Modifying Tubule Distribution in Tubule-Filled Composites by Using Polyurethane–Polydimethylsiloxane Interpenetrating Polymer Networks

Bor-Sen Chiou,[1] Andrew R. Lankford,[2] Paul E. Schoen[1]

[1]Center for Bio/Molecular Science and Engineering, Naval Research Laboratory, Washington, District of Columbia 20375-5348
[2]SFA, Inc., Largo, Maryland 20774

ABSTRACT: Microtubules that were made from a phospholipid and coated with copper to become electrically conductive were incorporated into a polyurethane–polydimethylsiloxane (PU-PDMS) interpenetrating polymer network. The tubule concentration ranged from 8 to 16 vol %, whereas the PDMS concentration ranged from 0 to 75 wt %. The composites' dielectric properties and morphology were characterized by using a vector network analyzer and an optical microscope. In the composites the tubules became segregated into the polyurethane phase and were excluded from the PDMS phase. This forced the tubules closer together and resulted in the sample being closer to percolation. Consequently, for a specific tubule concentration, the real part of the permittivity increased for higher PDMS concentrations. In addition, adding tubules changed the morphology of the matrix. The dispersed PDMS globules were smaller in the composites than in the neat interpenetrating polymer network. The reason was that the tubules increased the viscosity of the system, which prevented the smaller PDMS globules from coalescing to form larger globules. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1032–1038, 2003

Key words: polyurethane-polydimethylsiloxane; interpenetrating polymer networks; permittivity; tubules

INTRODUCTION

Previous studies have shown that using immiscible polymer blends can be an effective method for dramatically lowering the percolation threshold concentration of fillers in composite systems.[1–20] This threshold concentration occurs when a conducting network of fillers forms in the system, and the sample changes from insulating to conducting. Lowering the threshold concentration in immiscible blends can be accomplished by using several approaches. One involves localizing the filler in one of the two phases. This can be achieved by selecting polymers with specific surface tensions, thereby forcing the fillers to reside in one phase[3,15] The fillers become physically excluded from the other phase and are forced closer together. A second approach to reduce the threshold concentration involves localizing the filler at the interface of the blends. This produces much lower threshold concentrations than just localizing the filler in one phase. The interface localization can also be achieved by manipulating the surface tensions of the polymers.[3,15] In addition, interface localization can be controlled kinetically by applying the appropriate processing procedure.[5,12] For instance, the filler is first dispersed into the polymer with which it less strongly interacts. A second polymer is then added, and the sample is melt-blended. During blending the filler migrates toward the second polymer phase. The sample is eventually quenched when the fillers arrive at the interface of the two blends. For both types of selective localization to work, the phase containing the filler or the interface of the blends has to be continuous. This is termed double percolation, which denotes that sufficient filler is required to percolate in the preferred phase or at the interface, and furthermore, the preferred phase or interface has to be continuous.

The filler in these blend systems that is most commonly studied is carbon black. Very few studies have examined the effects of adding fibers to the systems. Fibers have high aspect ratios (length:diameter) and should produce composites with even lower percolation threshold concentrations than carbon black. In one study Sau et al.[21] added carbon fibers with an average length of 6 mm and an average diameter of 10 μm to a blend of acrylonitrile–butadiene rubber and ethylene–propylene–diene rubber. They found only slight changes in the percolation threshold concentration in those blends. Another study, by Zhang et al.,[14]

involved adding vapor-grown carbon fibers to a blend of high-density polyethylene and poly(methyl methacrylate). These carbon fibers had an average length of 10 μm and an average diameter of 0.2 μm. The fibers preferentially resided in the high-density polyethylene phase, resulting in reduced percolation threshold concentrations. In studies by Wu et al.[18,20] using the same vapor-grown carbon fiber/high-density polyethylene/poly(methyl methacrylate) system, it was found that adding only 1 wt % of polyethylene reduced the threshold concentration. The polyethylene did not form a continuous phase at this low concentration but instead adsorbed to the ends of the carbon fibers. In this way, the polyethylene acted as clamps for the fiber ends, thus forming interconnected fiber networks. The polyethylene was thought to preferentially adsorb at the fiber ends because these places contained rough carbon crystallite edges.

