Matrix Effects on Tubule Distribution and Dielectrics Properties of Tubule-Based Dielectrics

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ABSTRACT: The dielectric properties of composites containing copper-coated tubules in epoxy and polyurethane were characterized and interpreted in terms of contact angle and interfacial tension between the filler and the polymer matrix. The polyurethane samples had larger permittivity values than the epoxy samples over the entire tubule concentration range. The results suggested the tubules in polyurethane were more aggregated than those in epoxy and, consequently, the polyurethane samples were closer to percolation. This was inconsistent with the contact angle and interfacial tension data, because epoxy had larger contact angles and interfacial tension than polyurethane. Therefore, the contact angle and interfacial tension data could not be used to predict tubule distribution in composites. Also, the De Loor model provided a good fit to the permittivity data. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 53–57, 2005

Key words: biomaterials; composites; dielectric properties; surface energy; percolation

INTRODUCTION

Previous studies on polymer composites had shown that the polymer matrix could dramatically influence the filler distributions. In several studies involving carbon black composites,[1,2] the surface tension of the polymer matrix, and consequently, the interfacial tension between matrix and carbon black, had a large effect on the percolation threshold concentration. At the percolation concentration, the fillers form a sample-spanning network and the sample changes from an insulator to a conductor. The authors in the studies found that using polymer matrices with lower surface tensions can reduce the percolation concentration. A matrix with a surface tension of 30 dyn/cm had a percolation concentration of 0.04 filler volume fraction, whereas a matrix with a surface tension of 46 dyn/cm had a percolation concentration of 0.27 filler volume fraction.[1] The authors also determined that carbon black had a high surface tension of ~ 55 dyn/cm. Small differences in surface tensions between filler and matrix imply low interfacial tension. For such a case, interactions between the filler and polymer matrix should be favorable, resulting in more wetting of the filler by the polymer. Consequently, the fillers become more dispersed and the sample has a higher percolation threshold concentration. In contrast, large differences in surface tensions between filler and matrix imply high interfacial tension. For such a case, the interactions between filler and matrix become less favorable. This results in closer contact between fillers, leading to the sample having a lower threshold concentration. The authors of these studies proposed a model relating the percolation threshold concentration to the polymer–filler interfacial tension and the filler geometry.[1] Subsequently, the authors incorporated the effect of polymer viscosity into the model.[2,3] In addition, another group also proposed a model relating the percolation threshold concentration to the interfacial tension between polymer and filler.[3,4]

In a previous study involving tubule composites,[5] we found that varying the polymer matrices' surface tensions, and consequently, the interfacial tension between tubule and matrix, had no effect on the dielectric properties of the samples. For tubule composites, the permittivity had been shown to change rapidly as the tubule loading approached the percolation threshold concentration. In the study, we varied the interfacial tensions between the tubules and the polymer matrices from 0.8 to 16.8 mJ/m^2 and varied the tubule concentration from 6 to 14 vol %, with respect to monomers. We determined that, for a specific tubule concentration, all the samples had comparable permittivity values. This indicated the polymer matrix did not sufficiently affect the tubule distribution enough to alter the sample's permittivity value.

In this study, we expand on the previous study[5] by examining the effects of using polyurethane and epoxy matrices on the dielectric properties of composites containing copper-coated tubules. We measure the contact angles between the polymerizing matrices and copper as well as calculate the interfacial tensions between the fully cured matrices and copper. We then interpret the permittivity results in terms of the contact angle and interfacial tension data.

