

Effect of High Aspect Ratio Filler on Dielectric Properties of Polymer Composites: A Study on Barium Titanate Fibers and Graphene Platelets

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ABSTRACT

High aspect ratio fillers are predicted to increase the dielectric constant of polymer composites more efficiently than spherical fillers according to the rule of mixtures. Using high aspect ratio fillers is a promising route for creating high dielectric constant, low loss materials at a low filler volume fraction, for use as capacitor and electric field grading materials. In this work, two high aspect ratio fillers were mixed into a polymer matrix, and the dielectric properties of composites were studied. Barium titanate fibers were synthesized by electrospinning a sol-gel, followed by a heat treatment to obtain a perovskite crystal structure. The heat treatment conditions were found to be crucial for obtaining tetragonal barium titanate fibers with high dielectric constant. Graphene platelets were prepared by a thermal shock method, which was found to result in a larger dielectric constant. A combination of barium titanate and graphene platelets yielded the highest dielectric constant when used in a polydimethyl siloxane matrix. The increase in dielectric loss over the pure matrix was small when the volume fraction was below the percolation threshold of graphene platelets. Electric flux density-electric field (D-E) measurements showed a linear dielectric constant in barium titanate filled composites and higher loss when graphene was added. The ac breakdown strength was reduced compared to the neat polymer and was affected by filler aspect ratio. The mechanisms that lead to the observed phenomena are discussed.

Index Terms — Dielectric materials, dielectric breakdown, silicone rubber, permittivity

1 INTRODUCTION

FERROELECTRIC ceramic particles are widely used to increase the dielectric constant of polymer composites because of their high dielectric constant and low dielectric loss [1, 2]. However, the ability of spherical particles to increase the dielectric constant is small at low volume fractions according to the rule of mixtures [3]. Higher volume fractions lead to increased dielectric constant, but also to a reduction in electrical breakdown strength and mechanical properties [4-7]. Composites with high aspect ratio (AR) fillers are predicted to exhibit higher dielectric constant at lower loading [3], thereby potentially maintaining the mechanical properties and dielectric breakdown strength [5]. High aspect ratio fillers,

however, have not been studied as extensively as their spherical counterparts because of challenges in manufacturing high aspect ratio ferroelectric fillers [8, 9].

Electrospinning can afford barium titanate fibers with heat treatment [10-12]. The dielectric properties of these barium titanate fibers have, however, not been investigated. In order to create high dielectric constant BaTiO_3 , the tetragonal phase must be formed, which typically occurs at grain sizes larger than 100 nm [13-15]. In this work, a procedure to synthesize high dielectric constant tetragonal BaTiO_3 fibers with large grain size is presented. The dielectric properties of a polymer composite containing these BaTiO_3 fibers are investigated and discussed. By comparing the data with the theoretical prediction from the Maxwell Garnett rule of mixtures, the validity of the model to describe real composites can be illustrated. Also, the effect of filler aspect ratio on the

electrical breakdown strength is investigated and can be instructive for applications.

The alternative approach is to use conductive particles at a volume fraction close to the percolation threshold [16]. In this work, graphene platelet (GPL) was used to study the effect of high aspect ratio conductive fillers. Its plate like structure and high aspect ratio can lead to a very low percolation threshold. The dielectric behavior of three-phase-composites with both fillers was also studied at both low and high field strength.

2 EXPERIMENTAL

2.1 PREPARATION OF BARIUM TITANATE FIBERS

BaTiO₃ fibers were prepared by electrospinning a mixture that consisted of BaTiO₃ sol-gel and poly(vinyl pyrrolidone) (PVP, $M_w = 1,300,000$ grams/mol) solution [12]. Barium acetate (BaC₄H₆O₄, 5 mmol) was dissolved in acetic acid (3 ml). Then titanium isopropoxide (C₁₂H₂₈O₄Ti, 5 mmol) was added into solution under constant stirring. After that, a solution consisting of PVP (0.2g) and ethanol (3 ml) was added into the mixture. A clear pale yellow precursor was obtained by stirring the mixture. The precursor was loaded into a syringe for electrospinning. A positive voltage (16 kV) was applied on the needle tip of a syringe, and an aluminum foil was grounded as the counter electrode. The distance between the needle tip and the counter electrode was 25 cm, and the precursor was fed at a constant rate (30 μ l/min) by a syringe pump.

The electrospun BaTiO₃/PVP fibers had a diameter less than 1 μ m. The surface was smooth and the diameter was uniform along the fiber. Fibers were annealed in an oven at 500 °C for 12 h to remove the residual solvent and most of the PVP. They were then calcinated at high temperatures to crystallize. The high temperature treatment was optimized to develop large grains of tetragonal phase BaTiO₃ which possess a high dielectric constant [15], while avoiding sintering of the fibers. In the heat treatment process, different heating rates were used from 10 °C/min to larger than 2000 °C/min. The fast heating rate of larger than 2000 °C/min was achieved by inserting the sample into a preheated oven. The calcination temperature was varied between 600 °C to 1200 °C. The fibers were then cooled down to room temperature in air. During the above heat treatment, the PVP polymer was burned off which caused a reduction in the fiber diameter from 900 nm to approximately 500 nm, and a polycrystalline fibrous structure was obtained. Then the morphology and crystal structure of fibers were investigated. A scanning electron microscopy (SEM) picture of prepared BaTiO₃ fibers is shown in Figure 1a.