Most studies using polymer blends have involved melt-blending combinations of thermoplastics, rubbers, and thermoplastic elastomers. Melt blending entails high temperatures and high shear stresses that may be detrimental to brittle fillers. The melt-blending process usually requires temperatures in excess of 150°C. After blending the samples are compression-molded at even higher temperatures to produce uniform samples. In addition, these melt blends have high viscosities that require large shear stresses to mix properly. These high-stress conditions may cause fillers, such as the fibers, to break excessively.

One type of phase-separated polymer system that does not require a high processing temperature or have a high processing viscosity is a polyurethane–polydimethylsiloxane (PU–PDMS) interpenetrating polymer network. Only a few studies have focused on these polymers.[22–25] The system consists of a polyurethane network and a polydimethylsiloxane network that crosslink in the presence of, but independently of, each other. The monomers for each polymer can be mixed and subsequently cured at room temperature. In this way the sample does not experience the high processing temperatures associated with melt blending thermoplastics, rubbers, and thermoplastic elastomers. In addition, the polyurethane and polydimethylsiloxane monomers have low viscosities, which reduce the damage to any fillers resulting from the mixing process.

In this study we characterized the dielectric properties and morphologies of polyurethane–polydimethylsiloxane interpenetrating polymer networks containing copper-coated phospholipid tubules. The tubules preferred the polyurethane phase, creating different tubule distributions in samples with different PU–PDMS compositions. The varying tubule distributions then resulted in different dielectric properties. We varied the PDMS concentration and studied how this changed the dielectric properties of the samples. In
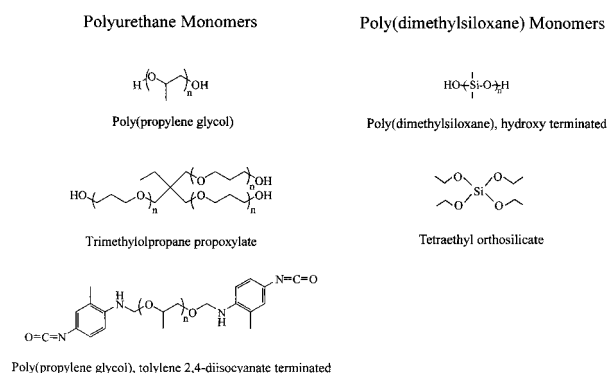

Figure 1 Chemical structures of polyurethane and polydimethylsiloxane monomers.

addition, we examined the morphology of the composites using optical microscopy.

EXPERIMENTAL

Sample preparation

A simultaneous interpenetrating polymer network of polyurethane and polydimethylsiloxane was prepared by adding the components all at once. The monomers for forming the polyurethane network consisted of poly(propylene glycol), a diol with a molecular weight of 425; trimethylolpropane propoxylate, a triol with a molecular weight of 308; and poly(propylene glycol), tolylene 2,4-diisocyanate terminated, a diisocyanate monomer with a molecular weight of 1000. The monomers for the polydimethylsiloxane network consisted of polydimethylsiloxane, hydroxy-terminated, with a molecular weight of 35,000, and tetraethyl orthosilicate. All the monomers were obtained from Sigma-Aldrich (St. Louis, MO). Their chemical structures are shown in Figure 1. The poly(propylene glycol), trimethylolpropane propoxylate, and polydimethylsiloxane, hydroxy-terminated, were dried in a vacuum oven at 60°C for 5, 3, and 2 h, respectively, before use. In addition to these monomers, the samples contained an antifoaming agent, AF-4 (BJB Enterprises, Tustin, CA), and a catalyst, tin(II) ethylhexanoate (Sigma-Aldrich).

The production and properties of the copper-plated lipid tubules have been described in previous studies.[26–29] The tubules were produced by first dissolving a phospholipid, 1,2-bis(tricosa-10,12-dinoyl)-sn-glycero-3-phosphocoline), in an ethanol–water solution. The temperature of the solution was then slowly lowered until hollow tubules started forming at around 35°C. The tubules were subsequently treated with a platinum catalyst. Finally, the tubules' surfaces were coated with copper through a commercial electroless plating process. The tubules had an average diameter of 1 μm and an average length of approximately 20–30 μm.

