close to the predicted value by Wiener bounds $\varepsilon_{r,wbmin} = 3.8$.

6.1.5 Conclusion

In this work, the anisotropy of dielectric samples with parallel and perpendicular aligned stripe structures was investigated. The two-phase mixture Wiener bounds theory was introduced to predict the dielectric properties of these two structures, and a difference in their dielectric constant was indicated. Waveguide samples with 6 perpendicular layers and 12 parallel layers were modelled by COMSOL Multiphysics and manufactured by 3D printing. The simulated and measured dielectric properties were compared to the predicted values. In general, the results were consistent with the values predicted by Wiener bounds, proving that an anisotropy effect does exist in samples with different alignments of dielectric materials. Particularly, the predicted, simulated and measured dielectric constants agreed very well for the parallel structured sample, but more dispersed for the perpendicular structured sample. The reason behind this discrepancy remains unclear, but it is conjectured that the discrepancy could be because of the effect the resonance peak observed at around 15.5 GHz which skewed the dielectric constant from its true value.

6.2 Power Divider Lens

6.2.1 Introduction

Transformation optics [5] is a novel concept that offers a method to manipulate wave propagation in materials by spatially arranging materials' electromagnetic

properties. When combined with metamaterials (can be broadly defined as materials with artificial electromagnetic properties), the transformation optics concept has inspired many electromagnetic applications such as perfect imaging [6], invisibility cloaking [7–9] and other types of novel light bending and guiding devices [10–13]. Some of these designs require negative refractive index metamaterials with the use of resonant split-ring structures. However, the strong dissipation and narrow bandwidth limitation in the materials needed to generate negative refractive indices severely restricts their application [14–16]. Therefore, the possibility of using all dielectric or positive refractive materials to realise transformation optics designs has been explored [17].

The Maxwell fish eye lens is one example of a perfect imaging application. The generalised Maxwell fish eye equation is [15]

$$n(r) = \frac{2}{r^{1-m} + r^{1+m}} \quad (6.3)$$

where $n(r)$ is the radial refractive index profile and m is a variable parameter which for the Maxwell fish eye lens is 1. In this work, a modified Maxwell fish eye lens with 11 concentric layers was proposed by our collaborators in Queen Mary University of London using all-dielectric materials with relative permittivity values in the range of 2.8 - 17. The lens profile was modified from the Maxwell fish eye [18] by setting $m = 0.95$ with the function of dividing an incoming beam into two sub-beams, as shown in Figure 6.13. The operating frequency of the lens was 15 GHz with the lens thickness of 3 mm. A continuous dielectric profile for the lens was first mapped from free-space and then discretized into individual layers by our collaborators. The complete mapped lens profile is presented in Figure 6.14. The outermost layer, the 11th layer, was not a functioning part of the lens, but a dielectric background in which we could observe the propagation of the sub-beams after being split.

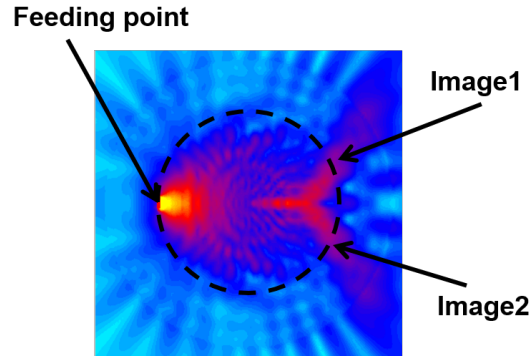


Figure 6.13: A simulation to show that a modified Maxwell fish eye lens functions as a power divider (by Rhiannon Mitchell-Thomas and Oscar Quevedo-Teruel)

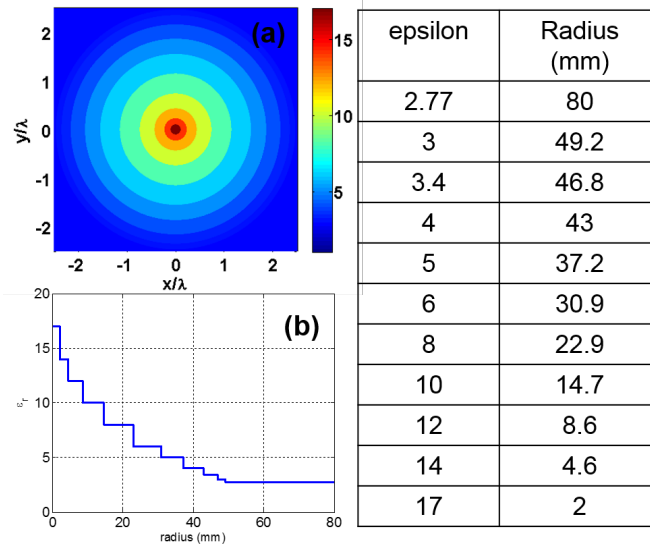


Figure 6.14: The proposed lens profile (a) the discretization plot (b), and the dielectric constant specification of individual layers listed in the chart (by Rhiannon Mitchell-Thomas and Oscar Quevedo-Teruel)

Pursuing an all dielectric materials approach for transformation optics applications is encouraged due to the lower loss and broadband nature of dielectric materials [17, 18], but the high demand for arbitrary values and customisation of permittivity poses a severe challenge for precise materials processing. The spatial wave manipulation and control over materials electromagnetic properties requires excellent homogeneity of the materials microstructure, as well as reliability and reproducibility of the processing route. For many years, suitable dielectric composite systems have been sought for customising device performance based on mixing ultra-high dielectric constant of inclusions with an easily processable

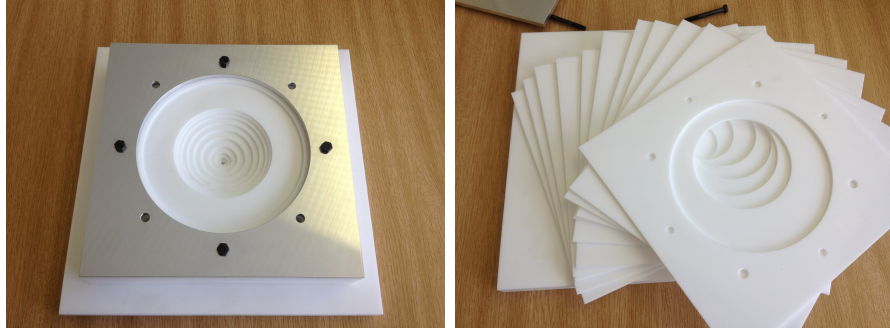


Figure 6.15: Pictures of the set of PTFE moulds used to cast the power divider lens

matrix, providing composites with a broad range of permittivity yet still being manufacturable by a scalable process [19, 20]. In this work, I combined my capability of accurately controlling the dielectric property of epoxy/BT composite materials demonstrated in the previous chapter with the power divider lens design to explore the possibility of applying a well-studied dielectric composite system to microwave applications.

6.2.2 Experimental

Lens manufacturing

Considering the concentric-layer structure of the power divider lens, an in-situ casting manufacturing route was proposed. A set of PTFE moulds with high dimensional precision (Figure 6.15) were used in this process. The set of moulds consists of a 20 mm thick PTFE base with a 2 mm radius hole drilled in the middle, eleven 3 mm thick PTFE slabs with through holes in the middle with radius from 2 mm to 80 mm in accordance to the design, and a 5 mm thick aluminium plate on top that can be bolted to the PTFE base to clamp the PTFE layer in position during casting. Having consulted the master curve of dielectric constants of epoxy/BT composites that was generated in Chapter 5, the list of BT volume fractions in epoxy/BT composites shown in Table 6.1 was proposed to manufacture the individual layers of the lens.

Table 6.1: Composition of epoxy/BT composites used for manufacturing individual layers of lens

Layer No. (outwardly)	Radius (mm)	Target ε_r	Volume fraction of BT (%)
1	2	17	42
2	4.6	14	36
3	8.6	12	30
4	14.7	10	25
5	22.9	8	20
6	30.9	6	12
7	37.2	5	9
8	43	4	5.4
9	46.8	3.4	2
10	49.2	3	0.9
11	80	2.8	0

The in-situ casting process goes as follows: I started from the smallest innermost section with radius of 2 mm, which is also the densest epoxy composite layer with an estimated BT volume fraction of 42%. This layer was cured in an oven at 60 °C for 24 h without degassing due to its high BT volume fraction. Once it was fully cured, the first PTFE mould layer was taken away, with the epoxy/BT composite cylinder anchored in the PTFE base for positioning purposes. The second PTFE mould layer was then put onto the base, leaving a cylindrical gap between the first epoxy/BT layer and the PTFE mould, into which the second lens layer would be cast. From this layer onwards, the epoxy/BT composites were poured into the gap and degassed for 30 min in a vacuum pump before being cured at 60 °C. After all 11 layers of the lens were cast in position, the lens was removed from the PTFE base and a thin layer of material from each side was sliced off using a lathe to create flat and smooth lens surfaces. Double-sided sticky tape was used to glue the lens on a metal base to facilitate sample mounting on the lathe. After lathing, the entire sample was submerged in acetone for a few hours for the lens to be detached from the tape naturally. Pictures showing the lens with all layers cast, and the lens right after being lathed, are shown in Figure 6.16.