2.2 PREPARATION OF GRAPHENE PLATELET (GPL)

The GPLs were obtained with a one-step thermal exfoliation and reduction of graphite oxide. In this method, graphite oxide is subjected to a thermal shock (rapid heating at a rate of larger than 2000° C/min) which exfoliates and reduces the graphite oxide into GPL. The GPL are several micrometers in the in-plane dimension and are comprised of ~3-4 graphene sheets within each platelet. The total platelet

thickness is less than 2 nm. A transmission electron microscopy (TEM) picture of prepared GPL is shown in Figure 1b.

2.3 PREPARATION OF COMPOSITES

Sylgard 184 (Dow Corning), consisting of poly(dimethyl siloxane) (PDMS) and a reinforcing silica filler was used as the polymer matrix. The calcinated BaTiO₃ fibers were mixed into the precursor Sylgard 184A using a FlackTek Speed Mixer at 3000 rpm for 10 minutes. Long fiber (AR = 15) composites were obtained by direct mixing of the calcinated BaTiO₃ fibers with the precursor resin. Medium length (AR = 6) fiber composites were prepared by adding alumina balls during the mixing process to break the fibers into shorter pieces. Calcinated fibers were also crushed in a mortar and pestle to obtain low aspect ratio fibers (AR = 3). The aspect ratio of the fibers was calculated from the average length and diameter, measured from optical microscopy and SEM images respectively. Composites were then prepared by carefully mixing the precursors Sylgard 184A (containing the fibers) and Sylgard 184B (crosslinker) at a ratio of 10:1 by mass, followed by curing in a mould at 150 °C for 24 h. The composites filled with GPLs were prepared through the same procedure, except that a 20 minute mixing time was used. Planar samples with a diameter of 3.175 cm and a thickness of approximately 300 μ m were obtained. Prepared samples were dried in an oven at 120 °C for 12 h prior to dielectric testing to remove any trapped moisture. Optical microscopy images showing the dispersion of fillers in the composites are shown in Figures 1c and 1d. Three phase composites containing both fillers were prepared using the same approach.

2.4 CHARACTERIZATION

Thermogravimetric analysis (TGA) was carried out to determine the weight fraction of BaTiO₃ fibers in the composites, using a TA Instruments Q50 thermogravimetric

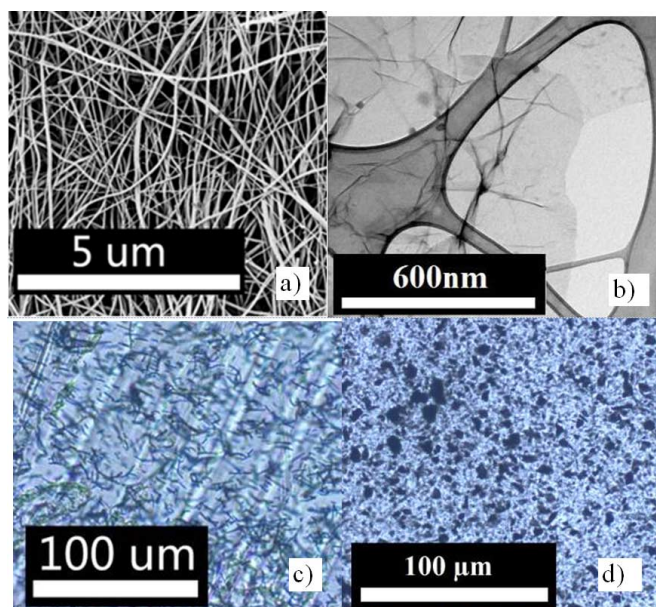


Figure 1. (a) SEM image of BaTiO₃ fibers; (b) TEM image of GPLs; (c) and (d) Optical microscope images showing dispersion of BaTiO₃ fibers and GPLs.

analyzer. Parameters from the literature and the manufacturer datasheet (BaTiO_3 density = 6.02 g/cm^3 , PDMS density = 1.03 g/cm^3) were used to calculate the filler volume fraction. The composite samples were tested in a Novocontrol alpha high resolution dielectric impedance analyzer for dielectric spectroscopy at room temperature. A frequency range from 10^{-1} to 10^6 Hz was utilized. AC breakdown tests were carried out at room temperature in dielectric oil (Dow Corning 561 silicone transformer fluid) at a frequency of 60 Hz. A voltage ramp rate of 200 V/s was used during the breakdown test. X-ray diffraction (XRD) 2θ scans were performed on a Bruker D8 Discover X-ray diffractometer to investigate the crystal structure. The morphology of the BaTiO_3 fibers was investigated using a Carl Zeiss Supra scanning electron microscope. Uncured composite was spin coated on a glass slide to align the fiber or GPLs along the glass slide plain. Then a stereo optical microscope was used to check the dispersion of fillers in composites as well as to measure the average fiber length. The electric flux density-electric field (D-E) measurement was taken in an ambient of dielectric mineral oil at 20°C following the ASTM standard D3487.