The composites were made in slightly different ways depending on their composition. The polydimethylsiloxane concentration was varied from 0 to 75 wt %, whereas the tubule concentration was varied from 8 to 16 vol %. The polyurethane part of the network had an isocyanate:hydroxyl (NCO:OH) ratio of 1.0 and a triol concentration that represented 25 mol % of the hydroxyl groups. Samples containing 25–75 wt % PDMS were made by first adding the monomers, AF-4, catalyst, and tubules together. The AF-4 and catalyst concentrations were 0.60% and 0.75%, respectively, by weight of monomers. This mixture was vigorously stirred for several minutes and then placed in a vacuum oven for degassing. The sample was degassed for 2 h and then placed between two aluminum plates. Spacers 1.3 mm thick were also inserted between the plates to produce samples with a convenient thickness. After 24 h the sample was removed from the plates and placed in a dry box saturated with nitrogen gas. The sample was allowed to cure for an additional 24 h. Finally, it was placed in a vacuum oven and cured under vacuum for a further 24 h at 60°C. Samples containing 0 wt % PDMS were produced in essentially the same way with a few minor differences. The AF-4 concentration was reduced to 0.30 % by weight of monomers. In addition, the samples were degassed for 1.5 h in the vacuum oven before being sandwiched between the aluminum plates.

Dielectric measurements

A vector network analyzer (HP8510, Hewlett-Packard, Palo Alto, CA) was used to measure the dielectric properties of the samples over a frequency range of 2–18 GHz. Each sample, approximately 1.3 mm thick and 7 mm in diameter, was placed in a coaxial measurement fixture. The S-parameters of all the samples were subsequently measured, and the Nicolson and Ross approach[30] was used to calculate the permittivity values.

Optical microscopy

An optical microscope (Leitz Wetzlar, Germany) was used to examine the morphology of the PU–PDMS interpenetrating polymer network and the composites. A thin slice of the sample was sandwiched between a glass slide and a cover slide. Micrographs were taken by using a camera attached to the microscope.

RESULTS AND DISCUSSION

The real (ε') and imaginary (ε'') parts of permittivity remained relatively constant for all samples over the frequency range examined in this study. This is shown
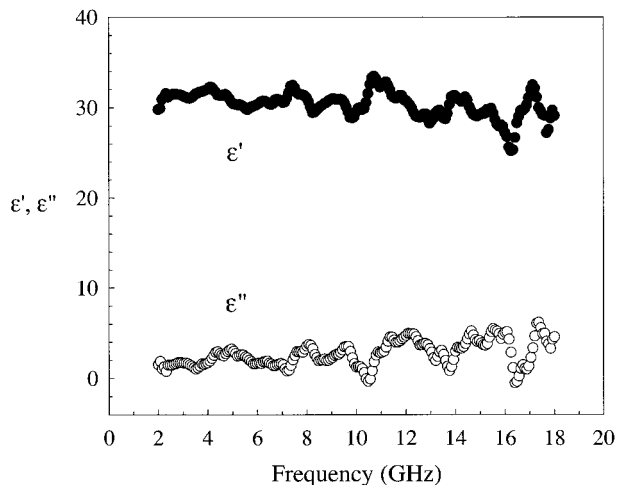

Figure 2 Real and imaginary parts of the permittivity as a function of frequency for a typical sample containing 12 vol % tubules and 50 wt % PDMS.

in Figure 2, which has a plot of the permittivities of a typical sample containing 12 vol % tubules and 50 wt % PDMS. The real part of the permittivity has a value of 30, which does not change much over the entire frequency range. The imaginary part of the permittivity also has a relatively constant value, but one that is much lower than the real part. Because the permittivites remained relatively constant, we only compare permittivities at a fixed frequency of 10 GHz for subsequent plots.

In addition, all our samples did not achieve percolation because the real part of the permittivity remained much larger than the imaginary part. As the sample approaches percolation, the imaginary part of the permittivity should increase in value dramatically, and the real part of the permittivity should reach its maximum value. This behavior had been found to occur for tubules incorporated in several different polymer matrices.[31,32] It had also been predicted using the effective-medium theory for conducting stick composites.[33] That our samples did not percolate indicates the tubules remained too far apart in the composites for sufficient contact or electron tunneling to occur.