EXPERIMENTAL

Sample preparation

Two types of polymer matrices were used to produce the tubule composites. The first was a commercial polyurethane product, LS-30, from BJB Enterprises (Tustin, CA). This consisted of a two-component system that cured at room temperature. Part A contained a polyurethane prepolymer resin, polyoxypropylene glycol polyol, 1,3-diisocyanatomethylbenzene terminated, whereas Part B contained a glycol and aromatic diamine solution in plasticizer. The two parts were mixed in a ratio of 45 parts by weight of A to 100 parts by weight of B. The second matrix was a commercial epoxy system. This consisted of the three following parts: Epon 815 from Shell (Tustin, CA), C3140 from Shell (Danbury, CT), and DER 736 from Electron Microscopy Sciences (Ft. Washington, PA). Epon 815 contained 86.5% of a bisphenol A/epichlorohydrin resin and 13.5% of n-butyl glycidyl ether. C3140 contained $\sim$ 84% of a dimer fatty acid polyamide and 16% of triethylenetetramine. DER 736 consisted of an epichlorohydrin–polyglycol product. The three parts were mixed in a 25 wt % Epon 815/50 wt % C3140/25 wt % DER 736 ratio.

The production of the tubules was described in previous publications.[6–9] In short, they were produced by first mixing a phospholipid, 1,2-bis(tricosa-10,12-dinoyl)-sn-glycero-3-phosphocoline, in an ethanol/water solution. The solution was slowly cooled until the phospholipid formed hollow cylindrical tubules at $\sim$ 40°C. The tubules were then coated with palladium, a metal plating catalyst. Finally, the tubules were coated with copper through a commercial electroless plating process. The tubules had an average diameter of 1 μm and an average length of 30 $\pm$ 22 μm.

All the tubule composite samples were produced in a similar way. The components of the polymer matrices and the tubules were added together all at once. The sample was mixed for several minutes before being placed between two aluminum plates. A 50-mil spacer was also placed between the plates to ensure the sample had the requisite thickness. The two plates were then clamped together and the sample was allowed to cure at room temperature for 24 h. After this point, the curing schedules for the polyurethane and epoxy samples became different. The polyurethane samples were placed in an N_2 filled box for at least one more week for further curing. On the other hand, the epoxy samples were placed in an oven and cured for an additional 24 h at 60°C. They were then taken out of the oven and placed in the N_2 filled box. The epoxy samples were allowed to cure for at least one more week at room temperature before any experiments were performed on them.

Contact angle measurements and surface tension calculations

Surface tension values of the epoxy, polyurethane, and copper foil were determined by performing contact angle measurements with a video contact angle system (VCA 2500, AST Products, Billerica, MA) using three test liquids. The copper foil (Pirelli Cables) was used as a model for the surface of the copper-coated tubules. The test liquids for contact angle measurements included triple-distilled water, formamide, and methylene iodide. Sessile drops containing 2 μL water, 2 μL formamide, and 1 μL methylene iodide were used in the measurements. Both the formamide and the methylene iodide were obtained from Sigma-Aldrich (Milwaukee, WI). The test liquid was initially placed on the sample's surface. A picture of the drop was taken after 10 s and the contact angle was then determined by using the instrument software. Once the contact angles were measured, the surface tension of the polymers and copper foil can be determined by using the harmonic mean method. The surface tension includes dispersion and polar components, which can be calculated by using[10]

$$\gamma_l(1+\cos\theta)=4\left(\frac{\gamma_l^d\gamma_s^d}{(\gamma_l^d+\gamma_s^d)}+\frac{\gamma_l^p\gamma_s^p}{(\gamma_l^p+\gamma_s^p)}\right) \qquad (1)$$

where γ_l is the test liquid's total surface tension, θ is the contact angle, γ_l^d is the test liquid's dispersion component of the total surface tension, γ_s^d is the sample's dispersion component of the total surface tension, γ_l^p is the test liquid's polar component of the total surface tension, and γ_s^p is the sample's polar component of the total surface tension. By using two test liquids with known surface tensions, the surface tension components of the sample can be calculated from eq. (1). This calculation was performed by using the instrument software.

The contact angles of the epoxy and polyurethane samples on copper foil during the curing process were measured by using the same video contact angle system. A drop of the sample was placed on the copper foil at a specific cure time. A picture of the sessile drop was taken and the contact angle was determined by using the instrument software.