3 RESULTS AND DISCUSSION

3.1 SINTERING EFFECT ON THE CRYSTAL STRUCTURE OF BARIUM TITANATE FIBERS

The goal of the heat treatment is to obtain tetragonal phase BaTiO_3 because it has a higher dielectric constant than cubic phase BaTiO_3 , and the grain size has a major influence on the crystal structure [15, 17, 18]. The grain size of the BaTiO_3 fibers is affected by the heating rate. Figure 2a shows XRD patterns that illustrate the effect of calcination temperature on the crystal structure of the BaTiO_3 fibers. After calcination at a temperature above 800°C , the XRD pattern is consistent with the XRD data of BaTiO_3 in the literature [11]. Above 1000°C , the impurity phase (mainly BaCO_3) [12] was removed as indicated by the absence of peaks below $2\theta = 30^\circ$. The influence of the heating rate on the BaTiO_3 crystal structure is shown in Figure 2b. A low heating rate (10°C/min) resulted in a symmetric (200) peak confirming cubic symmetry. The cubic crystal structure is facilitated by the smaller grain size (see Figure 3b and 3c) [14]. The low heating rate inhibited the diffusion process during crystal formation, resulting in small grains with pores between them (Figure 3c). At a heating rate of 200°C/min the asymmetric peak shape indicates the appearance of the tetragonal crystal phase, as evidenced by a (002) peak, although the cubic phase is still dominant. A very fast heating rate (larger than 2000°C/min) resulted in larger grains, as shown in Figure 3a, as a result of the fast crystal growth rate compared to the nucleation rate. It resulted in complete splitting of the (200) and (002) peaks, which indicates that most of the crystals are tetragonal phase as shown in Figure 2b. This increase in grain size was mitigated when an annealing temperature higher than 500°C was used prior to the calcinations due to the initiation of nucleation during the annealing process. The adhesion between the fibers and the silicone rubber matrix was good as shown in Figure 3d which is an image from a fracture surface. The good adhesion is clear because of the lack of debonding between the fiber and matrix.

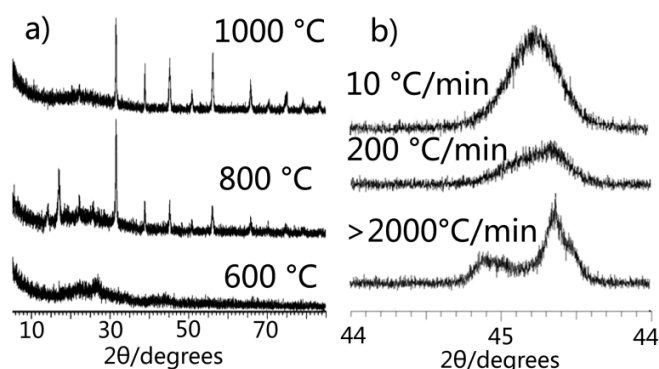


Figure 2. X-ray diffraction patterns of calcinated BaTiO_3 fibers a) influence of calcinations temperature; b) (200) and (002) peaks at $2\theta \sim 45^\circ$ for fibers subjected to different heating rates.

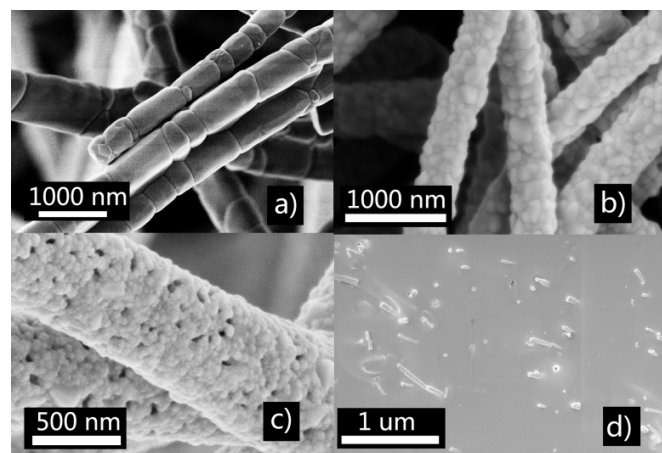


Figure 3. SEM images of BaTiO_3 fibers after different heat treatments: a) ramping rate: larger than 2000°C/min , calcinated during 5 min at 1200°C ; b) ramping rate: 200°C/min , calcinated during 120 min at 1000°C ; c) ramping rate: 10°C/min , calcinated during 120 min at 1000°C ; d) fractured surface of silicone rubber containing 1.6 vol. % BaTiO_3 fibers (AR = 15).

To optimize the formation of the high dielectric constant tetragonal phase while maintaining the fiber morphology, a rapid heating rate (larger than 2000°C/min) in combination with a short calcination step (5 min at 1200°C) was required. After the heat treatment, a polycrystalline bamboo-like structure was obtained as shown in Figure 3a. There is likely still some low dielectric constant cubic phase at the grain boundaries and surfaces due to a lack of constraint compared to the “ferroelectric core” in the bulk [14, 19], though the quantity is too small to be observed from the XRD data.

3.2 DIELECTRIC SPECTROSCOPY OF COMPOSITES FILLED WITH BARIUM TITANATE FIBERS

Dielectric spectroscopy (Figure 4a) shows an increased dielectric constant for the composites. Both the dielectric constant and loss factor increase with fiber aspect ratio and filler volume fraction, which is consistent with the rule of mixtures. The dielectric constant increased from 3 to 6.5 for the composites filled with 20 vol% of the lowest aspect ratio fibers (AR=3). The relative dielectric constant increase over the neat polymer is comparable to that of composites filled with spherical or irregular BaTiO_3 particles reported in the

literature [4-6]. Meanwhile, the high aspect ratio fiber (AR=15) leads to a significant increase in the composite relative dielectric constant to 12. The loss factor of all the tested composites is below 0.006, only an order of magnitude higher than that of the neat polymer. In the literature, 20 vol% of BaTiO₃ particles usually double the dielectric constant of pure polymer, which is similar to the effect of the lowest aspect ratio fiber in this work [4, 5, 20, 21].