As PDMS was incorporated into the polymer network, the real part of the permittivity increased markedly in value. This is shown in Figure 3, which has a plot of the permittivity as a function of tubule concentration for all the samples. The permittivity increased by 36%–41% for the 25 wt % PDMS samples over the tubule concentration range. Increasing the PDMS concentration to 50 wt % resulted in an additional incremental increase in permittivity values for most samples. For the 75 wt % PDMS samples, the permittivity values became 40%–78% larger than the samples without PDMS. The boost in permittivity seems to have become progressively smaller as we added more PDMS.
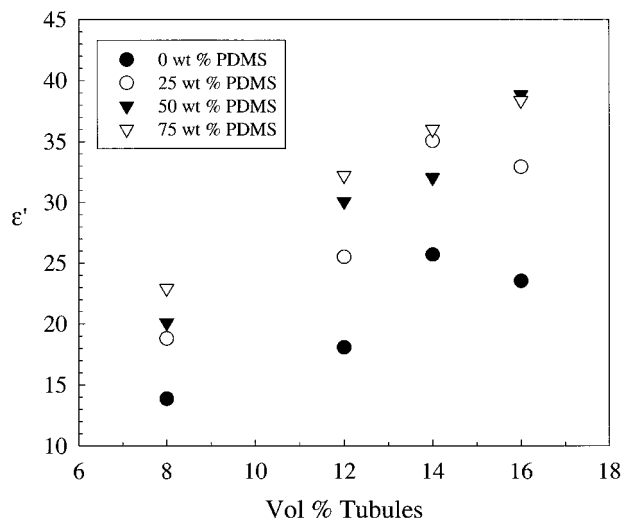
Figure 3 Real part of the permittivity as a function of tubule concentration for various PU–PDMS samples. The frequency was 10 GHz.

Figure 4 Optical micrograph of an uncured sample containing 4 vol % tubules and 40 wt % PDMS monomers. The micrograph was taken 1 h after the sample had been mixed.

The increase in permittivity after adding PDMS indicates a change in tubule distribution within the system. The data suggest the tubules preferred to reside in the polyurethane phase of the interpenetrating polymer network. Consequently, the tubules were excluded from the PDMS phase and were forced closer together, reducing the gaps between tubules. This resulted in a sample closer to percolation and a concomitant increase in permittivity.

Support for the idea that tubules preferentially localize in the polyurethane phase comes from examining how the tubules behaved before crosslinking could occur. We prepared a sample containing 40 wt % PDMS and 4 vol % tubules, but without any catalyst. Because crosslinking does not readily occur without the catalyst, the two phases can separate easily. After mixing the sample, we viewed it under an optical microscope. The result is shown in Figure 4 and indicates the tubules tended to favor the polyurethane monomer phase. In fact, the tubules accumulated in the polyurethane monomer phase and at the edges of the PDMS phase. Very few tubules were actually localized in the PDMS phase. We should note that the micrograph in Figure 4 represents the system 1 h after sample preparation. We waited this long to take the picture because this allowed for more phase separation to occur and subsequently produced a more distinctive picture. However, we could clearly see the tubules had already segregated into the polyurethane monomer phase immediately after mixing the sample. In any case, the result corroborates the dielectric data (see Fig. 3), which show the permittivity increases after introducing PDMS into the system.