Dielectric measurements

A vector network analyzer (Hewlett–Packard HP8510, Palo Alto, CA) was used to measure the dielectric properties of the samples over a frequency range of 2–18 GHz. Each sample, $\sim$ 1.3 mm thick and 7 mm in diameter, was placed in a coaxial measurement fixture. Their *S*-parameters were measured and the Nicolson and Ross approach was used to calculate the permittivity values.

RESULTS AND DISCUSSION

For all samples, the real part of the permittivity had a larger value than the imaginary part of the permittivity. This is shown in Figure 1 for a typical plot of the real and imaginary parts of the permittivity as a function of frequency. The sample in Figure 1 contains 18 vol % tubules in LS-30. In a previous study on tubule composites over the same frequency range as this study,[11] both the real and the imaginary parts of the permittivity were found to increase dramatically in value as the tubule loading approached the percolation threshold concentration in a vinyl composite. Above the percolation concentration, the imaginary part had a larger value than the real part of the permittivity. The much larger real part of the permittivity in Figure 1 indicated the sample had not reached percolation. Because this sample contained the highest tubule concentration in the study, all the other samples should also have tubule concentrations below the percolation threshold concentration.

The polyurethane composites had higher permittivity values than the epoxy composites for each tubule concentration. This is shown in Figure 2, where we plot the real part of the permittivity at 10 GHz as a
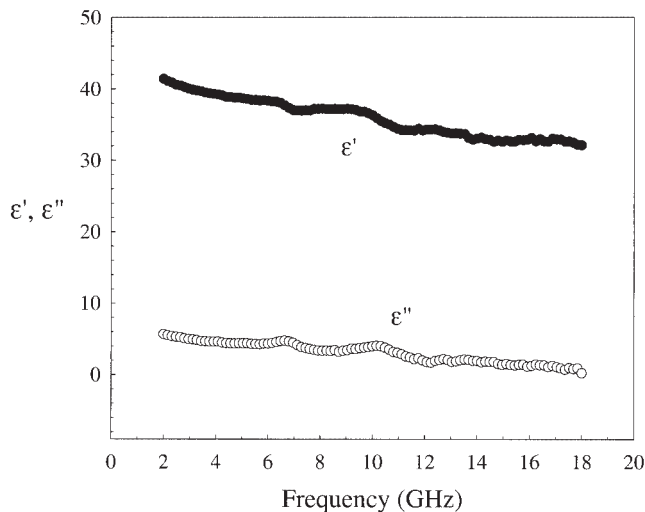
Figure 1 Typical plot of real and imaginary parts of permittivity as a function of frequency. The sample contains 18 vol % tubules in LS-30 matrix.
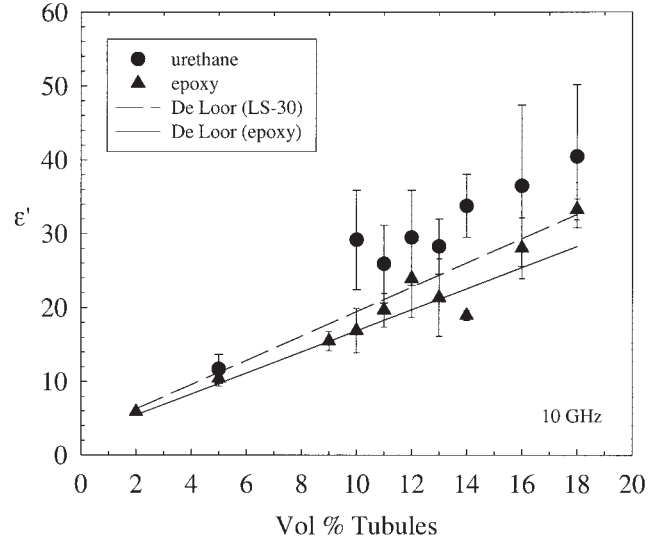
Figure 2 The real part of the permittivity as a function of tubule concentration for the polyurethane and epoxy samples. Also shown are the De Loor model predictions. The frequency is 10 GHz.

function of tubule concentration for the various samples. We decided to compare the permittivities at a frequency of 10 GHz because all the samples had relatively constant real parts of the permittivity over the entire frequency range. From Figure 2, we see that, at lower tubule loadings, both polyurethane and epoxy samples had comparable permittivities. However, at higher tubule loadings, the polyurethane samples consistently had greater permittivity values.