The dielectric constant of composites with randomly orientated ellipsoidal fillers can be described by the Maxwell-Garnett expression [3]

$$\varepsilon_{eff} = \varepsilon_e + \varepsilon_e \frac{\frac{f}{3} \sum_{j=x,y,z} \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_e + N_j(\varepsilon_i - \varepsilon_e)}}{1 - \frac{f}{3} \sum_{j=x,y,z} \frac{N_j(\varepsilon_i - \varepsilon_e)}{\varepsilon_e + N_j(\varepsilon_i - \varepsilon_e)}} \quad (1)$$

Where ε_{eff} is the dielectric constant of the composite, ε_i and ε_e are the dielectric constants of the filler and matrix respectively, f is the filler volume fraction and N_j is the depolarization factor of ellipsoids in the x, y and z direction. For needle shaped fillers, where the radii $a_x > a_y = a_z$, a simple expression of N_j is

$$N_j = (\ln((1+e)/(1-e)) - 2e)(1-e^2)/2e^3 \quad (2)$$

$$e = \sqrt{1 - a_y^2/a_x^2} \quad (3)$$

The data is compared with the Maxwell-Garnett model due to the similarity of the filler geometry. In the literature the reported dielectric constant of BaTiO₃ ranges from 1000 to 5000 [15, 18] when the grain size is larger than 200 nm. Although the actual dielectric constant of the BaTiO₃ fiber is unknown, the change in composite dielectric constant is very small when the filler dielectric constant increases from 1000 to 5000 according to equation (1). For example, when changing the filler dielectric constant from 1000 to 5000, the composite dielectric constant increases from 5.39 to 5.47 in a 10 vol% composites with a filler AR of 5. A dielectric constant of 1000 is assumed for BaTiO₃ fibers in the fitting using equation (1), and a comparison between the experimental data and fitting is shown in Figure 4b. The fitting gives effective ARs of 3, 5, and 8 for the fibers that have measured ARs of 3, 6, and 15, respectively. The difference between the fitting and the actual AR is larger as the filler AR increases.

The Maxwell Garnett equation is usually accurate at low filler volume fraction. However, there are three major differences between the model and the real composite. First, real fibers have curvature. High AR fillers have a larger tendency to curve in the composite, which explains the drop of the effective AR. Secondly, the polydispersity of the fiber aspect ratio may affect the dielectric constant. Although no literature was found to describe the effect of AR polydispersity on the mixing rules, it is possible that the higher AR fibers are affected more than their low AR counterparts. Finally, high AR fillers have more grain boundaries in their bamboo structure. These low dielectric constant grain boundaries separate the high dielectric constant fiber into many lower aspect ratio sections. The segment length is the same for all the fibers, however, the stronger alignment of the segments in the high AR fibers can give an “effective aspect

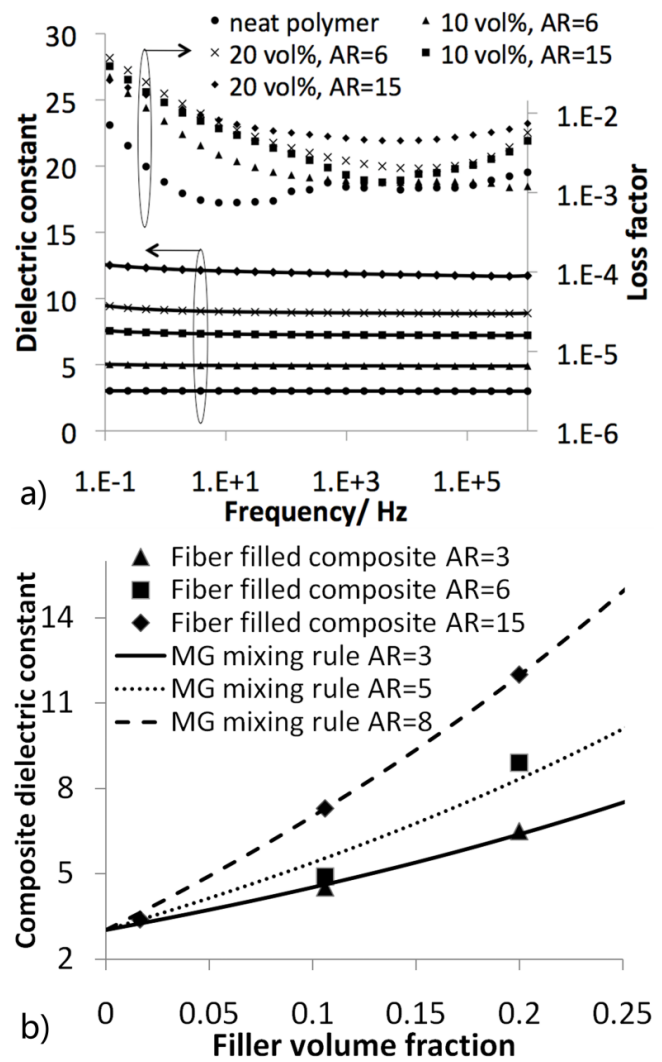


Figure 4. a) Dielectric spectroscopy of BaTiO₃ fiber/ silicone rubber composites and b) Experimental data compared to Maxwell-Garnett rule of mixtures for different aspect ratios.

ratio” that is larger than that in the low AR ones, but smaller than the actual AR. For the reasons stated above, the Maxwell-Garnett equation cannot predict the dielectric constant of composites with high aspect ratio fillers potentially due to the curvature, the AR polydispersity and the polycrystallinity.

3.3 DIELECTRIC CONSTANT OF COMPOSITES FILLED WITH GRAPHENE PLATELETS

The dielectric constant and dissipation factor of composites filled with GPLs are shown in Figure 5. Both the dielectric constant and dissipation factor exhibit a large increase at a small volume fraction of GPLs. The sheet morphology and high aspect ratio of GPLs lead to a low percolation threshold of less than 0.01 in volume fraction. The large dissipation factor above the percolation threshold is caused by the leakage current. The high dielectric constant can be explained by percolation theory [22], which describes the critical behavior of composites when the volume fraction of conductive fillers approaches the percolation threshold. However, a large dissipation factor is usually not desired in electrical applications.