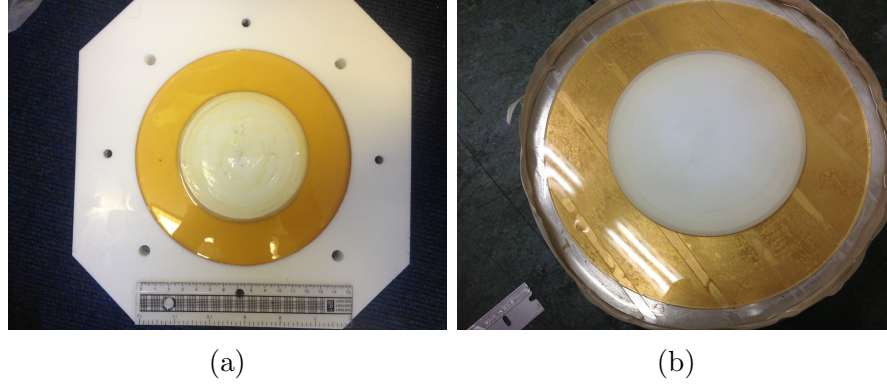


Figure 6.16: Pictures of the manufactured lens before (a) and after (b) lathing

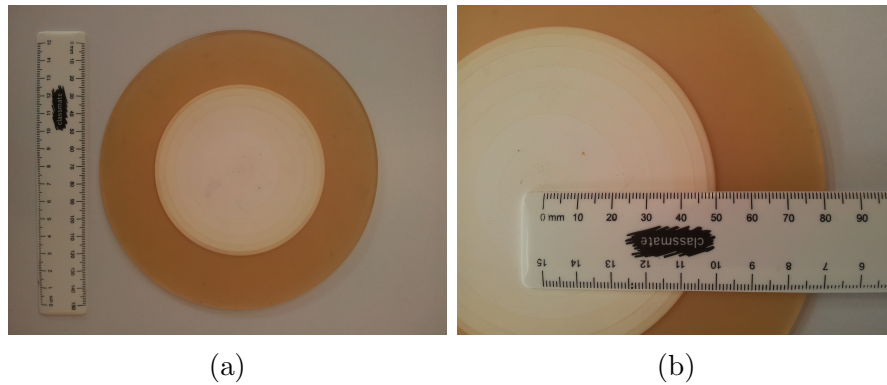


Figure 6.17: Pictures of the completed lens showing good interface quality between layers as well as good dimensional precision

The revealed cross-section of the lens after lathing showed good interface quality between individual layers, with visible boundaries and no air gaps. The only mismatch between the manufactured lens and the design was that in order to remove enough materials off the lens surfaces to achieve flat surfaces, the end product had a thickness of 2.5 mm instead of 3 mm as originally designed, which the lens' designers suggest could change the functional frequency of the lens. The new operating frequency calculated by our collaborator was 18 GHz instead of the originally proposed 15 GHz. Pictures of the completed lens are shown in Figure 6.17.

During the in-situ casting, for each layer of the lens being manufactured some extra material was used to prepare up to 5 waveguide samples to confirm the true dielectric properties of this layer. The comparison of the target dielectric

constant and measured dielectric constant of each layer is illustrated in Figure 6.18. In general, a good match between target and measured dielectric constant

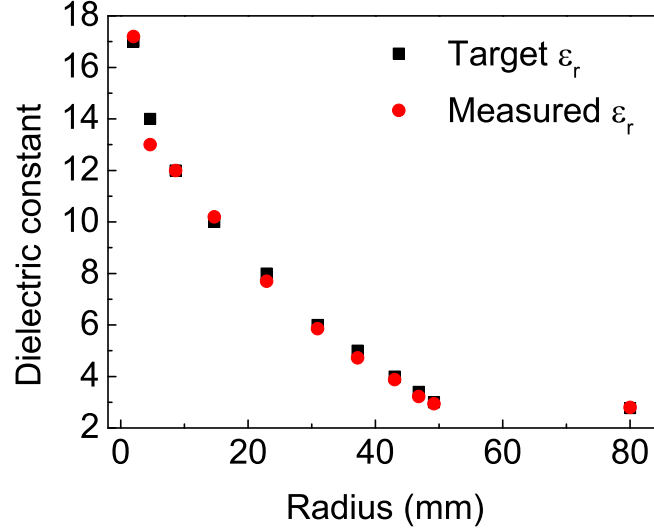


Figure 6.18: Graph comparing the target and measured dielectric constant of individual layers of the lens

was found for the entire lens, except for a slight deviation for lens layer No.10 (the target dielectric constant was 14, while the actual measured dielectric constant was 13). The microstructure of the epoxy/BT materials at various compositions used to manufacture lens layers was also examined by microtomy and SEM, all showing same homogeneous distribution of barium titanate particles as shown in Chapter 5. The lens is a good demonstrator of my capabilities in controlling the macroscopic dielectric property of composite materials with excellent microscopic homogeneity.

Lens' testing

The lens was tested by near-field microwave imaging systems in both of our collaborating universities – Queen Mary University of London and the University of Exeter. The near-field imaging system consists of a two-port VNA (Vector Network Analyzer), transmitter and receiver devices, a metal base on which the lens was sitting (ideally in perfect contact), and some absorbing materials surround-

ing the lens. Two type of transmitters (monopole and waveguide transmitter) and monopole receivers were adopted and compared in this work. The monopole transmitter was constructed by exposing a quarter-wavelength of the inner conductor of a coaxial cable (the exposed length was about 14 mm). Waveguide transmitters, including a standard Ku band rectangular waveguide and a modified K band rectangular waveguide, were also tested to compare with the results of the monopole transmitter. Monopole transmitters generate an isotropic radiation pattern, whereas waveguide transmitters are more directive [21]. However, monopole transmitters have the advantage of small physical dimensions that allows more precise position of the excitation source than with waveguide transmitters, especially in our case where the source ideally should be placed on the interface between the dielectric background and the lens. On the other hand, the isotropic radiation pattern of the monopole source could compromise the image quality, particularly giving decreased signal-to-noise ratio [21] when comparing with a waveguide transmitter. Whichever type of transmitter was used, fundamental drawbacks exist in the near-field imaging system due to cross coupling between the transmitter and receiver through the surrounding air and the possibility of collection of unwanted scattered fields [21]. Depending on the loss in the media, serious attenuation could also aggravate the difficulty in data acquisition. A digitally controlled monopole receiver moved along a zig-zag pattern with preset step sizes to perform the data collection. Three lens tests were conducted using slightly different set-ups in this work: 1) monopole transmitter; 2) Ku band waveguide transmitter; 3) modified K band waveguide transmitter.

The first test was taken immediately after the lens was manufactured using a monopole transmitter in the University of Exeter (Figure 6.19). The monopole receiver was placed right above the interface between the lens and the dielectric background scanning a plane at $z = 3$ mm, which was thus 0.5 mm away from the lens surface. The scan was performed over an area of 190 mm x 190 mm at

a step size of 1 mm measuring over a frequency range of 5 - 40 GHz.

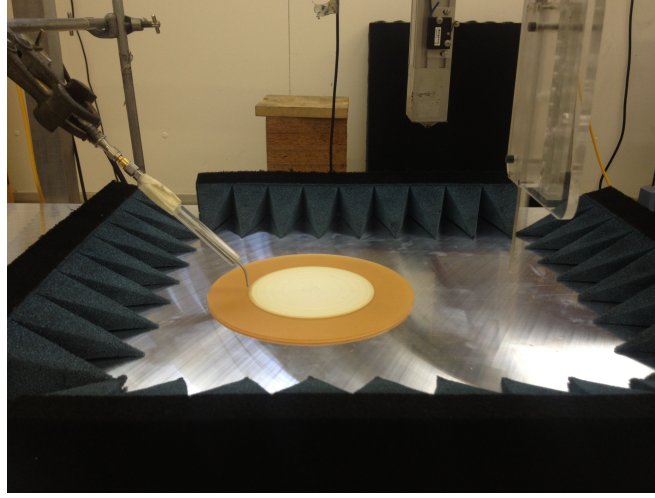


Figure 6.19: First lens test in Exeter using a monopole source

To reduce the cross coupling between the transmitter and receiver, as well as to test if a more directive antenna (i.e. waveguide) would interact better with the 2D dielectric variation of the lens, we changed to a waveguide transmitter with a piece of absorbing material attached on the outlet to block space waves in the second test, and a modified waveguide transmitter with a taper on the top and an epoxy wedge inserted in the third test. The second and third tests were done in an anechoic chamber in Queen Mary University of London about one year later. Pictures of the second lens test scene are shown in Figure 6.20. The receiver was scanned across the region of $x = (-25, 125)$ mm, $y = (-100, 100)$ mm at step size of 1 mm (the origin was aligned to the lens centre) over frequency range of 15 to 18 GHz.