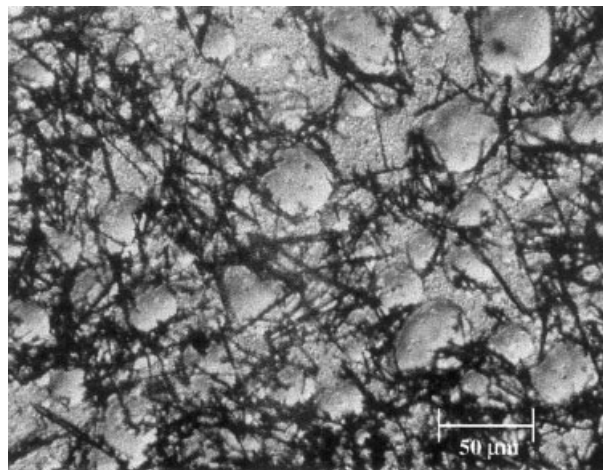We can further test the assumption that tubules reside primarily in the polyurethane phase by recalculating the tubule concentration for samples containing PDMS. This new tubule concentration is calculated by assuming all tubules are located only in the polyurethane phase. Therefore, the recalculation involves just the polyurethane volume and excludes the PDMS volume. The results are shown in Figure 5, which has a plot of the real part of the permittivity as a function of the recalculated tubule concentrations for all samples. Figure 5 also includes the sample standard deviation for each datum. The results indicate that permittivities for the samples containing no and some PDMS follow the same curve. This is especially evident for tubule concentrations between 8 and 16 vol %. The results provide further evidence that the tubules do reside primarily in the polyurethane phase.
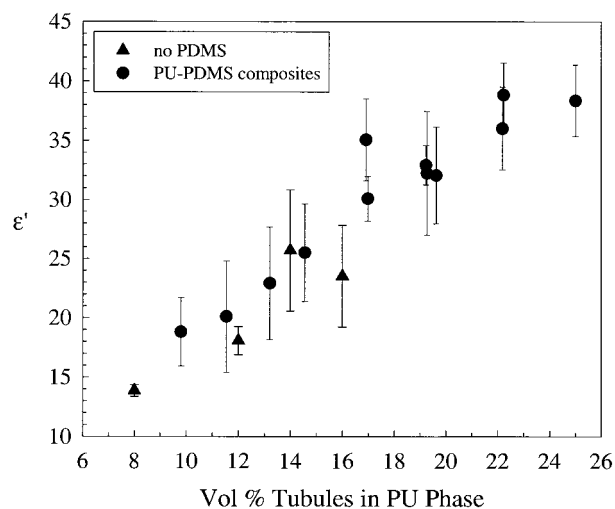

Figure 5 Real part of the permittivity as a function of the recalculated tubule concentration for all samples. The new tubule concentration was calculated by assuming all tubules reside in the polyurethane phase. The frequency was 10 GHz.
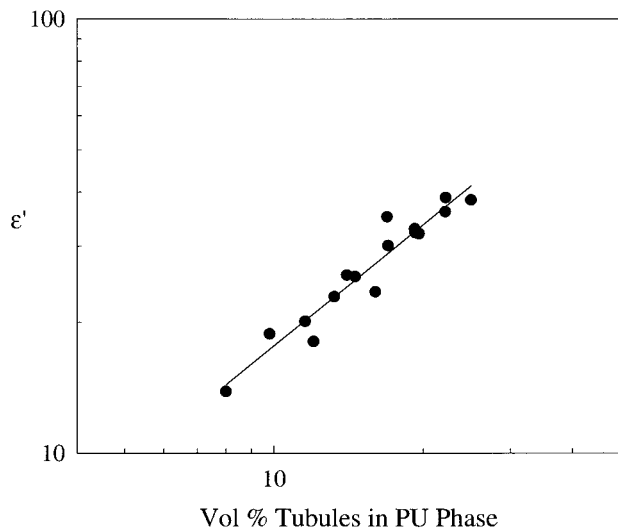
Figure 6 Power law plot of the real part of the permittivity as function of tubule concentration on a log–log scale. The frequency was 10 GHz.

We can best fit the data from Figure 5 to a power law of the form:

$$\varepsilon' = Ac^n \qquad (1)$$

where ε' is the real part of the permittivity, A is a constant, c is the tubule concentration (vol %), and n is the exponent. A power law indicates that a plot of the real part of the permittivity as a function of the tubule concentration on a log–log scale should be linear. The slope is then n and the intercept is log(A). This plot is shown in Figure 6, with n and A calculated as 0.93 and 2.1, respectively. Although extrapolation of data may prove to be inaccurate, this empirical model can nevertheless provide a rough permittivity estimate for tubule concentrations that may be experimentally inaccessible. For instance, high tubule loadings can create extremely viscous systems that become very difficult to process and manufacture into reproducible samples.