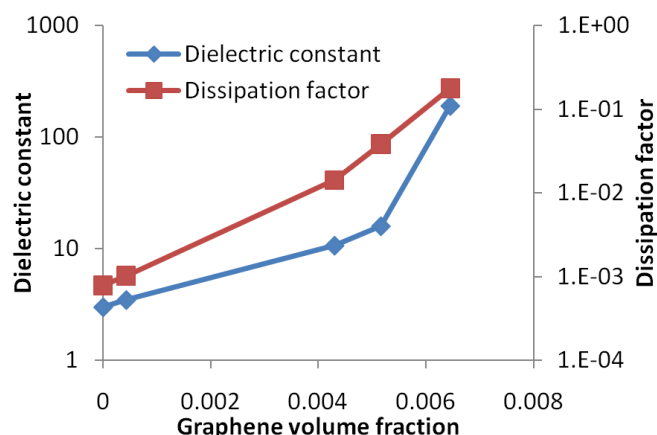


Figure 5. Dielectric constant and dissipation factor of composites filled with various volume fractions of GPLs. The testing frequency is 60 Hz.

High aspect ratio conductive fillers such as carbon nanotubes [23] and carbon fibers [24] have been used to prepare high dielectric constant composites. The rule of mixtures predicts that 2-dimensional GPLs will increase the dielectric constant at even a lower volume fraction due to their sheet structure and high aspect ratio. The dielectric properties of graphene-filled composites were not reported until recently [25]. In our work, the GPLs prepared by the thermal shock method have a smaller thickness, and thus the percolation was reached at a lower volume fraction.

3.4 DIELECTRIC SPECTROSCOPY OF COMPOSITES FILLED WITH BOTH FILLERS

A GPL volume fraction of 0.0043 was chosen for the three-phase composite with both fillers. At this loading, the dielectric constant is improved with only a moderate increase in the dissipation factor. The dielectric spectroscopy of several representative composites is shown in Figure 6. The slope in the loss factor is small indicating little contribution from the conduction current. The relative dielectric constant increase over the neat polymer is significantly larger than that of the composites filled with spherical fillers. The increase in dielectric constant of the composites is summarized in Fig. 7. By adding 0.43 vol% of GPLs into the BaTiO₃ fiber/PDMS composites, the dielectric constant was further increased to 13.7 and 18.6 for 10 vol% and 20 vol% BaTiO₃ fiber composites respectively.

The dissipation factor of the composites is shown in Fig. 6b. The dissipation factor of the composites is about one order of magnitude higher than that in the neat PDMS. Generally the dielectric loss increases with the volume fraction of fibers and the GPLs. Adding 0.43 vol% of GPLs into the BaTiO₃ fiber composites results in an increased dissipation factor that is, however, not higher than the pure GPL/PDMS composites. By combining the two types of fillers, the three-phase composite shows a larger dielectric constant than either of the two-phase composites without a further increase in loss factor.

In the three-phase composites reported in the literature [24, 26, 27], a combination of conductive fillers and high dielectric constant ceramic fillers is generally used. Considering the ceramic-polymer composite as the base matrix, percolation theory is applicable when adding conductive fillers. By using

high aspect ratio ceramic fillers to increase the dielectric constant of the base matrix, the dielectric constant of the final composites is further enhanced while maintaining a low filler volume fraction.

3.5 D-E MEASUREMENT

The high voltage behavior of materials was investigated through D-E measurements. Both BaTiO₃ fiber composites and three-phase composites were tested under several field conditions below the breakdown strength of materials. Figure 8 shows the results for each composite under the highest measured field.

The relative permittivity was calculated using an approach found in the literature [28]. The real dielectric constant for composites is listed in Table 1. From the literature, ferroelectric ceramics such as barium titanate usually exhibit a nonlinear dielectric constant. Depending on the microstructure and crystal morphology, the dielectric constant of barium titanate can either increase [29] or decrease [30] with increasing field strength. In our result, however, the dielectric constant remains unchanged at elevated electrical field. The difference between the one-phase ceramics and the composites

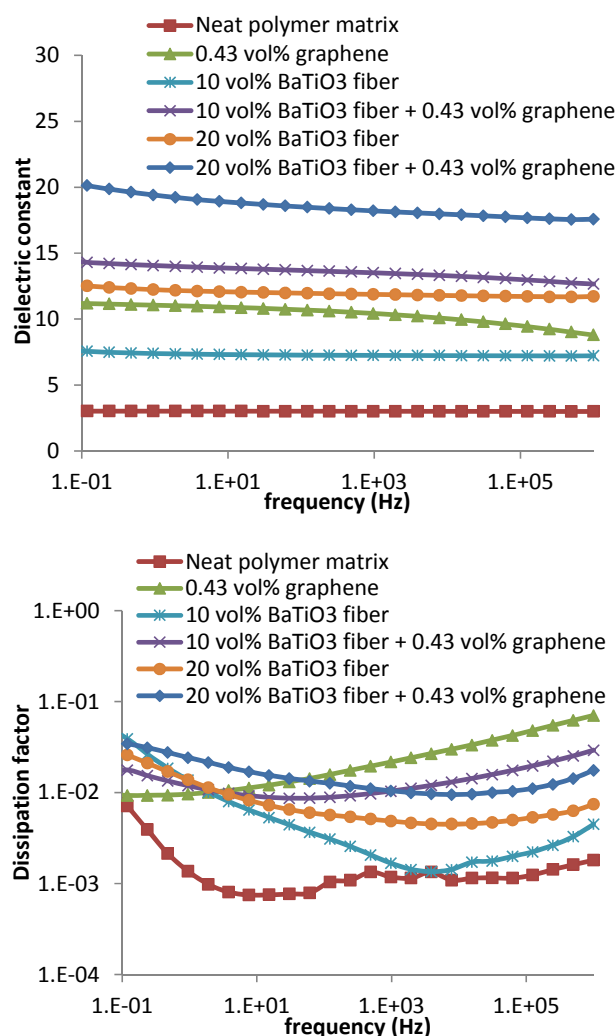


Figure 6. Dielectric spectroscopy at 60 Hz of composites filled with BaTiO₃ fibers and GPLs, showing (a) permittivity and (b) loss factor.