This modified waveguide transmitter structure was proposed by the collaborators in Queen Mary to introduce a smoother transmission of waves from waveguide into the lens. The schematics of the modified waveguide and a picture revealing the internal structure are shown in Figure 6.21. At the end of the waveguide (K band WR-51 for 15 - 22 GHz), a taper was machined to tune the width of the waveguide from 6.5 mm to the lens thickness 2.5 mm by slicing the top material off at an calculated angle and soldering back a copper layer. To facilitate energy

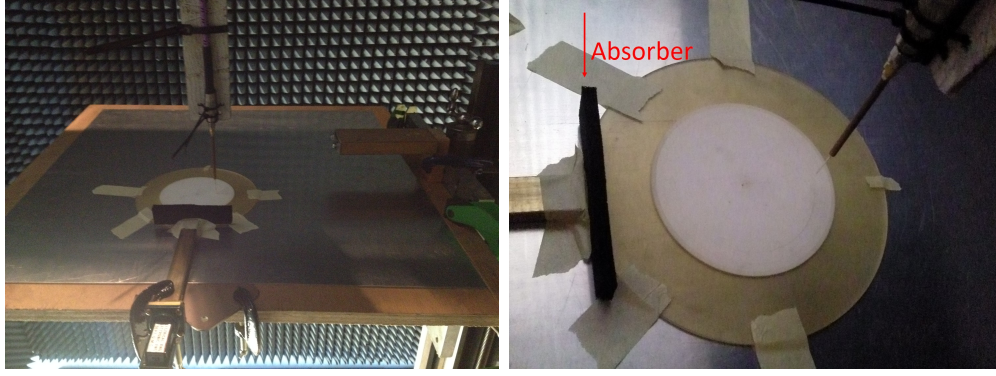


Figure 6.20: Second lens test in the University of Queen Mary in an anechoic chamber using waveguide excitation with absorbing materials to block space waves

channelling from the waveguide into the lens, a 2.5 mm thick prismatic epoxy block with the length of roughly one wavelength was inserted into the tapered section. The end of the epoxy block entirely filled the waveguide leaving no air gap, and was glued to the edge of the lens by polishing a flat surface. In addition, to help the epoxy block align inside the waveguide, a 3 mm long platform with constant width of 2.5 mm was constructed at the end of the waveguide. The completed fixture of the modified waveguide with the lens and a metal cover is shown in Figure 6.22 (a). Two experimental set-ups were carried out in the third lens test; with and without the metal cover. A picture of the third lens test scene with no cover is shown in Figure 6.22 (b). The metal cover was installed by bolting the top and bottom metal pieces together to press flat the deformed lens. The measurements took place in an anechoic chamber in the Queen Mary University of London, scanning an area of $x = (-60, 100)$ $y = (-100, 100)$ for the no cover set-up and an area of $x = (82, 122)$ $y = (-100, 100)$ for the metal cover set-up at a step size of 1 mm (origin was the lens centre) over frequency range of 15 - 19 GHz.

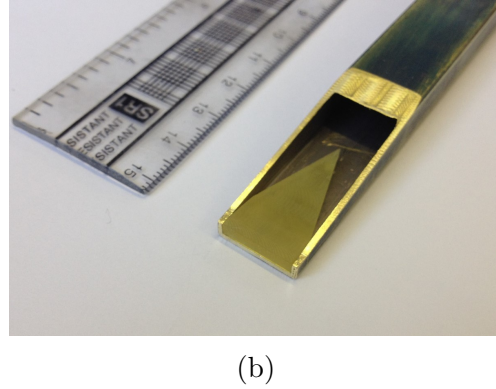
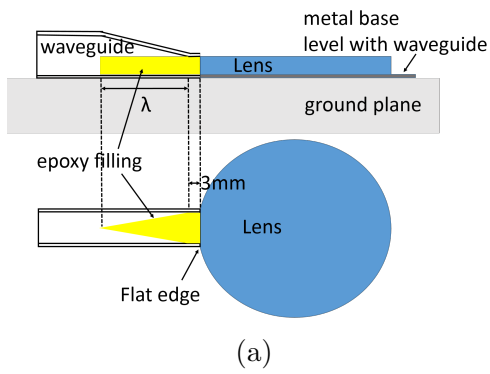


Figure 6.21: Schematics of the third lens test set-up (a) and picture of the modified waveguide inner structure before the metal top was sealed back on (b)

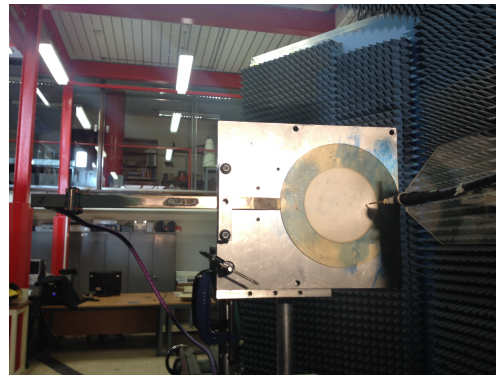
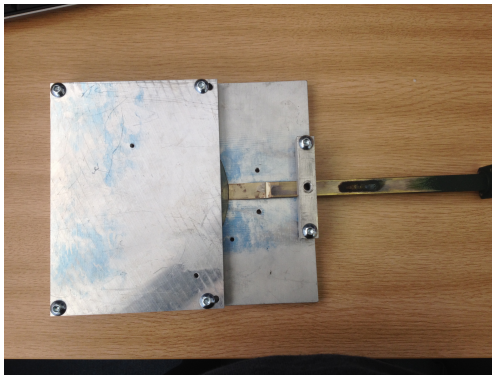


Figure 6.22: The modified waveguide fixture with lens and a metal cover (a); the second lens test with the no cover in anechoic chamber in the University of Queen Mary (b)

6.2.3 Simulation

3D models simulating these three lens tests were constructed in the COMSOL Multiphysics RF module. All models employed hemispherical perfectly matched layer (PML) domains with an outer radius of 165 mm situating outside the air domain to absorb incident radiation without producing reflections [3]. The thickness of the PML was set to be 20 mm. Scattering boundary conditions were applied to the hemispherical exterior boundaries. The lens was built in the x-y plane, perpendicular to the z axis. Its bottom centre was located at the origin. A perfect electric conductor was chosen for geometrical boundaries at $z = 0$, representing the metallic base in the actual test. A free tetrahedral mesh was applied to all domains with the exception of the PML. A swept mesh of five elements through the thickness was applied to the PML. The maximum element size of the free tetrahedral mesh was calculated as one fifth of the local wavelength equivalent to $3e8/(18e9*n*5)$ mm (where n was the refractive index of the dielectric medium and the calculation was based on the highest frequency 18 GHz) for all dielectric domains. The calculated mesh sizes for our simulations are listed in Table 6.2. A fine mesh with maximum element size of 1 mm and minimum element size of 0.1 mm was applied to port domains or boundaries. Measured dielectric properties, including the loss tangents of all dielectric layers of the lens, were used to specify the materials properties in these simulations to replicate the real lens testing environment as closely as possible. Simulated electric field z component (E_z) distributions in the same scanning area at the cut plane of $z = 3$ mm as in the experiments were exported in a grid spreadsheet with step size of 1 mm. Raw data files were then plotted in Matlab. The specification for the individual models are described below:

Table 6.2: Maximum element size setting for all dielectric domains in COMSOL model

Domain	Dielectric constant ε_r	Maximum element size (mm)
Air	1	3.3
Lens layer 1	18	0.78
Lens layer 2	13	0.92
Lens layer 3	12	0.96
Lens layer 4	10	1.05
Lens layer 5	8	1.18
Lens layer 6	6	1.36
Lens layer 7	5	1.49
Lens layer 8	4	1.67
Lens layer 9	3.4	1.81
Lens layer 10	3	1.92
Lens layer 11	2.8	1.99

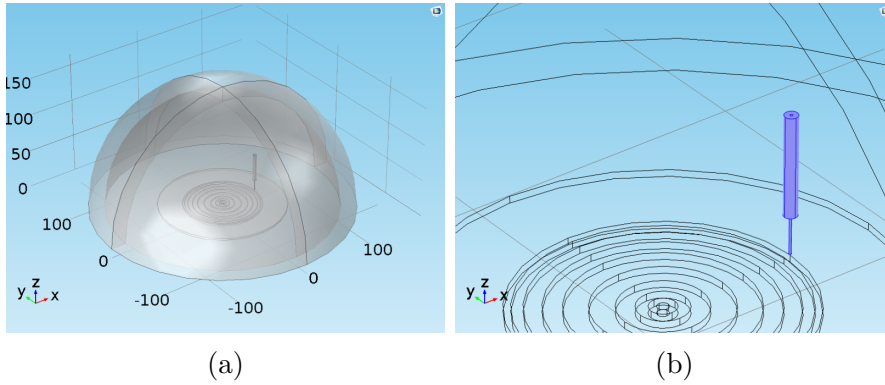


Figure 6.23: 3D COMSOL model of the first lens test using a monopole source, which is highlighted in (b)

Monopole source

The snapshots of the constructed 3D model for the first lens test using a monopole transmitter are shown in Figure 6.23. A coaxial cable, with inner conductor radius of 0.5 mm and outer conductor radius of 2.5 mm, was constructed as the monopole transmitter, by exposing the inner conductor. The exposed end of the monopole was placed 0.5 mm above the lens (i.e., $z = 3$ mm), right above the interface between the 10th and 11th layer of the lens (i.e., between the dielectric background and the actual lens). PTFE was selected for the layer between the

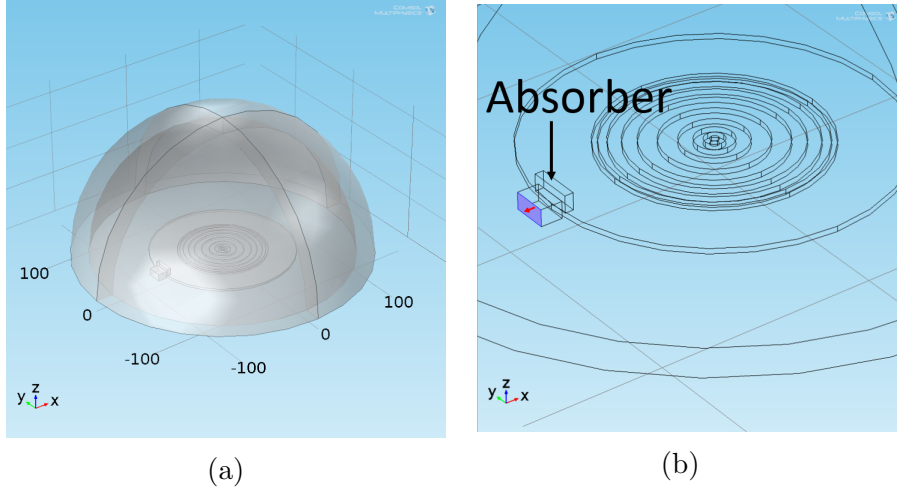


Figure 6.24: 3D COMSOL model of the second lens test using a waveguide transmitter. The rectangular port is highlighted in (b) with a piece of absorber blocking part of the outlet

inner and outer conductors. Perfect electric conductor conditions were applied to all inner and outer conductor boundaries. A lumped port condition was set at the ring surface on the far end of the monopole source. The type of the lumped port was coaxial and the terminal type was also coaxial. Wave excitation was at this port. Parametric solver was used to solve the model over a frequency range of 12 - 18 GHz at a step size of 1 GHz.

