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Preparation, microstructure and microwave dielectric properties of sprayed PFA/barium titanate composite films

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Abstract

Frequency dependence of the dielectric properties of polymer-ferroelectric composites at different bands of microwave frequencies was investigated in this work. Perfluoroalkoxy (PFA) / barium titanate (BaTiO₃) nanocomposite films were prepared by spray deposition. The spraying process was scaled up to fabricate large area (max. 160 mm x 160 mm) uniform composite sheets out of which a controlled bonding process was introduced to form composite blocks. The microstructure of the composite films was examined by SEM with a microtome sample preparation method to evaluate the effectiveness of the spraying process at producing uniform particle distributions. The dielectric properties of the composite films with various BaTiO₃ loadings were characterised by an Impedance Analyzer at frequencies between 10 Hz and 1 MHz and Vector Network Analyzer at 12 - 18 GHz respectively. The Lichtenecker mixing rule was incorporated to fit the measured dielectric constant data, which gives estimates of dielectric constant of the BaTiO₃ nanometer sized particles to be 895 and 571 at 10 kHz and 15 GHz respectively. In comparison, the composite effective dielectric constant was approximately reduced by 25% at 10 kHz than that at 15 GHz.

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1. Introduction

Polymer-ferroelectric composite films are widely used for electronics at microwave frequencies (up to a few MHz) including capacitors and other energy storage devices [1, 2, 3], as well as for high frequency applications ($> \text{GHz}$) in the telecommunications industry such as for beam steering, antennas and electromagnetic interference devices [4, 5, 6]. Combining the advantages of the easy processability and 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 [7, 8]. 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 [9]. 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 micrometer 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.

Although data has been reported for the dielectric constant of polymer-ferroelectric composite films at low frequencies, very limited reference data can be found for high frequency measurements of the same materials. In part this is due to sample preparation difficulties for the high frequency measurements [10]. For composite films, capacitance measurements using an impedance analyzer is the conventional way to obtain dielectric constant data [11, 12, 13], which unfortunately is only suitable for measurements up to 1 GHz. Attempts

have been made to measure the dielectric performance of composite films at high frequencies using resonator or free space techniques [14, 15]. However, both of these two techniques suffer from intrinsic drawbacks that significantly limit their application for routine high frequency measurements. The resonator method is not suitable for monitoring the dielectric performance over a continuous frequency band whereas the free space technique is very demanding on equipment and hence is expensive to apply for routine measurements [16]. In contrast, the transmission/reflection technique is ideal for easy and continuous dielectric measurement at high frequencies. However, for a typical waveguide measurement in the Ku band (12.4 GHz - 18 GHz), samples are required to be the order of a mm thick in order to guarantee reliable measurements, and this poses a challenge for film samples that normally have thicknesses in the nm to μm range. In this work, we have designed a carefully monitored hot pressing method to create reproducible samples from sprayed composite films for high frequency waveguide measurements. Thermoplastic/BT composite films up to 120 μm thick were stacked and hot-pressed at a temperature just above polymer melting temperature to build up a sufficient sample thickness for a reliable waveguide measurement without altering the microstructure of the material. Dielectric properties of the polymer-ferroelectric composite films were measured and compared at low frequencies (100 Hz - 1 MHz) and at high frequencies (12 - 18 GHz) in our work.

Industrial applications of polymer-ferroelectric composite films require accurate control and prediction of the dielectric performance. Several theoretical models are available to predict the dielectric properties of composite systems, and their validity tested by curve fitting to experimental data [11, 17, 18, 19, 20, 21]. 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 nanometer sized particles in a composite, since it is difficult to measure the dielectric properties of the nanometer sized particles alone. This is a useful procedure because the dielectric constant of nanometer sized ceramic

particles is expected to deviate significantly from that measured in bulk ce-
 60 ramics due to the three dimensional clamping effect in bulk ceramics [1]. For
 instance, from data fitting using the Lichtenecker [22] and Jayasundere & Smith
 [20] equations dielectric constant values an order of magnitude lower have been
 reported at 100 kHz for barium titanate particles (282 for 0.25 μm particles)
 than for bulk ceramics (~ 2000) [17]. In our work, the Lichtenecker equation
 65 was used to fit the measured dielectric constants of PFA/BT nanocomposite
 films at 10 kHz and 15 GHz to allow us to estimate the dielectric constant of
 the nanometer sized barium titanate particles.