We next examine the morphology of the PU–PDMS interpenetrating polymer network with and without tubules. The PDMS phase separates from the PU and forms dispersed globules at lower PDMS concentrations. Because the polyurethane crosslinks faster than the PDMS, it forms the continuous phase. When the polymers crosslink, the globules become trapped in the matrix. This is shown in Figure 7, which presents an optical micrograph of a sample containing 25 wt % PDMS. The PDMS globules have a wide distribution of diameters. These range from about 5 to 25 μm in diameter, similar to those found in other PU–PDMS systems.[22,23]

The sample's morphology changed dramatically after adding tubules to the system. The PDMS globules
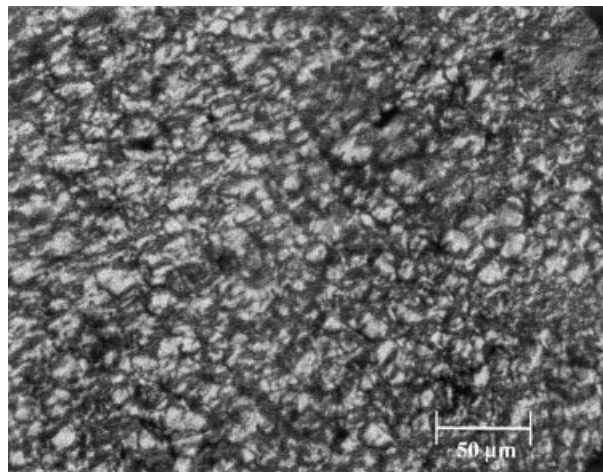

Figure 7 Optical micrograph of neat PU–PDMS interpenetrating polymer network containing 25 wt % PDMS.

became much smaller in the presence of the tubules. This is shown in Figure 8, which depicts an optical micrograph of a sample containing 8 vol % tubules and 25 wt % PDMS. Most of the PDMS globules now have diameters of less than 10 μm, much smaller than those found in the neat PU–PDMS sample shown in Figure 7. This effect has also been observed for systems containing carbon black in various thermoplastics.[7] The authors of that study attributed the decrease in size of the dispersed phase to an increase in viscosity after adding more filler to the system. This also applies to our system because the samples became more viscous with more tubules. The increased viscosity prevented the smaller PDMS globules from coalescing to form larger globules. Subsequently, the sample crosslinked, thereby locking the smaller globules into the matrix. We also examined under the microscope samples containing higher PDMS concen-
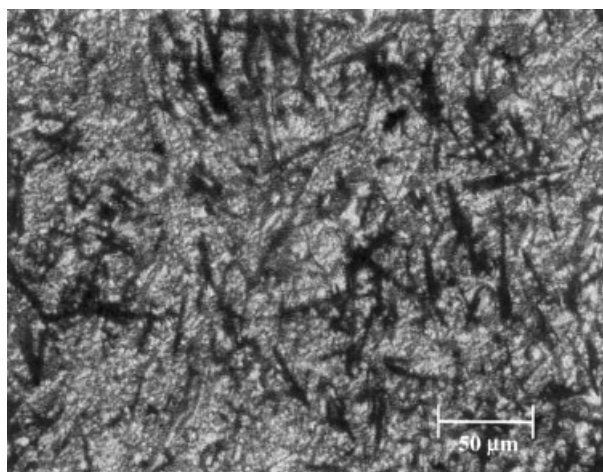

Figure 8 Optical micrograph of a PU–PDMS interpenetrating polymer network composite containing 8 vol % tubules and 25 wt % PDMS.
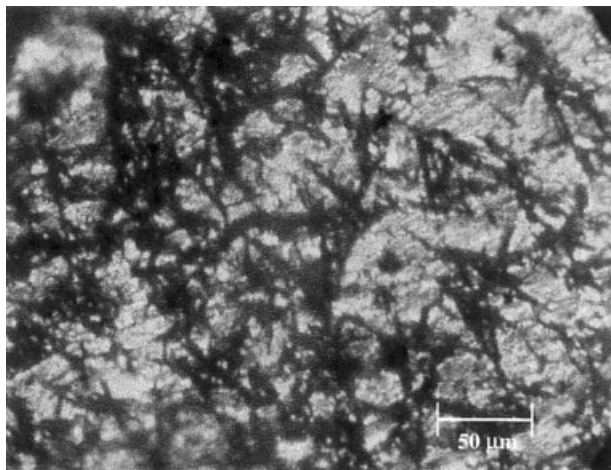
Figure 9 Optical micrograph of a PU–PDMS interpenetrating polymer network composite containing 14 vol % tubules and 25 wt % PDMS.

trations. However, we could not tell much of a difference between those samples and the one shown in Figure 8.