We can compare the experimental permittivity data to a model that predicts the permittivity as a function of filler loading and geometry. De Loor[12,13] developed one such model for a composite with a dielectric matrix and spheroid conductors as fillers. In this model, the complex permittivity of the composite, ε, can be determined by[12,13]

$$\varepsilon = \varepsilon_1 \left[1 + \frac{1}{3} v_2 \sum_{i=a,b,c} \frac{1}{A_i} \right] \tag{2}$$

where ε_1 is the complex permittivity of the matrix, v_2 is the filler volume fraction, and A_i is the depolarization factor along the *a*, *b*, and *c* axes of the spheroid. For this model, it is assumed that the permittivity of the medium immediately surrounding the filler is equal to that of the matrix. Therefore, this model applies to composites with lower filler loadings. For prolate (needlelike) spheroids, similar to the tubules, where $a > b = c$,[14]

$$A_a = \frac{-1}{p^2 - 1} + \frac{p}{(p^2-1)^{3/2}} \ln[p + (p^2-1)^{1/2}] \tag{3}$$

Here, A_a is the depolarization factor along the a axis and $p = a/b$ or the aspect ratio of the tubules. The other two depolarization factors can be determined from[14]

$$A_b = A_c = \frac{1}{2}(1 - A_a) \qquad (4)$$

In eq. (2), we let $\varepsilon' \sim \varepsilon$ and $\varepsilon_1' \sim \varepsilon_1$ because the imaginary parts of the permittivity have small values for all the samples. We determined ε_1' to be equal to 3.0 and 2.6 at 10 GHz for the polyurethane and epoxy matrices, respectively. We also set the aspect ratio, p, to be equal to the mean tubule length divided by the mean tubule diameter in each sample. In a previous study,[15] we determined the mean tubule length to remain $\sim 21\ \mu m$ for samples containing 5–16 vol % tubules. The mean tubule diameter is $\sim 1\ \mu m$. Consequently, we let $p = 21$ for all the samples. After substituting these values into the De Loor model, we can compare the model predictions with the experimental data. This is shown in Figure 2. The model seems to provide a better fit to the epoxy samples than to the polyurethane samples. However, the model is very sensitive to the tubule aspect ratio. For instance, if we set the aspect ratio equal to 23 μm for all samples, the model provides good fits to both the polyurethane and the epoxy samples. In addition, the model only incorporates the mean tubule length and does not take into account the wide tubule length distribution found in the samples.[15] Despite these drawbacks, the De Loor model provides a fairly good fit to the data.