2. Experimental

Perfluoro alkoxy (PFA) / BT nanocomposite films were prepared by spray
 70 deposition. Spraying is a convenient and economical manufacturing method 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 with minimum equipment maintenance re-
 quired and is suitable for efficient small quantity spraying when compared with
 75 spin-coating which causes significant waste of precursor materials [23]. This
 spray deposition technique has been shown in previous work [24, 25] 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 thicknesses exceeding 100 μm while still
 80 maintaining good surface quality. The thermoplastic fluoropolymer perfluoro
 alkoxy (PFA) was chosen as the polymer matrix because of its good chemical
 resistance, high temperature resistance (due to a high melting point of over 300
 $^{\circ}\text{C}$) and stable dielectric performance at microwave frequencies [26].

2.1. Materials

85 PFA from 3M Dyneon was chosen as the polymer matrix for spraying, and
 has a melting temperature of 306 $^{\circ}\text{C}$. It is available as a 50 vol% PFA water

suspension containing PFA particle sizes around 80 nm. BT particles (300 nm, 99.9 %, tetragonal) supplied by Nanoamor were used as the ceramic filler. The choice of most suitable particle size and phase for the BT particles was made
 90 with the aim of providing a high dielectric constant filler material that is also compatible with the spraying process. The spraying process requires stable suspensions which we achieved by dispersing BT particles homogeneously in PFA water suspensions. Big BT particles or poor stability of the composite suspensions caused blockage in the spray nozzle tip - a 0.023 inch diameter
 95 orifice. Therefore, BT particles as small as possible would be preferred, but taking into consideration that peak dielectric constant values were reported for BT ceramics with grain size 700-800 nm with the dielectric constant gradually decreasing for smaller grain size[27]. When the grain size is less than 100 nm, the crystal phase of BT changes from tetragonal to cubic at room temperature
 100 and hence shows a much lower dielectric constant. Thus the BT particle sizes should be as close to 700-800 nm as possible and be tetragonal phase to obtain highest dielectric constant. Considering these two opposing requirements, we chose the smallest BT particles we could source that had the tetragonal phase, which are 300 nm. Dispex A40 (BASF, Germany), an ammonium salt of acrylic
 105 polymer, was used as a dispersant to help stabilise the aqueous PFA and BT suspension.

2.2. Spray deposition

. PFA/BT composite films with filler to matrix volume ratios up to 40% (corresponding to BT volume percent of 28.6%) and with thickness ranging from a
 110 few μm to over 100 μm were prepared by spraying using pneumatic atomizing nozzles. A diagram of the spraying process is shown in Fig. 1. Composite suspensions were prepared by mixing the PFA water suspension, BT particles and 2wt% of Dispex A40 under ultrasonication for ~ 1 h. The well-mixed composite suspension was subsequently fed into the spray nozzle by a syringe pump
 115 driven at a controllable, constant speed. The liquid droplets were atomised at the nozzle outlet by compressed air at high pressure. The atomisation formed