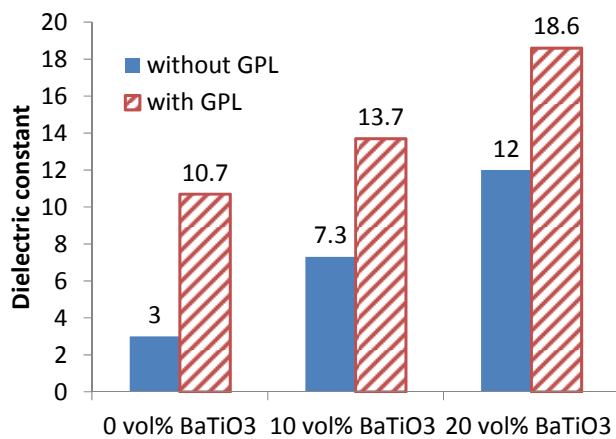


Figure 7. Dielectric constant at 60 Hz of composites filled with various volume fractions of BaTiO₃ fibers, with and without addition of GPLs.

is attributed to the field distribution in the composites. The large dielectric constant of BaTiO₃ fibers leads to a field concentration in the polymer phase and reduced electric field in the ceramics. When the field in the ceramics is less than the “threshold field” [29], a linear dielectric constant is expected.

The degree of hysteresis is more pronounced at higher field. The three-phase composite also has a larger loop area, compared to the BaTiO₃ composite. It indicates a higher dielectric loss, which matches with the dielectric spectroscopy data under low field conditions.

Table 1. Real Relative Permittivity of Composites at Elevated Field.

ac field (kV/mm)	20 vol% BaTiO ₃ fibers	20 vol% BaTiO ₃ fibers +0.43 vol% GPLs
Low field ^a	12	18.6
2	11.9	17.5
5	11.7	18.1
7.5	11.8	-

^aThe value of low field (about 3 V/mm) dielectric constant is from the dielectric spectroscopy measurement.

3.6 AC BREAKDOWN STRENGTH

The ac breakdown strength of both BaTiO₃ fiber/PDMS composite and GPL/PDMS composite is shown in Figure 9. For the fiber composites, it decreases with increasing fiber volume fraction and fiber aspect ratio. The breakdown strength of GPL composite is even lower than the lowest of the BaTiO₃ fiber composites. This effect can be explained by the stress concentration at the interfaces between the fillers and the polymer matrix. When the high dielectric constant or high conductivity fillers are added into the polymer, the electrical field in the polymer around the fillers is much larger than that in the bulk. The most stressed part should be close to the fiber tips or the edge of GPLs and the local stress should increase with filler aspect ratio. Breakdown is more likely to be initiated at these highly stressed regions than in the bulk polymer, so a reduction in the overall breakdown strength is expected. The other candidate mechanism, defects at the filler-polymer interface, can be eliminated considering the good adhesion between the fiber and polymer as shown before. Also the number of defects is not likely to be proportional

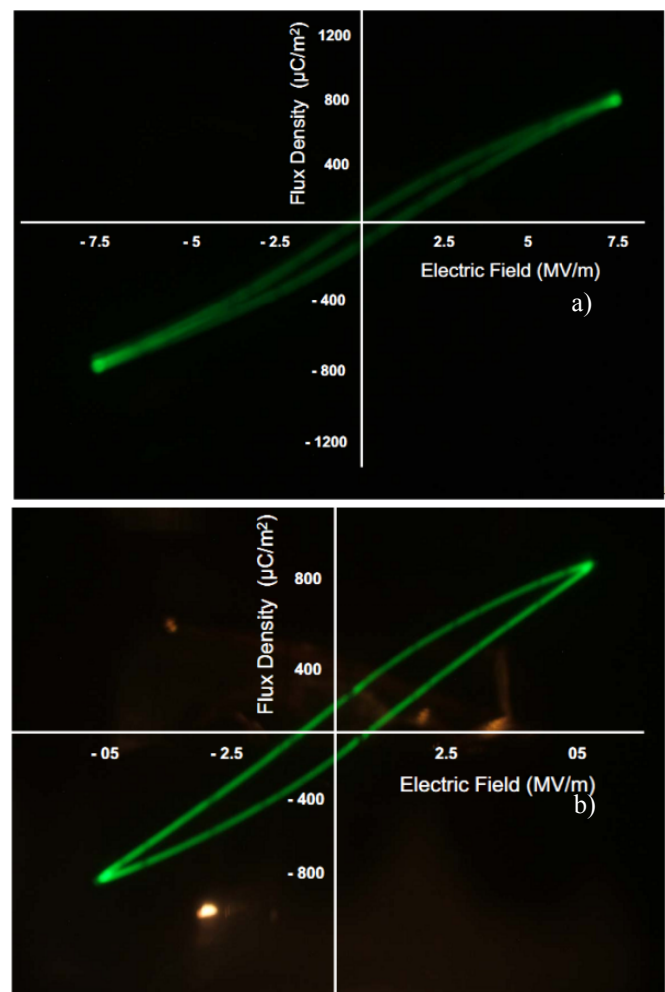


Figure 8. D-E measurement of (a) 20 vol% BaTiO₃ fibers composite and (b) 20 vol% BaTiO₃ fibers+0.43vol% graphene filled composite. Note the scale difference of the applied electric fields.