Waveguide source

The snapshots of the constructed 3D model of the second lens test using a waveguide transmitter with a piece of absorbing material blocking part of the outlet are shown in Figure 6.24. A 10 mm long block with the same Ku band waveguide dimension of 15.8 x 7.9 mm was created to imitate the waveguide transmitter. Port condition was applied to the surface at the far end of the waveguide, marked by a red arrow in Figure 6.24 (b). The type of port was rectangular with TE_{01} mode excitation on. The waveguide was placed close to the edge of the lens just like in the actual lens test. Another block sitting above the lens, leaving a 1 mm gap and flush with the end of waveguide, was constructed to represent the absorber

used in the actual test. A relative permittivity of 1, relative permeability of 1 and electrical conductivity of 0.5 S/m were assigned as the material properties for the absorber, as is normal for the usual absorbing materials used in anechoic chamber experiments [22]. The four surfaces forming the waveguide, excluding the inlet and the outlet, were set to be perfect electric conductors. This model was also solved at frequencies of 12 - 18 GHz at a step size of 1 GHz.

Modified waveguide source

The snapshots of the constructed 3D model of the third lens test using a modified waveguide transmitter with a transition taper are shown in Figure 6.25. A 50 mm long block with standard K band waveguide dimension of 13 mm x 6.5 mm was first built as the waveguide transmitter. The same rectangular waveguide port condition was applied to the far end of the waveguide, marked by a red arrow in Figure 6.25(c). At the other end, a slope turning the height of the waveguide from 6.5 mm to 2.5 mm over a distance of 21 mm was created. A 2.5 mm thick, 21 mm long prismatic block was inserted into the waveguide. A flat surface slightly wider than the width of waveguide was cut on the lens to which the prismatic block could be attached. Five metallic surfaces of the modified waveguide, including the slope but excluding the inlet and the outlet, were set as perfect electric conductors. Two experimental settings were simulated with the modified waveguide transmitter: the metal top setting (Figure 6.25(a)) and the no cover setting (Figure 6.25(b)). In the metal top setting, a 150 mm x 160 mm x 3 mm aluminium block was placed in contact with the top surface of the lens slightly away from the waveguide transmitter and flush with the end of the lens.

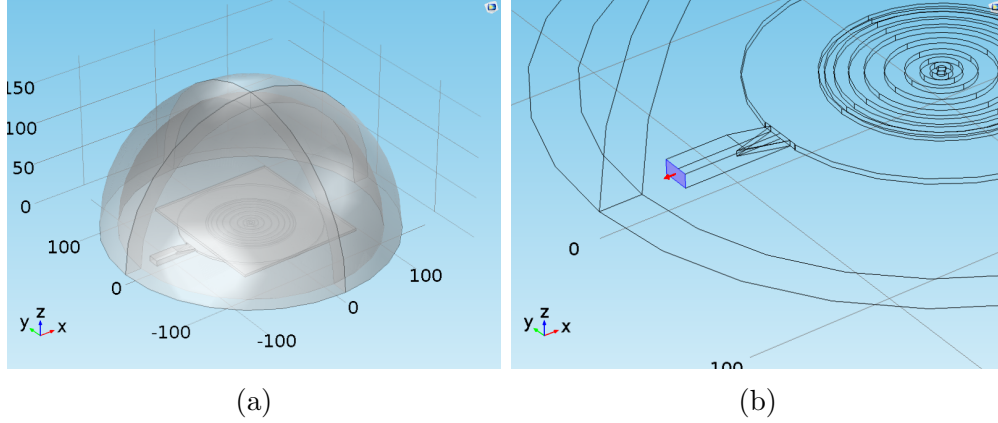


Figure 6.25: 3D COMSOL model of the third lens test using modified waveguide source (highlighted in (b)) creating a transition section for better energy channelling between the waveguide and the lens

6.2.4 Results and discussion

Monopole source

Plots of the amplitude and instantaneous electric field, i.e., E_z , the component perpendicular to the propagation plane at 15 and 18 GHz, in the first lens measurement using a monopole transmitter are shown in Figure 6.26. The Comsol simulation results for the same scenario are shown in Figure 6.27 for comparison. The lens was centred at the origin in all plots, and the two dashed circle overlays mark the position of the lens (the inner circle) and the dielectric background (the outer circle).

Comparing the experiment and simulation results, the measured electric field distribution within the lens area (before reaching the dielectric background) matched relatively well with the simulation. The waves were guided to converge at the edge of the power divider lens in the amplitude plots, and phase separations were clearly seen in the instantaneous plots. In the areas corresponding to the dielectric background in the E_z amplitude plots, the simulation shows the expected two main beams with sidelobes visible on either side of each beam and in the central region between the two beams. This compares reasonably well with the original simulations performed by collaborators at QMUL (Figure 6.13). A similar

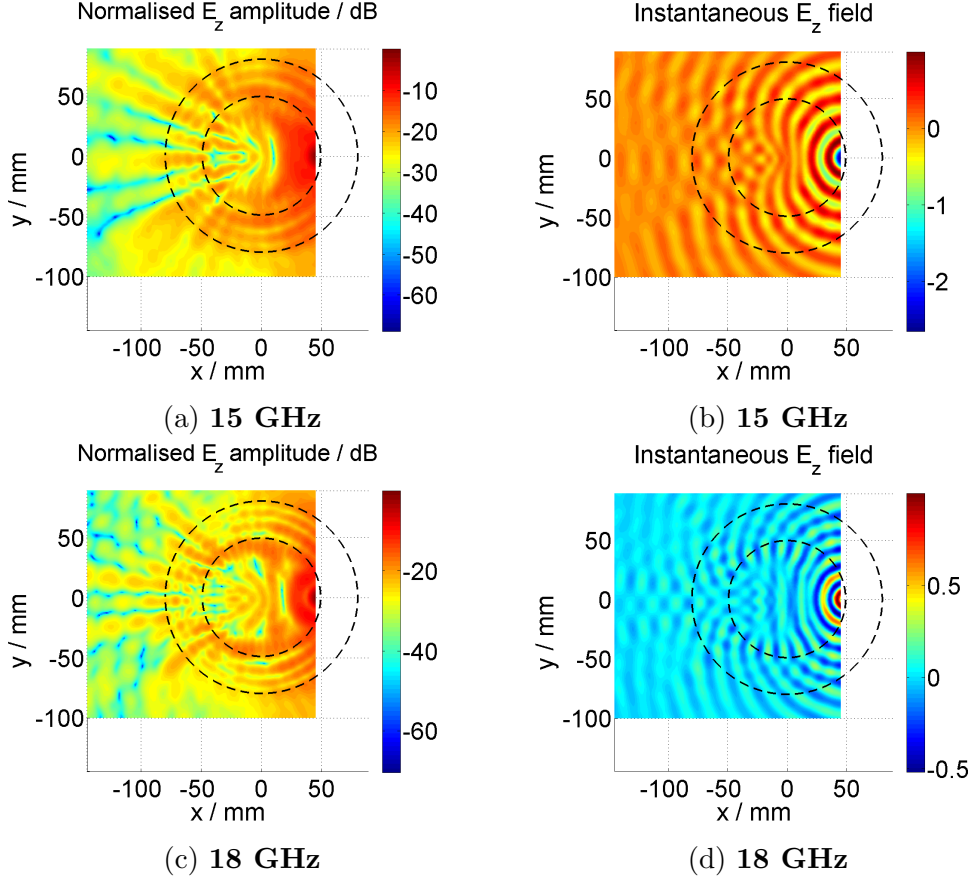


Figure 6.26: Experimental result of the first lens test using the a monopole transmitter (a)(b) E_z amplitude (V/m) plot and instantaneous E_z field plot measured at a plane of $z = 3$ mm at 15 GHz, (c)(d) and 18 GHz

distribution can be seen in the experimental data but the relative amplitude of the sidelobes with respect to the main beams seems to be greater when compared to the simulation results. According to the simulation results (Figure 6.27(a) and (c)), the wave propagation in the lens appears to be better restricted to the lens area with less energy radiated at the outside at 18 GHz than at 15 GHz and the divided two main sub beams came out of the lens at a narrower angle at 18 GHz.