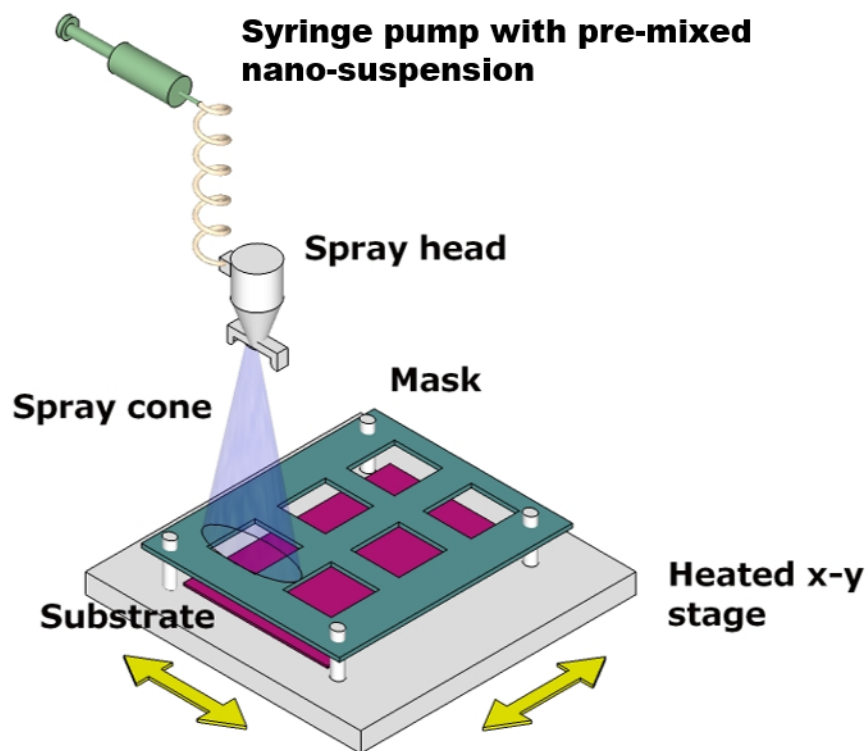


Figure 1: Illustration of the spraying deposition process

a cone of fine mist that deposited on the surface of glass substrates sitting on a mobile hotplate preheated to 95 °C. The hotplate moved under computer control according to a pre-set pattern in the x-y plane. The height of the spraying nozzle above the hotplate of between 10 - 15 cm, atomisation pressure of typically 300 kPa, suspension feed rate of 2 - 4 mL/min and the hotplate moving pattern were all carefully optimised to obtain good quality films. Quality was determined by a consistent thickness, color and surface roughness across the full area of the film. Following thorough drying on the hot plate, sprayed composites were then melt-processed in a belt furnace at 380 °C for 30 min. For low frequency measurements, premetallised (Au) glass slides were used as the spray substrate and another layer of Au was deposited on top of the composite film through shadow masks. For higher frequency measurements, 200 mm x 200 mm

glass plates were used, and the composite films were carefully removed from the
 130 glass substrates by submerging the whole sample in water until the composite
 films detached spontaneously from the glass substrate, followed by drying.

2.3. Hot pressing

Maximum 160 mm x 160 mm 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
 135 a heated die within a specially designed hot press with an initial load of 25 Kgf
 evenly applied. 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 mea-
 surements of the pressurizing ram from a linear variable displacement transducer
 140 (LVDT) to avoid excessive heating or pressing. The sample was heated to just
 above the PFA melting 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,
 suitable for the high frequency waveguide measurements.

2.4. Characterisation

The crystal structure of the BT particles was confirmed by X-ray diffrac-
 tion using a Philips PW1729 $\theta - 2\theta$ diffractometer. The particle size of BT
 was observed under SEM and analysed with a Zetasizer Nano ZS (Malvern In-
 struments). As-received BT particle / water suspensions and de-agglomerated
 150 BT particle water suspensions after ultrasonication with 2 wt% of Dispersant
 for ~ 1 h were prepared and examined by Zetasizer. Zeta potentials
 were also measured as an important indicator of the stability of the suspensions.