to filler aspect ratio at certain filler volume fraction. At higher filler volume fraction, the electrical stress concentration is more severe and the probability of finding

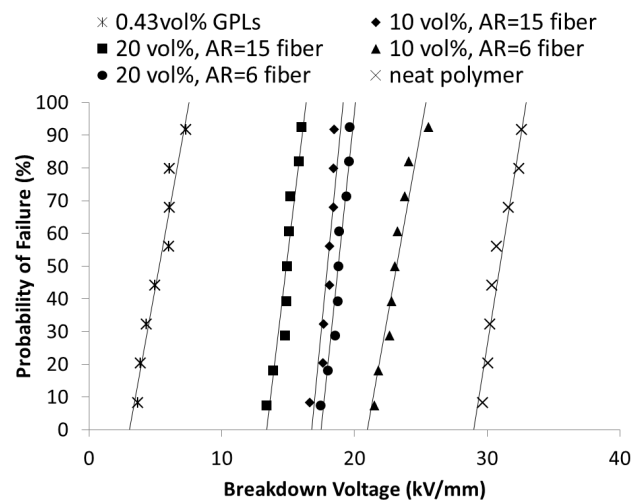


Figure 9. Probability of failure in dielectric breakdown tests from the Weibull distribution of neat PDMS, BaTiO₃ fiber/ PDMS composites and GPLs/PDMS composites

an enhanced local field is larger in the polymer matrix [31]. So the breakdown strength also reduces with increasing filler volume fraction. The breakdown strength of the GPL composite is lower than all the BaTiO₃ fiber composites, which can also be attributed to the higher aspect ratio and conductivity of GPLs and their sheet morphology. Note that the volume fraction of the tested GPL composite is below the percolation threshold, which should not raise the tendency for thermal runaway compared to the BaTiO₃ fiber composites. Consequently, the stress concentration is still the dominating mechanism.

SUMMARY AND CONCLUSION

A method to synthesize high dielectric constant, high aspect ratio BaTiO₃ fibers by electrospinning and a subsequent heat treatment is reported. A high heating rate was found to be the key to preparing the desired tetragonal phase of BaTiO₃ while still maintaining the fiber morphology. Higher aspect ratio BaTiO₃ fibers were found to increase the composite dielectric constant by more than a factor of two, compared to correspondingly shorter fibers or spherical particles, in combination with a very moderate increase in the loss factor. The rule of mixtures failed to predict the high aspect ratio fillers due to their curvature, polycrystallinity and AR polydispersity.

The GPLs alone can increase the dielectric constant at a very low filler volume fraction. However, the loss increased dramatically when the loading reached the percolation threshold. By combining those two fillers and avoiding the percolation of GPLs, the highest dielectric constant was reached without further increasing the dissipation factor. The dielectric constant remains unchanged under high voltage since the field in the ferroelectric ceramic filler is lower than the threshold field for non-linearity. The reduction in breakdown strength was attributed to the stress concentration at the fiber tips.

This method can be potentially used to prepare mechanically robust, high dielectric constant/ low loss composite materials for various electrical applications.