For the instantaneous E_z plots, a major difference between the simulation and experimental results was that in the simulation (Figure 6.27(b) and (d)) the divided sub-beams were strong in amplitude and had a weak space wave (transmitted directly from the point source) background, therefore the propagation of the sub-beams beyond the lens could be easily recognised. In the experiment

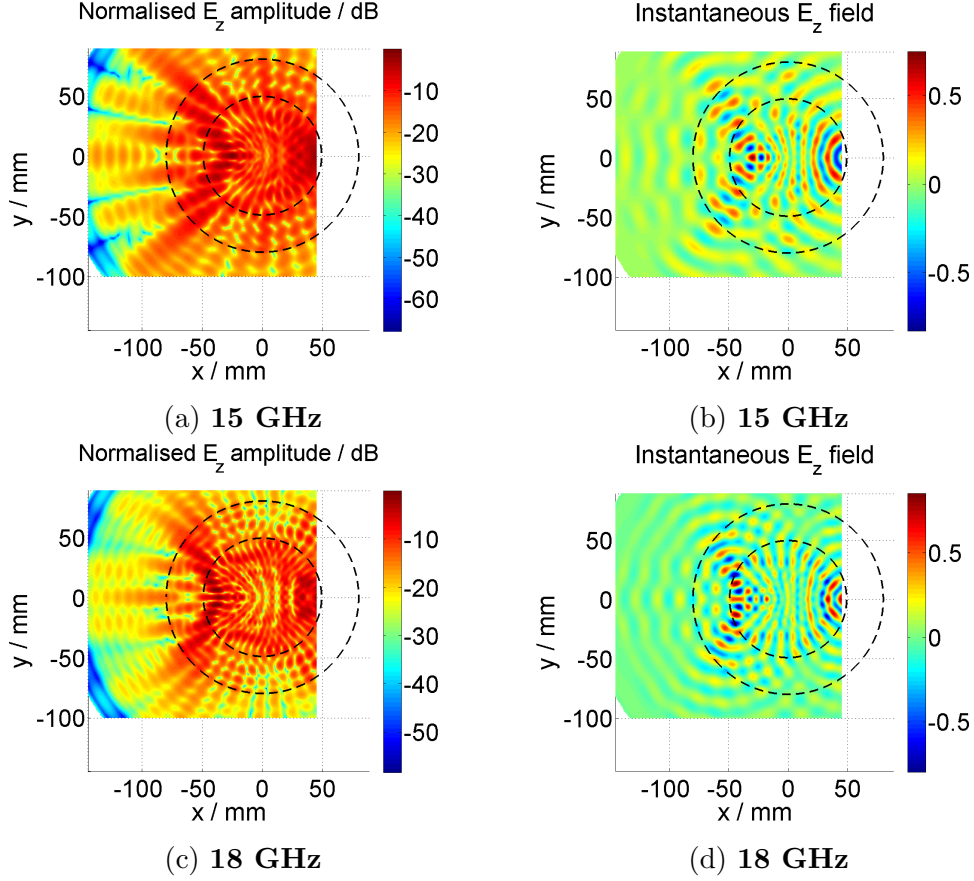


Figure 6.27: Simulation results of the first lens test using the monopole transmitter (a)(b) E_z amplitude (V/m) plot and instantaneous E_z field plot measured at plane of $z = 3$ mm at 15 GHz, (c)(d) and 18 GHz

(Figure 6.26 (b) and (d)) however, the divided sub-beams were so weak in comparison to the space wave that the overlap between the two could only be vaguely distinguished. The reason for this mismatch could be multi-fronts including that the strong cross coupling between the receiver and transmitter (which was not used in simulations) developed a strong space wave which made the detection of the sub-beams more difficult, and/or the wave was more strongly attenuated inside the lens than predicted by the simulation due to high dielectric losses in the selected materials; reflection from the local environment (even though absorbers were used to minimise reflections, it is impossible to remove them entirely) interfered with the detection of the sub-beams.

To quantitatively compare the split beams outside of the dielectric back-

ground, arc scan was performed on both the experimental and simulation results at 15 and 18 GHz to detect the normalised E_z amplitude at a distance of $r_1 = 70$ mm (in the dielectric background) and $r_2 = 90$ (outside the dielectric background) away from the lens centre over an angular range of $\phi = (-60, 60)$ degrees, as sketched in the insert in Figure 6.28. A shift in the central position of the experiment arc plot away from the origin (0 degree) was observed in all four plots, which accounts for part of the mismatch between simulation and experiment data. The shift is probably caused by problems in monopole positioning in the experiment that the monopole was not aligned at the exact position of $x = 49.2$ mm.

Although showing some mismatch with the simulation data, all plots exhibit reasonably good agreement between simulation and experiment in terms of the number and the angle of the peaks. Waves within the dielectric background ($r = 70$ mm) show better symmetry in the experiment data than waves outside the dielectric background ($r = 90$ mm) at both frequencies. The arc plots indicate clearly that the angle of the split beams coming out of the dielectric background in experiment correspond reasonably well with those in the simulation at both frequencies, but the relative amplitude of the sidelobes with respect to the main beams are bigger than outside the dielectric background. The main beams in all four experiment arc plots have comparatively similar amplitude with the sidelobes, inconsistent with the simulation arc plots. The deteriorated symmetry of the waves after propagating into air could suggest imperfection in the device's spherical geometry. To conclude, in the first lens test using a monopole transmitter, waves were detected in the experiment to split into sub beams at about the right number and angular position as the simulation suggests in and outside the dielectric background at both 15 and 18 GHz. The position and shape of the split beams are not perfectly symmetrical and the asymmetry is worse outside the dielectric background than within. The biggest inconsistency between the

experiment and simulation arc plots comes from the amplitude ratio of the main sub-beams to sidelobes. None of the experiment arc plots show dominant amplitude in the main sub-beams as seen in the simulation prediction. This could be caused by imperfect composition profile of the manufactured lens. Another possible explanation relating to the measurement is that simulations use a much greater power input than in experiment (1 W vs. 10 mW) which means a greater measuring precision is required for measuring attenuated waves after propagating along the lens in experiment to show real contrast.

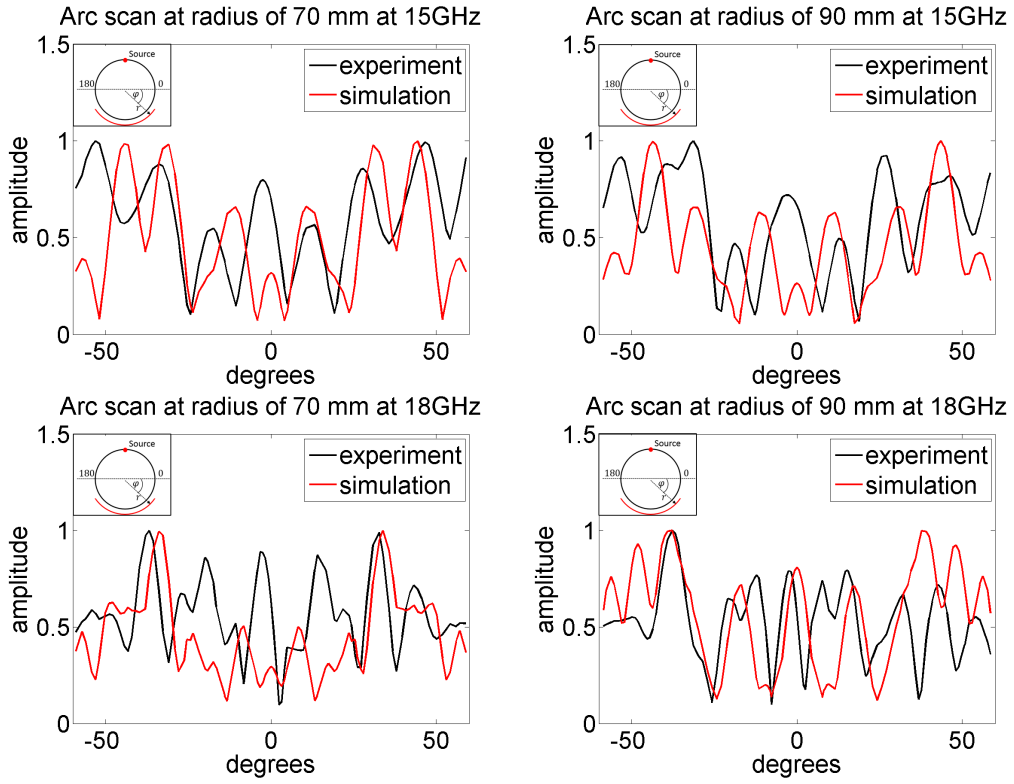


Figure 6.28: Arc scan from -60 to 60 degrees of normalised E_z amplitude of experiment and simulation results at 15 GHz and 18 GHz at radius of 70 mm and 90 mm

Waveguide source

The experimental and simulation results of the amplitude and instantaneous E_z plots at 15 and 18 GHz in the second lens measurement using a waveguide transmitter are shown in Figure 6.29 and Figure 6.30 respectively. In contrast to the

previous monopole transmitter results, using a waveguide transmitter resulted in two strong and clearly identifiable split main beams in the amplitude plots due to better directivity of the waveguide. Unfortunately, details about the wave propagation inside and outside the lens were less resolved as in the first lens test. Inside the power divider lens, the wave propagation using a waveguide transmitter showed a different profile than using monopole source, which might be influenced by the position in which the waveguide and monopole transmitters were placed. Although we see some suggestion of the waves being bent and converged in Figure 6.29 (a) and (c) but miss the evidence of the initiation of two sub-beams radiating outwards as in Figure 6.30 (a) and (c). The reason why we could not detect the confined and continuous propagation of the two divided beam from the lens to the dielectric background using either the monopole transmitter or waveguide transmitter experiments remain to be explained.