The microstructures of the sprayed films with various loadings were exam-
 ined by scanning electron microscopy (SEM) in a JEOL 840F. Samples were
 155 prepared by submerging the glass slide and the composite film in liquid nitro-
 gen, then snapping instantly after removal from liquid nitrogen to achieve brittle
 fracture cross-sections. More elaborate sample preparation designed to better

reveal particle agglomeration by eliminating interference from the surface texture of the polymer matrix was achieved by microtomy with a diamond blade in a Leica Ultracut E microtome. This provided a smooth cross-section of the composite surfaces in which agglomerates could be more easily resolved. The film cross-sections were coated with 2.5 nm thick platinum layers before SEM observation.

Thermogravimetric analysis was also conducted on the composite films to assess the effect of filler materials on composites' thermal stability. The mass residue of the composites following high temperatures is also provided as a complementary study of the real composition of composite films at milligram scale.

For low frequency dielectric characterisation, capacitance measurements up to 1 MHz were conducted on a Solartron SI 1260 Impedance Analyzer. Sprayed films were sandwiched between two Au electrodes to create mini-capacitors. For each film, 4 to 14 measurements were taken at various positions. Calculation of the dielectric constant (ϵ_r) and loss tangent ($\tan \delta$) values required measurement of the area of each mini-capacitor, and the thickness of the film using a Dektak surface profilometer.

High frequency measurements (from 12 GHz to 18 GHz) were carried out using a two-port Vector Network Analyser (VNA, HP 8510C Agilent) and a standard Ku band waveguide with sample dimensions of 15.8 mm x 7.9 mm x 2 mm connected to the VNA with phase-stable cables. Block samples cut into these exact dimensions were carefully press-fitted into the waveguide. The complex relative permittivity and relative permeability were extracted from the measured S-parameters using the Nicolson-Ross-Weir method [28].

3. Results and Discussion

3.1. Size and crystal structure characterisation for BT particles

SEM image of as-received BT powders particle size measurements before and after the deagglomeration process measured by Zetasizer are shown in Figure 2.

Particle agglomeration is seen in the SEM image. The average suspension particle diameter in Zetasizer measurement was $1.5\ \mu\text{m}$ for as-received BT powders which reduced to 420 nm when the combination of dispersant and ultrasonication was applied. A corresponding zeta potential $\zeta = -25.5\ \text{mV}$ was also obtained by Zetasizer measurement which suggested good stability of the dispersion [25]. There is a practical limit to the BT loading in the spraying technique because addition of the particles increased the viscosity of the composite suspension. Very viscous composite suspensions cause blockage to the nozzle tip and drastically increase the surface roughness of the final composite films. A rough film surface with micro-holes or cracks results in short-circuits between the bottom and top electrodes over a critical frequency. In this study, the highest practicable BT:PFA volume ratio was 0.4 beyond which good quality films could not be achieved.

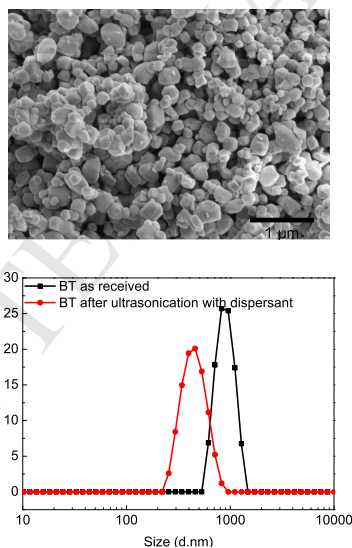


Figure 2: SEM image of as-received BT powders (top) and Zetasizer measurements for as-received BT powder water suspension and de-agglomerated BT powder water suspension after ultrasonication with dispersant Dispex A40 (bottom)

To enhance the overall dielectric constant of our composites, tetragonal nanometer sized BT particles were chosen, and the tetragonal phase was con-

205 firmed from the XRD results in Figure 3. All the resulting peaks shown in which could be assigned to the tetragonal form of BaTiO_3 , with the characteristic splitting of (200) peaks visible in the inset around $2\theta = 45^\circ$. It is well known that dielectric properties of BT powders are dependent on both crystal structure and particle size [1, 29]. Transition from the tetragonal to cubic structure reduces the permanent dipole and dielectric constant of BT, while particle size reduction would induce this phase transition at a lower temperatures.