We next examined why the polyurethane composites have higher permittivity values than the epoxy samples. First, the matrix permittivity of the polyurethane is $\sim 15\%$ larger than that of epoxy. As seen in the De Loor model, the matrix permittivity appears as a multiplicative factor, so, all other things being equal, the permittivities of the two composites should differ by $\sim 15\%$ at all loadings. In addition, we were concerned with how the polymerizing media interacted with copper during the cure process, so we measured their contact angles with respect to copper at different cure times. Before we did this, we first measured the contact angles of the individual components in the
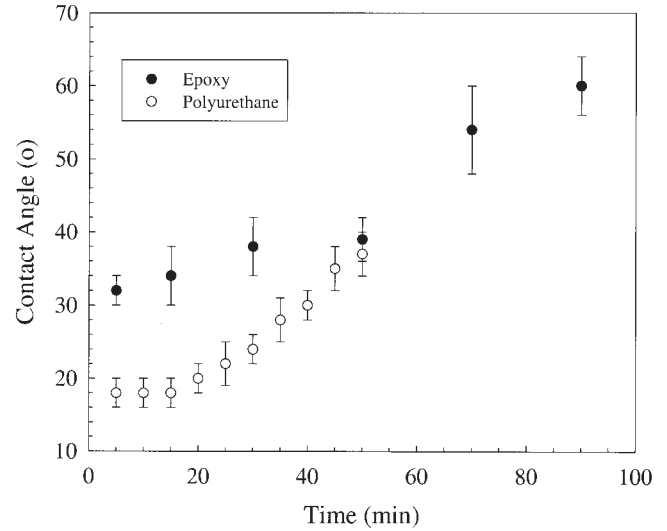
Figure 3 Contact angles of polymerizing samples with copper foil as a function of cure time.

epoxy and polyurethane formulations. This is shown in Table I. For the most part, the epoxy components have higher contact angles than the polyurethane components. We then mixed the components together and determined the contact angles of the epoxy and polyurethane samples during curing. This is shown in Figure 3, where we plot the contact angles of the polymerizing liquid as a function of cure time. After 5 min of curing, the epoxy sample had a contact angle of 32°, whereas the polyurethane sample had a contact angle of 18°. This would suggest that the copper particles should tend to aggregate at lower loadings in the epoxy, leading to larger permittivities. As curing progressed, contact angles for both samples increased, with the epoxy sample continuing to have larger values over the cure times. The difference between the two, however, decreased significantly. The results in Table I and Figure 3 indicated that the polyurethane better wetted the tubules than the epoxy, but that this difference decreased substantially during cure.

We also wanted to check whether the polyurethane still wetted the tubules better, and consequently had lower interfacial tensions, than epoxy throughout the entire cure process. The reason we needed to do this was because we were only able to measure the contact angles until the sample began to gel and the viscosity became too high. At this point, however, the tubules may still be able to rearrange themselves and affect the final distribution profile. To ensure the polyurethane–tubule interfacial tension remained lower for the entire cure process, we needed to determine the interfacial tensions between the fully cured polymers and copper. To calculate these values, we first measured the surface tensions of the fully cured polymers and copper. These values are listed in Table II. Both polymer matrices and copper have similar total surface

TABLE I
Contact Angles of Individual Components from Epoxy and Polyurethane Formulations

	Component	Contact angle (°)
Polyurethane	Part A	33 ± 3
	Part B	11 ± 5
Epoxy	Epon 815	40 ± 3
	Der 736	28 ± 2
	C3140	45 ± 9

TABLE II
Surface and Interfacial Tensions of Polyurethane, Epoxy, and Copper

	Dispersive (dyn/cm)	Polar (dyn/cm)	Total surface tension (dyn/cm)	Interfacial tension (dyn/cm)
Polyurethane	30.8	11.5	42.3	—
Epoxy	27.2	13.9	41.1	—
Copper	38.5	2.9	41.4	—
Polyurethane-Cu	—	—	—	6.0
Epoxy-Cu	—	—	—	9.2

tensions, but the polymers have higher polar components. We can calculate the interfacial tension from the individual surface tension values by using the harmonic mean method[10]

$$\gamma_{12} = \gamma_1 + \gamma_2 - 4\left[\frac{\gamma_1^d\gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^p\gamma_2^p}{\gamma_1^p + \gamma_2^p}\right] \quad (5)$$

where γ_{12} is the interfacial tension between species 1 and 2, γ_1 is the total surface tension of species 1, γ_2 is the total surface tension of species 2, γ_1^d is the dispersion component of species 1, γ_2^d is the dispersion component of species 2, γ_1^p is the polar component of species 1, and γ_2^p is the polar component of species 2. Table II contains the interfacial tension values between each polymer matrix and copper. The polyurethane samples do have a lower interfacial tension than the epoxy samples.