Because the waveguide transmitter was placed on the outer edge of the dielectric background, a certain portion of the wave was transmitted along the edge of the dielectric background as seen in the amplitude plots of Figure 6.29 (a) and (c). Two strong sub-beams were detected in the experimental data at 15 GHz (Figure 6.29 (a)) but at a slightly narrower angle than in the simulation (6.30 (a)). The main sub-beams were not as well defined at 18 GHz in Figure 6.29 (c) and the instantaneous plot Figure 6.29 (d) was heavily disrupted compared to the simulation results. The significant mismatch between the simulation and experiment results for the second lens test using a waveguide transmitter could be due to serious deformation of the lens in the 10 months between manufacturing and testing, and the fact that for the waveguide transmitter tests the lens was mounted vertically so that achieving perfect contact between the lens and the metal base was questionable.

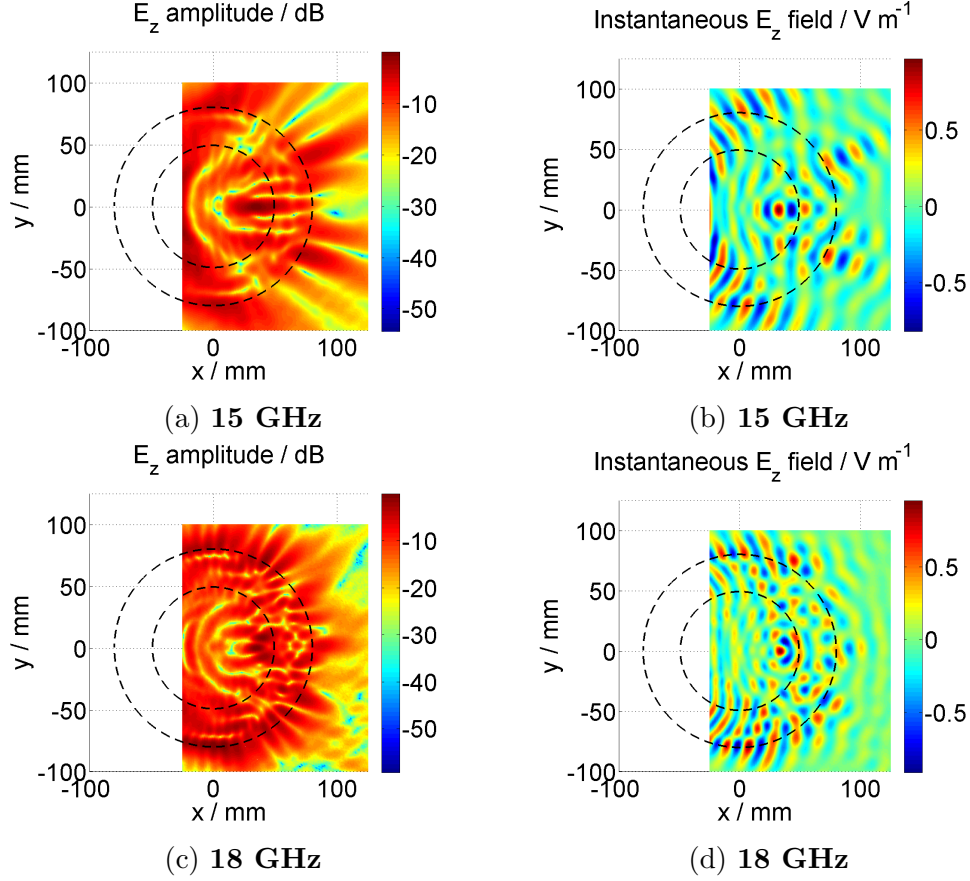


Figure 6.29: Experimental result of the second lens test using a waveguide source. (a)(b) E_z amplitude (V/m) plot and Instantaneous E_z field plot measured at plane of $z = 3$ mm at 15 GHz (a)(b) and 18 GHz (c)(d)

Modified waveguide source

The experimental and simulation results of amplitude and instantaneous E_z plots at 15 and 18 GHz in the third lens test with no cover on top using the modified waveguide transmitter are shown in Figure 6.31 and Figure 6.32 respectively. One obvious improvement compared to the second lens test was less waves were radiated transmitted along the edge of the dielectric background particularly close to the waveguide source suggesting the modified waveguide structure helped with suppressing the space wave. A much clearer profile of wave propagation was found in the amplitude plots of this experiment, showing how waves were bent and channelled across the lens. However, the directions of wave propagation deviate badly from the simulation. Such deviation could be result of progressed lens

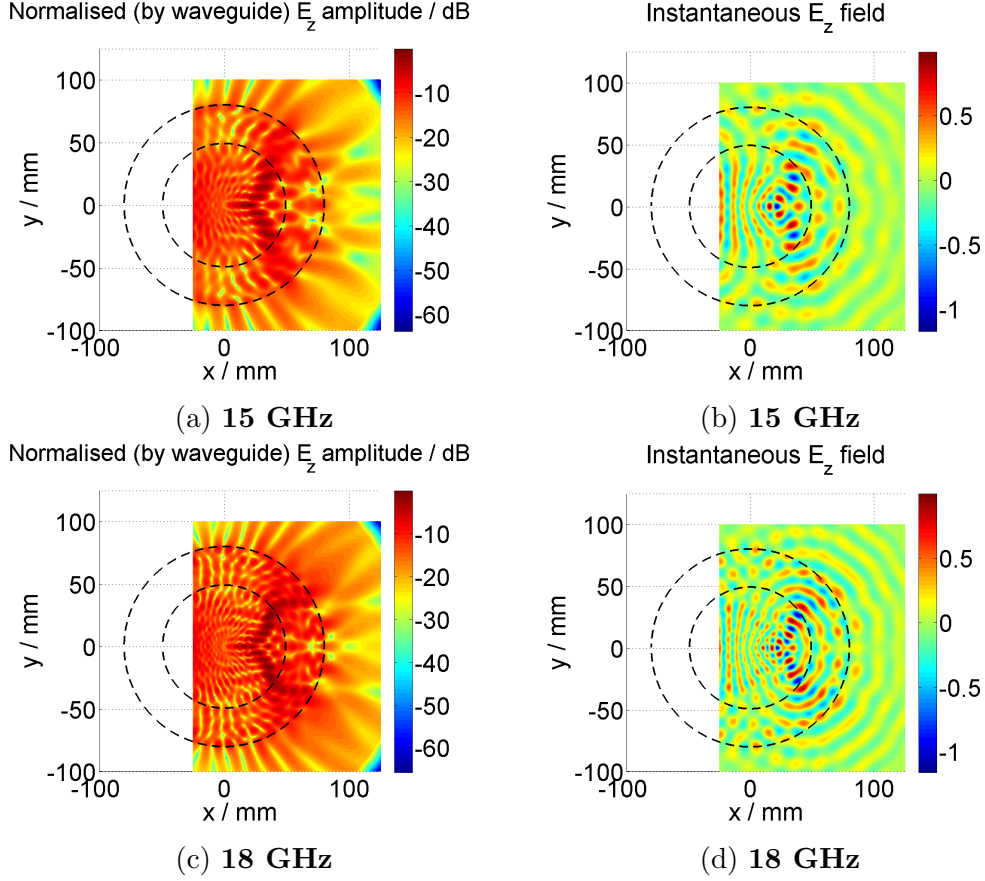


Figure 6.30: Simulation result of the second lens test using waveguide source: (a)(b) E_z amplitude (V/m) plot and instantaneous E_z field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d)

deterioration after another 5 months of time between the second and third lens test and lens handling to attached the modified waveguide feed in the meantime.

To keep the lens pressed down against the metal base and test the effect of using modified waveguide transmitter, a metal cover was devised to clamp the lens to the metal bottom as discussed previously. The experimental and simulation results for the metal top set-up are shown in Figure 6.33 and Figure 6.34 respectively. Clear evidence of two main sub-beams was visible in both the amplitude and instantaneous E_z field plots in the experimental data, which indicates that adding a metal top to press the lens flat improved the results. The angle of the two sub-beams were in good agreement with the simulation prediction