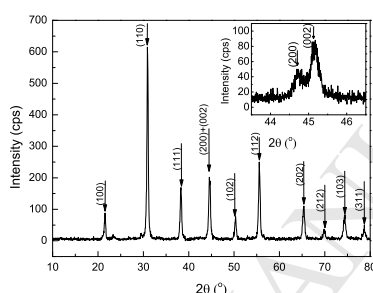


Figure 3: XRD plots of as-received barium titanate nano-powders. The main figure is the overall scan from 10 to 80° , and the insert of a detailed scan around 45° confirms the characteristic splitting of the (200) and (002) peaks for tetragonal crystal symmetry.

3.2. SEM characterisation of PFA/BT composite films

210 BT particle distribution in the PFA / BT composite films were examined by SEM as shown in Figure 4. 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 freeze fracture
 215 samples for cross-sectional analysis was no longer feasible due to weak attachment between the film and the glass substrate. However, in the SEM images of the microtome-prepared cross-sections of composite films, any BT agglomerates could be easily revealed. An example of poor BT distribution is seen in 4 (e) and (f) for a composite with BT:PFA volume ratio of 0.1 (corresponding to BT
 220 volume percent of 9.1%), where BT clusters with diameters as large as 5 microns could be identified. Localised large particle agglomerates would result not

only in patchy dielectric performance but also sedimentation of the composite suspension during the spraying process when large areas (long spraying times) were required. After introducing high power ultrasonication combined with the application of Dispex A40, the BT distribution was much improved and the composite films were almost agglomerate-free.

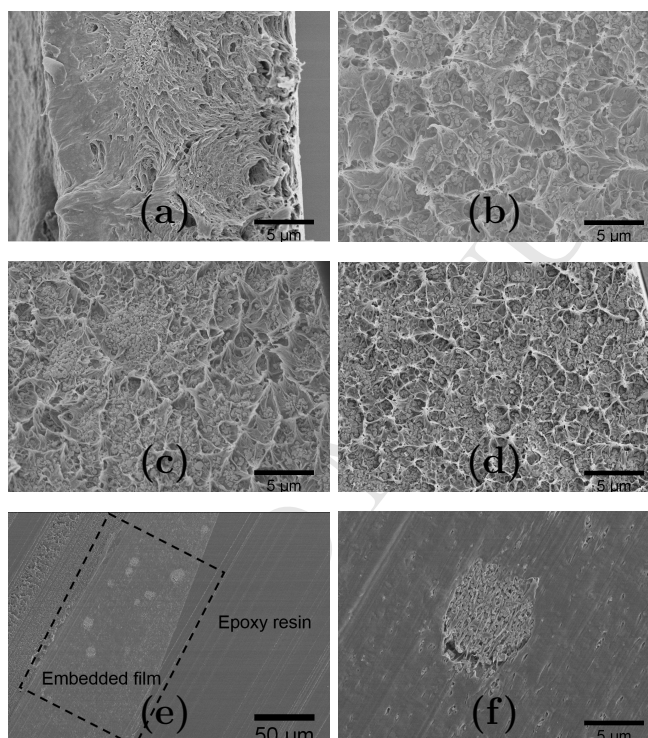


Figure 4: SEM images of freeze-fractured cross-sections of PFA-BT composite films at (a) BT:PFA (v/v)= 0.05 (BT volume fraction of 0.048) (b) BT:PFA (v/v)= 0.1 (BT volume fraction of 0.091) (c) BT:PFA (v/v)= 0.2 (BT volume fraction of 0.167) (d) BT:PFA (v/v)= 0.3 (BT volume fraction of 0.231);(e) and (f) are microtome-prepared cross-sections of BT:PFA (v/v)= 0.1 composite film at different magnifications