For samples with higher tubule concentrations, the PDMS globules became even smaller in size. This is shown in Figure 9, which presents an optical micrograph of a sample containing 14 vol % tubules and 25 wt % PDMS. The PDMS globules are even smaller than those seen in Figure 8 for the sample containing 8 vol % tubules. One reason for this behavior is the larger increase in viscosity at the higher tubule concentration.

Many immiscible polymer blends containing carbon black have shown large decreases in their percolation threshold concentrations. When we used the PU–PDMS interpenetrating polymer networks to produce tubule composites, we did not find such a large effect on their dielectric properties. The main reason for this behavior involves the sizes of the tubules compared to those of the carbon black fillers and the dispersed phases. The average particle sizes of the carbon black fillers used in the percolation studies ranged from 15 to 30 nm. In contrast, the average tubule length was 3 orders of magnitude larger than the average carbon black size. The carbon black was, therefore, usually much smaller than the dispersed phases in the blends. When carbon black fillers preferentially localized in one phase or at the interface of the blends, they became excluded from large amounts of continuous volume. This forced the fillers to come much closer together. For our samples, this did not occur to as large an extent. Because the tubules were larger than the PDMS globules (see Figs. 8 and 9), they could not be excluded from sizable continuous volumes. Consequently, the tubules were forced together only moderately, resulting in smaller changes in the dielectric properties. These scale effects were also found in other

studies involving carbon fibers. Sau et al.[21] discovered that adding carbon fibers to a blend of acrylonitrile–butadiene rubber and ethylene–propylene–diene rubber resulted in only slight changes in the percolation threshold concentration. The fibers were larger than the tubules used in this study, suggesting they may also have been larger than the dispersed phases. However, the authors did not present any micrographs showing the morphology of the samples. Therefore, the fibers may not have preferentially localized in one phase. In another study involving carbon fibers, Zhang et al.[14] found substantial reduction in the percolation threshold concentration after adding fibers to a polyethylene/poly(methyl methacrylate) blend. In this case the fibers used were smaller than our tubules. Moreover, the fibers were smaller than the dispersed phases, and they became localized in the polyethylene phase.

CONCLUSIONS

We used a polyurethane–polydimethylsiloxane (PU–PDMS) interpenetrating polymer network to manipulate the tubule distribution in tubule composites. In the PU–PDMS interpenetrating polymer network the PDMS formed dispersed globules at lower PDMS concentrations. When tubules were incorporated into the system, they preferred to reside in the polyurethane phase and became excluded from the PDMS phase. This forced the tubules closer together and produced a system closer to percolation. Consequently, at a specific tubule concentration, the permittivity increased for higher PDMS concentrations. For example, samples containing 75 wt % PDMS had their permittivities boosted by 40%–78% relative to samples without any PDMS. In addition, adding tubules to the system dramatically changed the morphology of the matrix. The PDMS globules in composites became smaller than those found in the neat interpenetrating polymer network. This resulted from an increase in viscosity after the addition of more tubules to the system. The increased viscosity prevented the small PDMS globules from coalescing to form larger globules. Subsequently, the polymers crosslinked, and the small globules became trapped in the matrix.

References

1. Geuskens, G.; Gielens, J. L.; Geshef, D.; Deltour, R. Eur Polym J 1987, 23, 993.
2. Geuskens, G.; De Kezel, E.; Blacher, S.; Brouers, F. Eur Polym J 1991, 27, 1261.
3. Sumita, M.; Sakata, K.; Asai, S.; Miyasaka, K.; Nakagawa, H. Polym Bull 1991, 25, 265.