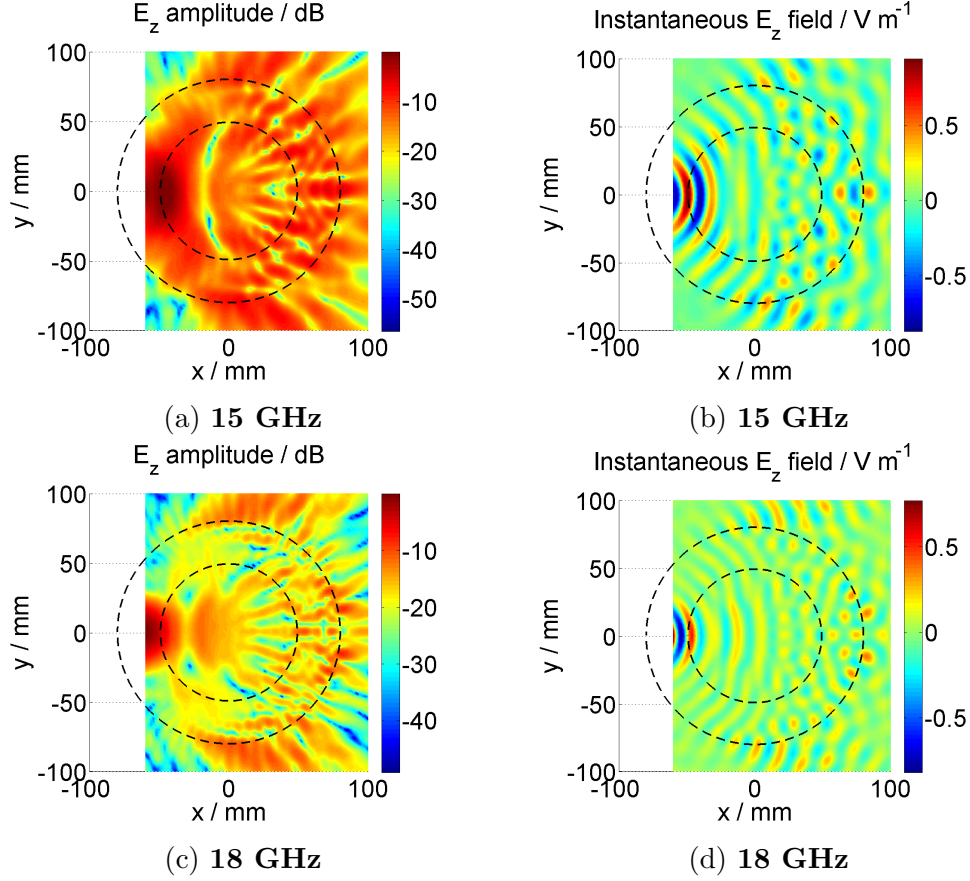


Figure 6.31: Experimental results of the third lens test using a modified waveguide source with no cover. (a)(b) E_z amplitude (V/m) plot and instantaneous E_z field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d)

at both 15 and 18 GHz. The main inconsistency between the experimental and simulation results was that the number of split waves in the amplitude plots in the experiment is more than in the simulation where small beams were merged into major beams, especially at 18 GHz. In these plots, waves transmitted in the central area were more significant in the experiment than in the simulation.

6.2.5 Conclusion

An all dielectric power divider lens employing a radial gradient dielectric profile to realise beam splitting was proposed by our project collaborator. The lens required a fine discretisation of dielectric constant with a narrowest difference of 0.4 between two layers, which increased the difficulty in lens manufacturing. The lens

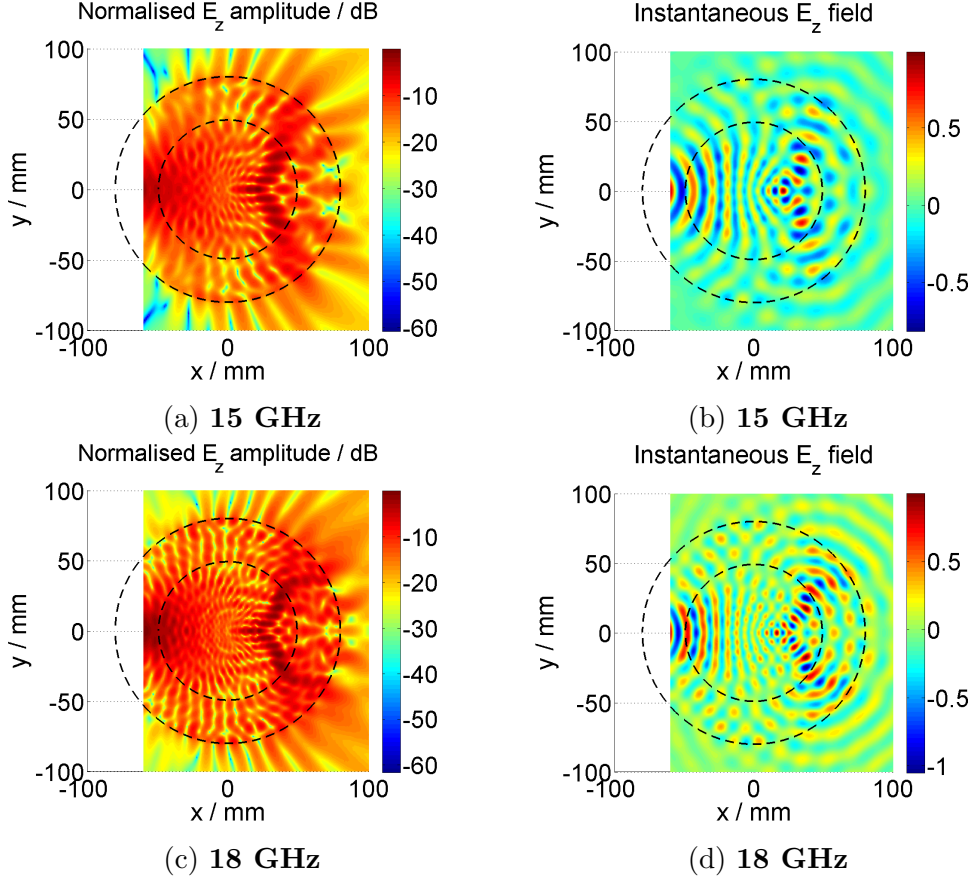


Figure 6.32: Simulation result of the third lens test using modified waveguide source with no cover: (a)(b) E_z amplitude (V/m) plot and Instantaneous E_z field plot measured at plane of $z = 3$ mm at 15 GHz (a)(b) and 18 GHz (c)(d)

was successfully manufactured by in-situ casting. The dielectric constants of the manufactured individual layers of the lens were verified by waveguide measurement, and showed good match with the target values. The manufactured power divider lens possessed good surface and interface properties. The thickness of the lens, although evenly distributed, was 0.5 mm thinner than the original design due to manufacturing limits. The reduced thickness was predicted to shift the functioning frequency of the lens from 15 GHz to 18 GHz. This effect was considered in the lens testing.

Three measurements using two different types of transmitters (monopole and waveguide) were conducted on the lens in this work, and corresponding simulations for each measurement were also done in COMSOL to compare with the

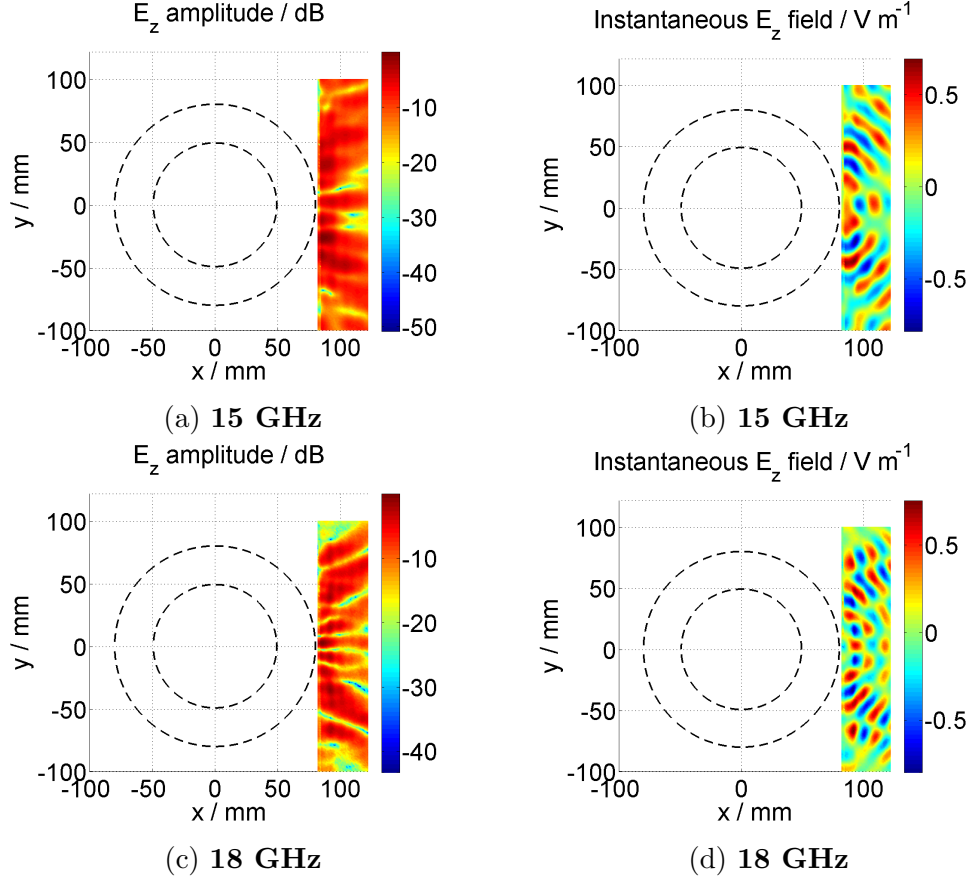


Figure 6.33: Experimental result of the third lens test using a modified waveguide source with metal top. (a)(b) E_z amplitude (V/m) plot and instantaneous E_z field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d)

experimental results. In the results where the lens was tested without a metal cover on top, we achieved the best result in the first lens test using a monopole transmitter which is very likely due to the excellent lens condition at that time as the lens was freshly fabricated. All sub-beams detected on the outside of the dielectric background were at angles consistent with the simulation predictions but the main sub-beams did not show the largest amplitude. The second and third lens test introduced a more directive waveguide transmitter and took place nearly 1 year later, and the seriously deformed lens condition increased the difficulty of determining the lens true performance under a waveguide source. Although all experiment results showed signs of the wave being guided through curved paths to the other side of the lens, details of split two sub-beams propagating outward