3.3. Thermogravimetric analysis

To test the thermal stability of the composite films, thermogravimetric analyses of samples with varying compositions were conducted on a Perkin Elmer Diamond TG/DTA machine (Figure 5). PFA started to decompose at *ca.* 400

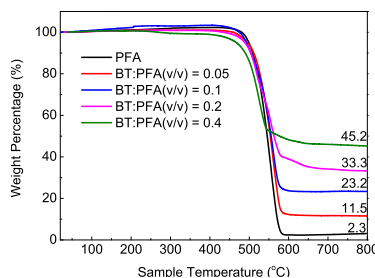


Figure 5: TG/DTA measurements of composite films with different compositions. The numbers at the end of each data line are the measured residual mass after removal of the PFA

°C and was almost completely removed from the system above 600 °C. The nominal weight percentages of BT in the tested composite samples are 0, 12.0, 21.4, 35.2, 52.1 respectively compared to what were marked in the graph as the measured results. There was only minor disagreement between the TGA measurements of residual BT weight fraction and the nominal compositions, which can be explained by variation due to the very small sample size tested in the TGA measurements (~ 2 mg), possible particle agglomeration and powder sedimentation during spraying.

3.4. Low frequency dielectric properties characterisation

Several capacitance measurements were taken on each film, and the typical dielectric performance of PFA / BT composite films with increasing ceramic loading between 100 Hz and 1 MHz is shown in Figure 6. There was relatively stable dielectric performance over the frequency range for films with lower BT loadings. As the BT:PFA volume ratio increased, the decrease in dielectric constant becomes obvious towards 100 Hz. A similar relaxation effect for titanate-polymer composites between 10 Hz and 1 kHz was reported in [30]. The dielectric constant and loss tangent measurements at 10 kHz for composite films with different BT loadings are compared in Figure 6 where each data point is an average of 4-14 measurements taken on each film sample, and the standard deviation of measurements taken on each film are plotted as error bars. The scattering in measurements taken on each film can be significant

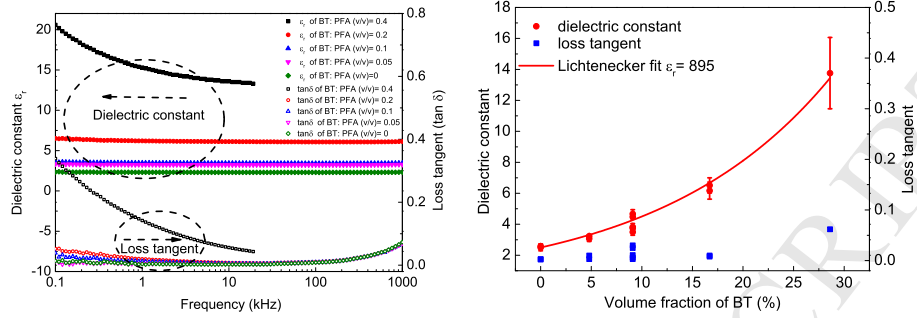


Figure 6: Dielectric measurements at low frequencies for PFA / BT composite films with varying volume ratios of barium titanate (left); dielectric constant and loss tangent of PFA / BT composite films at 10 kHz plotted against BT volume fraction and fitted using Lichtenecker equation (right)

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 (corresponding to BT volume percent of 9.1%), which might be related to the sedimentation effects during spraying as discussed before. Possible factors that might contribute to the reproducibility of 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 films. The Lichtenecker or logarithmic mixing law [22] shown in Equation 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 and ϵ_f was varied to achieve the best-fit.