The contact angle and interfacial tension data indicated the polyurethane better wetted the tubules and had a lower interfacial tension than the epoxy over the entire cure process. This suggested the polyurethane samples should have more dispersed tubules and a higher percolation threshold concentration. Consequently, for a specific tubule concentration, the polyurethane sample should have a lower permittivity value than the epoxy sample. However, we obtained the opposite results. This can be seen in Figure 2. In a previous study on tubule composites,[5] we found that the composites had comparable permittivity values even though the samples had different contact angle and interfacial tension values. It appears that interfacial tension differences of the order we have measured in these samples cannot be used to predict how the tubules distribute in the composite. This contradicted previous studies[1,2] that showed the matrix surface tension had a large influence on filler distribution. However, in a recent study, Wu et al.[16] also found that interfacial tension between polymer and filler might not be the primary predictor of how fillers distribute in the composite. They studied carbon black in immiscible polymer blends and discovered that the filler preferentially dispersed in the polymer with the lower glass transition temperature rather than the lower interfacial tension. Clearly, more studies need to be done to clarify the effects of interfacial tensions, their changes during curing, and the time needed for the composites to reach equilibrium while these changes are occurring.

CONCLUSIONS

The polyurethane composites containing copper-coated tubules had higher permittivity values than the epoxy samples. These results were inconsistent with the contact angle and interfacial tension measurements. The polyurethane samples had smaller contact angles and a lower interfacial tension with copper than the epoxy samples. This implied the tubules should be more dispersed in a polyurethane matrix. The more dispersed tubules should result in the sample being farther from percolation and having lower permittivity values. We found the opposite result, with the polyurethane samples having larger permittivities over the tubule concentration range. This suggested that contact angle and interfacial tension results could not be used, without further examination of curing effects, to predict tubule distribution in these samples.

References

1. Miyasaka, K.; Watanabe, K.; Jojima, E.; Aida, H.; Sumita, M.; Ishikawa, K. J Mater Sci 1982, 17, 1610.
2. Sumita, M.; Abe, H.; Kayaki, H.; Miyasaka, K. J Macromol Sci Phys 1986, B25, 171.
3. Lux, F. J Mater Sci 1993, 28, 285.
4. Wessling, B. Synth Met 1988, 27, A83.
5. Chiou, B. S.; Lankford, A. R.; Schoen, P. E. J Appl Polym Sci 2003, 88, 3218.
6. Yager, P.; Schoen, P. E. Mol Cryst Liq Cryst 1984, 106, 371.
7. Georger, J. H.; Singh, A.; Price, R. R.; Schnur, J. M.; Yager, P.; Schoen, P. E. J Am Chem Soc 1987, 109, 6169.
8. Schnur, J. M.; Price, R.; Schoen, P.; Yager, P.; Calvert, J. M.; Georger, J.; Singh, A. Thin Solid Films 1987, 152, 181.
9. Zabetakis, D. J Mater Res 2000, 15, 2368.
10. Wu, S. Polymer Interface and Adhesion; Marcel Dekker: New York, 1982.
11. Browning, S. L.; Lodge, J.; Price, R. R.; Schelleng, J.; Schoen, P. E.; Zabetakis, D. J Appl Phys 1998, 84, 6109.
12. De Loor, G. P. Appl Sci Res 1954, 3, 479.
13. van Beek, L. K. H. In Progress in Dielectrics; Birks J. B., Ed.; CRC Press: Cleveland, 1967; p 69.
14. Altshuller, A. P. J Phys Chem 1954, 58, 544.
15. Chiou, B. S.; Lankford, A. R.; Schoen, P. E. J Appl Phys to appear.
16. Wu, G.; Asai, S.; Sumita, M.; Yui, H. Macromolecules 2002, 35, 945.