4. Sumita, M.; Sakata, K.; Hayakawa, Y.; Asai, S.; Miyasaka, K.; Tanemura, M. Colloid Polym Sci 1992, 270, 134.

5. Gubbels, F.; Jerome, R.; Teyssie, P.; Vanlathem, E.; Deltour, R.; Calderone, A.; Parente, V.; Bredas, J. L. Macromolecules 1994, 27, 1972.

6. Soares, B. G.; Gubbels, F.; Jerome, R.; Teyssie, P.; Vanlathem, E.; Deltour, R. Polym Bull 1995, 35, 223.

7. Gubbels, F.; Blacher, S.; Vanlathem, E.; Jerome, R.; Deltour, R.; Teyssie, P.; Teyssie, P. Macromolecules 1995, 28, 1559.

8. Tchoudakov, R.; Breuer, O.; Narkis, M.; Siegmann, A. Polym Eng Sci 1996, 36, 1336.

9. Gamboa, K. M. N.; Ferreira, A. J. B.; Camargo, Jr., S. S.; Soares, B. G. Polym Bull 1997, 38, 95.

10. Tchoudakov, R.; Breuer, O.; Narkis, M.; Siegmann Polym Eng Sci 1997, 37, 1928.

11. Zhang, M. Q.; Yu, G.; Zeng, H. M.; Zhang, H. B.; Hou, Y. H. Macromolecules 1998, 31, 6724.

12. Gubbels, F.; Jerome, R.; Vanlathem, E.; Deltour, R.; Blacher, S.; Brouers, F. Chem Mater 1998, 10, 1227.

13. Feng, J.; Chan, C. M. Polym Eng Sci 1998, 38, 1649.

14. Zhang, C.; Yi, X. S.; Yui, H.; Asai, S.; Sumita, M. J Appl Polym Sci 1998, 69, 1813.

15. Mamunya, Y. P. J Macromol Sci Phys B 1999, 38, 615.

16. Calberg, C.; Blacher, S.; Gubbels, F.; Brouers, F.; Deltour, R.; Jerome, R. J Phys D: Appl Phys 1999, 32, 1517.

17. Foulger, S. H. J Polym Sci, Part B: Polym Phys 1999, 37, 1899.

18. Wu, G.; Asai, S.; Sumita, M. Macromolecules 1999, 32, 3534.

19. Cheah, K.; Forsyth, M.; Simon, G. P. J Polym Sci, Part B: Polym Phys 2000, 38, 3106.

20. Wu, G.; Asai, S.; Sumita, M.; Yui, H. Macromolecules 2002, 35, 945.

21. Sau, K. P.; Chaki, T. K.; Khastgtir, D. Polymer 1998, 39, 6461.

22. Ebdon, J. R.; Hourston, D. J.; Klein, P. G. Polymer 1984, 25, 1633.

23. Ebdon, J. R.; Hourston, D. J.; Klein, P. G. Polymer 1986, 27, 1807.

24. Klein, P. G.; Ebdon, J. R.; Hourston, D. J. Polymer 1988, 29, 1079.

25. Ali, S. A. M.; Hourston, D. J.; Manzoor, K.; Williams, D. F. J Appl Polym Sci 1995, 55, 733.

26. Yager, P.; Schoen, P. E. Mol Cryst Liq Cryst 1984, 106, 371.

27. Georger, J. H.; Singh, A.; Price, R. R.; Schnur, J. M.; Yager, P.; Schoen, P. E. J Am Chem Soc 1987, 109, 6169.

28. Schnur, J. M.; Price, R.; Schoen, P.; Yager, P.; Calvert, J. M.; Georger, J.; Singh, A. Thin Solid Films 1987, 152, 181.

29. Zabetakis, D. J Mater Res 2000, 15, 2368.

30. Nicolson, A.M.; Ross, G.F. IEEE Trans Instrum Meas 1970, IM-19, 377.

31. Browning, S. L.; Lodge, J.; Price, R. R.; Schelleng, J.; Schoen, P. E.; Zabetakis, D. J Appl Phys 1998, 84, 6109.

32. Chiou, B. S.; Mera, A. E.; Zabetakis, D.; Lankford, A. R.; Schoen, P. E. J Appl Phys, submitted.

33. Lagarkov, A. N.; Sarychev, A. K. Phys Rev B 1996, 53, 6318.