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REFERENCES

- [1] Y. Rao, S. Ogitani, P. Kohl, and C. P. Wong, "Novel polymer-ceramic nanocomposite based on high dielectric constant epoxy formula for embedded capacitor application", *J. Appl. Polym. Sci.*, Vol. 83, pp. 1084-1090, 2002.
- [2] G. Subodh, V. Deepu, P. Mohanan, and M. Sebastian, "Dielectric response of high permittivity polymer ceramic composite with low loss tangent", *Appl. Phys. Lett.*, Vol. 95, pp. 062903-062903, 2009.
- [3] A. Sihvola and E. Alanen, "Studies of mixing formulae in the complex plane", *IEEE Trans. Geosci. Remot. Sens.*, Vol. 29, pp. 679-687, 2002.
- [4] Y. Bai, Z.-Y. Cheng, V. Bharti, and H. Xu, "High-dielectric-constant ceramic-powder polymer composites", *Appl. Phys. Lett.*, Vol. 76, pp. 3804-3806, 2000.
- [5] K.-C. Cheng, C.-M. Lin, S.-F. Wang, S.-T. Lin, and C.-F. Yang, "Dielectric properties of epoxy resin-barium titanate composites at high frequency", *Mater. Lett.*, Vol. 61, pp. 757-760, 2007.
- [6] S. Cho, J. Lee, J. Hyun, and K. Paik, "Study on epoxy/BaTiO₃ composite embedded capacitor films (ECFs) for organic substrate applications", *Mater. Sci. Eng. B*, Vol. 110, pp. 233-239, 2004.
- [7] T. Hu, J. Juuti, H. Jantunen, and T. Vilkman, "Dielectric properties of BST/polymer composite", *J. Eur. Ceram. Soc.*, Vol. 27, pp. 3997-4001, 2007.
- [8] N. Guo, S. DiBenedetto, and P. Tewari, T. J. Marks "Shape, and Interfacial Effects on Leakage Current Density, Permittivity, and Breakdown Strength of Metal Oxide - Polyolefin Nanocomposites: Experiment and Theory", *Chem. Mater.*, Vol. 22, pp. 1567-1578, 2010.
- [9] L. F. Chen, Y. P. Hong, X. J. Chen, Q. L. Wu, Q. J. Huang, and X. T. Luo, "Preparation and properties of polymer matrix piezoelectric composites containing aligned BaTiO₃ whiskers", *J. Mater. Sci.*, Vol. 39, pp. 2997-3001, 2004.
- [10] D. Li, J. T. McCann, Y. Xia, and M. Marquez, "Electrospinning: A Simple and Versatile Technique for Producing Ceramic Nanofibers and Nanotubes", *J. Am. Ceram. Soc.*, Vol. 89, pp. 1861-1869, 2006.
- [11] J. McCann, J. Chen, D. Li, Z. Ye, and Y. Xia, "Electrospinning of polycrystalline barium titanate nanofibers with controllable morphology and alignment", *Chem. Phys. Lett.*, Vol. 424, pp. 162-166, 2006.
- [12] J. Yuh, J. Nino, and W. Sigmund, "Synthesis of barium titanate (BaTiO₃) nanofibers via electrospinning", *Mater. Lett.*, Vol. 59, pp. 3645-3647, 2005.
- [13] M. Leonard and A. Safari, "Crystallite and grain size effects in BaTiO₃", *Proceedings of the Tenth IEEE International Symposium on Applications of Ferroelectrics*, Vol. 2, pp. 1003-1005, 1996.
- [14] K. Uchino, E. Sadanaga, and T. Hirose, "Dependence of the Crystal Structure on Particle Size in Barium Titanate", *J. Am. Ceram. Soc.*, Vol. 72, pp. 1555-1558, 1989.
- [15] S. Wada, H. Yasuno, T. Hoshina, S. M. Nam, H. Kakemoto, and T. Tsurumi, "Preparation of nm-Sized Barium Titanate Fine Particles and Their Powder Dielectric Properties", *Jpn. J. Appl. Phys.*, Vol. 42, pp. 6188, 2003.
- [16] C. Pecharróman and J. S. Moya, "Experimental Evidence of a Giant Capacitance in Insulator-Conductor Composites at the Percolation Threshold", *Adv. Mater.*, Vol. 12, pp. 294-297, 2000.
- [17] D. Kuo, "Dielectric behaviours of multi-doped BaTiO₃/epoxy composites", *J. Eur. Ceram. Soc.*, Vol. 21, pp. 1171-1177, 2001.
- [18] T. Takeuchi et al., "Grain size dependence of dielectric properties of ultrafine BaTiO₃ prepared by a sol-crystal method", *J. Mater. Sci.*, Vol. 32, pp. 4053-4060, 1997.
- [19] F. S. Yen, H. I. Hsiang, and Y. H. Chang, "Cubic to tetragonal phase transformation of ultrafine BaTiO₃ crystallites at room temperature", *Jpn. J. Appl. Phys.*, Vol. 34, pp. 6149, 1995.
- [20] R. Popielarz, C. K. Chiang, R. Nozaki, and J. Obrzut, "Dielectric Properties of Polymer/Ferroelectric Ceramic Composites from 100 Hz to 10 GHz", *Macromolecules*, Vol. 34, pp. 5910-5915, 2001.
- [21] Y. Kobayashi, A. Kurosawa, D. Nagao, and M. Konno, "Fabrication of barium titanate nanoparticles-polymethylmethacrylate composite films and their dielectric properties", *Polym. Eng. Sci.*, Vol. 49, pp. 1069-1075, 2009.
- [22] A. Efros and B. Shklovskii, "Critical behaviour of conductivity and dielectric constant near the metal-non-metal transition threshold", *Phys. Status Solidi B*, Vol. 76, pp. 475-485, 1976.
- [23] C. Yang, Y. Lin, and C. W. Nan, "Modified carbon nanotube composites with high dielectric constant, low dielectric loss and large energy density", *Carbon*, Vol. 47, pp. 1096-1101, 2009.
- [24] Z. Dang, "Study on dielectric behavior of a three-phase CF/(PVDF+BaTiO₃) composite", *Chem. Phys. Lett.*, Vol. 369, pp. 95-100, 2003.
- [25] J. Yu, X. Huang, C. Wu, and P. Jiang, "Permittivity, thermal conductivity and thermal stability of poly (vinylidene

fluoride)/graphene nanocomposites", IEEE Trans. Dielectr. Electr. Insul., Vol. 18, pp. 478–484, 2011.

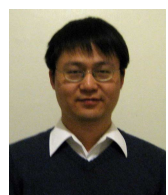
- [26] Z.-M. Dang, Y. Shen, and C.-W. Nan, "Dielectric behavior of three-phase percolative Ni–BaTiO₃/polyvinylidene fluoride composites", Appl. Phys. Lett., Vol. 81, pp. 4814, 2002.
- [27] L. Qi, B. I. Lee, W. D. Samuels, G. J. Exarhos, and S. G. Parler, "Three-phase percolative silver–BaTiO₃–epoxy nanocomposites with high dielectric constants", J. Appl. Polym. Sci., Vol. 102, pp. 967–971, 2006.
- [28] J. Robertson and D. Hall, "Nonlinear dielectric properties of particulate barium titanate–polymer composites", J. Phys. D: Appl. Phys., Vol. 41, pp. 115407, 2008.
- [29] D. Hall, "Review nonlinearity in piezoelectric ceramics", J. Mater. Sci., Vol. 36, pp. 4575–4601, 2001.
- [30] L. Curecheriu, M. T. Buscaglia, V. Buscaglia, Z. Zhao, and L. Mitoseriu, "Grain size effect on the nonlinear dielectric properties of barium titanate ceramics", Appl. Phys. Lett., Vol. 97, pp. 242909, 2010.
- [31] J. P. Calame, "Finite difference simulations of permittivity and electric field statistics in ceramic-polymer composites for capacitor applications", J. Appl. Phys., Vol. 99, pp. 084101, 2006.



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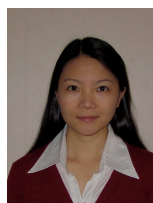


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