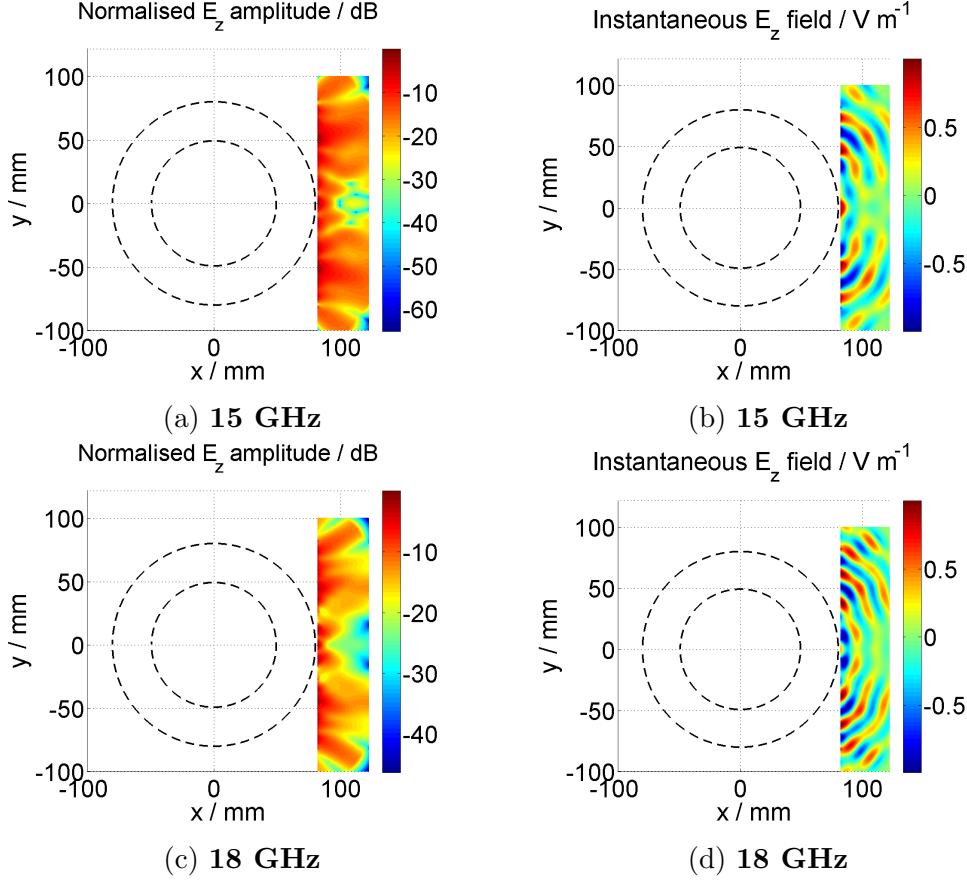


Figure 6.34: Simulation result of the third lens test using a modified waveguide source with metal top. (a)(b) E_z amplitude (V/m) plot and instantaneous E_z field plot measured at plane of $z = 3$ mm at 15 GHz, and 18 GHz (c)(d)

continuously were not detected. The enhanced directivity of the waveguide transmitter increased the intensity of the sub-beams, which made the main sub-beams more recognisable, but lost details about the wave propagation. To force the lens sit in perfect contact with the metal base, a metal top was used to press the lens flat between two metal layers in the third lens test, and two split beams were clearly detected in the experiment which agreed well with the simulation results.

All in all, we found that the manufactured power divider lens performed to split the incoming beam into sub-beams in the tests whether a monopole or waveguide transmitter was used. However, this demonstrator lens was not able to generate the two dominant sub beams aimed at in the design, and losses in the dielectric materials as well as difficulties and delays in deciding how to measure

the performances of the this novel device may both have contributed to this result.

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Chapter 7

Conclusions and Suggestions for future work

In this work, I have explored several manufacturing methods to fabricate different types of polymer/ceramic composites for electromagnetic customisation at microwave frequencies. The main conclusions drawn in this work include:

- PFA/BT composite films with BT loadings up to 26 vol% have been fabricated by spraying. The spraying process has been optimised to produce good quality, small (glass slide) and large (160 mm x 160 mm) area films with thickness up to 100 μm .
- A uniform distribution of BT nano-particles within the PFA matrix has been confirmed by microstructural examination of PFA/BT composite films by microtomy and SEM, as well as by thermogravimetric analysis.
- The dielectric properties of the sprayed PFA/BT composite films were measured by impedance analyser and waveguide methods (samples prepared with the help of a well controlled hot pressing process) over both a low frequency range of 100 Hz - 1 MHz and over a high frequency range of 12 - 18 GHz. The Lichtenecker or logarithmic mixing rule that had good agreement

to both sets of data was used to give estimates of the dielectric constant of the barium titanate nano-powders over these two frequency ranges.

- At 10 kHz, dielectric constants from 2.5 to around 14 have been achieved for PFA/BT composites with a BT dielectric constant estimate of 2072 given by the Lichtenecker fit.
- At 15 GHz, dielectric constants from 2 to around 6 have been achieved for PFA/BT composites with a BT dielectric constant estimate of 517 given by the Lichtenecker fit.
- The estimated dielectric constants of BT powder are consistent with the reported values for bulk BT ceramics, but higher than the estimated values using mixing rules by others. A reduction of about 30 % in the effective dielectric constant of the PFA/BT composites at high and low frequencies has been observed in my measurement data, which give some insight to the frequency dependence of the dielectric properties of PFA/BT composites - data which is rarely reported in the literature.
- Epoxy/BT composite blocks with BT loadings up to 40 vol% have been fabricated by casting in this work to produce systematic data for permittivity customisation. Other ceramic powders such as BST and CT have been briefly investigated as lower loss ceramic alternatives.
- The casting process has been optimised to produce block samples with uniform composition and stable dielectric properties. Vacuum degassing was used to remove air bubbles trapped in the epoxy composites with ceramic loadings lower than 30 vol%. Homogeneous distribution of powders within the matrix was confirmed by microstructural examination.
- The dielectric properties of epoxy/BT composite blocks were measured by a waveguide technique at 12 - 18 GHz. Dielectric constants from 3 to 18 have

been achieved for these epoxy/BT composites, with dielectric constants from 3 - 12 being achieved in a controllable and predictable way, which offers the capability of permittivity customisation over this range.

- Various mixing rules have been studied and used to fit the dielectric constant data for these epoxy/BT composites, and the Yamada equation was found to best fit the data, with the morphology factor, n , chosen properly. A dielectric constant estimate of 360 for micron sized BT powders was given by the Yamada equation based on the experimental data on these composites.
- An effective surface treatment process using a silane coupling agent was developed to facilitate ceramic dispersion in epoxy resin. This was a critical step for preparing homogeneous epoxy/BST composites with stable dielectric properties, as the BST powders often showed severe agglomeration.
- Epoxy/BST and epoxy/CT composites were found to have lower losses than their compositionally equivalent epoxy/BT counterparts, but at the cost of slightly lower dielectric constants. The 20 vol% epoxy composites showed loss tangent value of 0.06, 0.05 and less than 0.03 for BT, BST and CT fillers respectively.
- Advanced applications of anisotropic dielectrics and a power divider lens were explored, utilising the permittivity customisation capability described above. Anisotropic ABS and ABS/BT composite blocks were fabricated by 3D printing, and the concentric layers of an index-gradient epoxy/BT composite lens was built by in-situ casting.
- 3D printed ABS and ABS/BT composite blocks showed a clear anisotropic dielectric effect when the dielectric layers were aligned parallel and perpendicular to the electric field. The experimental results also agreed well with simulation results from COMSOL Multiphysics.

- A power divider lens employing a concentric 11-dielectric-layer structure was cast layer by layer with epoxy/BT composites at pre-calculated loadings. The lens was tested in three different 2D near-field microwave imaging systems in the University of Exeter and Queen Mary University of London. The simulations of the lens performance was built in COMSOL Multiphysics and compared with the experimental results. A reasonable agreement between the experiment and simulation results was achieved in the first lens test using a monopole transmitter. More discrepancies were found on the following tests, probably due to the lens ageing and deformation over time.

To summarise, different polymer/ceramic composites were investigated and manufactured in this work by spraying, casting and 3D printing to pursue flexible control over the dielectric properties of composites. This control was tested in advanced applications of anisotropic dielectrics and a 2D index-gradient power divider lens. The spatial arrangements of composites with designated dielectric properties has proved to be effective in manipulating wave propagation at microwave frequencies. For future work, dielectric composites with a wider and more precisely defined dielectric constant range can be pursued, which might involve selection of dielectric components with higher dielectric constants and optimisation in the manufacturing process to produce very stable and homogeneous composite mixtures. Use of high dielectric constant polymers is expected to help elevate the dielectric constant of the composites, while low loss polymers should be selected in applications requiring low loss. Combining the dielectric range of these composites has been shown to be possible, and the geometric flexibility of future manufacturing methods will be the key to realising transformation optics applications. 3D printing would be a promising manufacturing method to meet this goal with its superior control over sample geometries. We have demonstrated examples of using 3D print to fabricate complex geometry samples with in-house customised composite filaments. The key limitations in 3D

printing index-gradient dielectric samples are restricted dielectric constant range achievable as the filaments get too brittle to print when too much high dielectric constant fillers are loaded, and unstable dielectric properties of the composite filaments. More advanced EM customisation applications can be explored to test the effectiveness of EM manipulation of such dielectric composites.