$$\log \epsilon_{eff} = f \log \epsilon_f + (1 - f) \log \epsilon_m \quad (1)$$

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. It is worth mentioning that in addition to Lichtenecker mixing law, a few other common laws including Maxwell-Garnett, Bruggeman, Jayasundere-Smith, Ya-

mada were tried and the Lichtenecker mixing law was the only one that gave
 270 a converged fitting. The estimated dielectric constant for the BT nanometer
 sized particles based on the converged fitting was 895. This value is reasonable
 for this particle size in this frequency range compared to the normally quoted
 dielectric constant for bulk barium titanate of 2000 [1, 31], but higher than some
 other reported estimates: for example Cho et al. estimated 282 for 0.25 μm BT
 275 particles for epoxy/BT composites [17].

3.5. High frequency dielectric properties characterisation

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,
 280 but with residual layer boundaries visible after pressing which proved that the
 hot pressing method is adequate in producing reliable block samples. 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
 285 composites with various loadings are compared in Figure 7, and best-fitting of
 the data again using the Lichtenecker mixing law gave an estimated dielectric
 constant of the BT particles of 517. This simple pressing process could be
 readily applied to building graded-index layered structures for thermoplastic
 polymer-based composites.

290 A comparison of the dielectric constant 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 8. There was a significant difference in the dielectric constant of
 the composites in the low frequency and high frequency measurements, which is
 consistent with previous reports of bulk BT behaviour. The dielectric constant
 295 drop of PFA/BT composites at high and low frequencies could be related to the
 change in polarisation mechanisms. At low frequencies both atomic and dipolar
 polarisations contribute to the dielectric constant, whereas at high frequencies
 only atomic polarisation occurs [32]. It is thus understandable that there is a

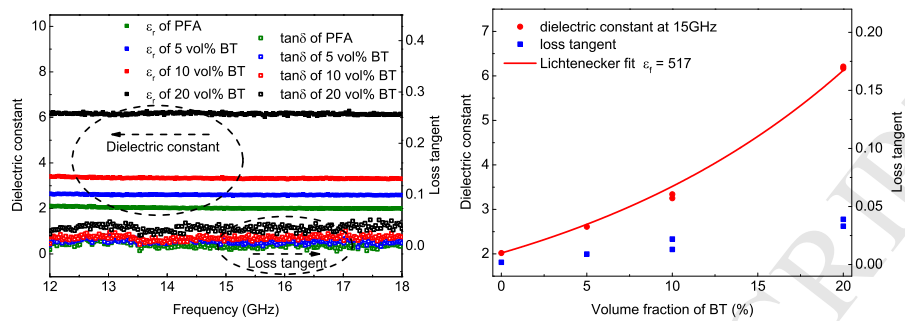


Figure 7: Dielectric measurements at high frequencies for PFA / BT composite blocks with varying volume ratios of barium titanate (left); dielectric constant and loss tangent of PFA / BT composite films at 15 GHz plotted against BT volume fraction and fitted using Lichtenecker equation (right)

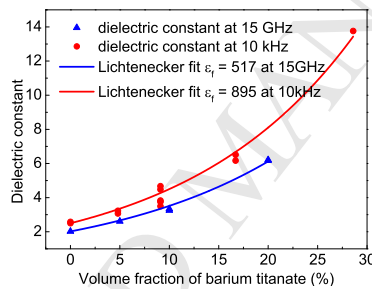


Figure 8: Comparison of low frequency and high frequency dielectric constants of sprayed PFA-BT composite films

reduction in dielectric constant of our composites by about 25% in the lower and
 300 higher frequency ranges. 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
 305 layers which averages out the sheet-to-sheet variations.

4. Conclusions

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
 310 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 particles in the different frequency ranges, and yielded 895 and 572 at 10 kHz and 15 GHz, respectively. These estimated dielectric constants are generally higher than other people's
 315 estimation from composite data using mixing rules. There was a reduction of about 25 % in the effective dielectric constant of the PFA / BT composites at high frequency measurements 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
 320 of high k materials are being developed.

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