

ELECTRICAL CONDUCTIVITY OF A GRAPHITE BASED COMPOSITE AS AFFECTED BY THE DEGREE OF MIXEDNESS OF GRAPHITE IN THE ELASTOMERIC MATRIX

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Dedicated to the memory of our friend and colleague Dr. Rahmi Yazici (1949-2000)*

Abstract

The development of the electrical properties of composites as a function of the degree of mixedness of graphite distributed into a plasticized thermoplastic elastomer (Kraton with mineral oil plasticizer) is investigated. A wide-angle x-ray diffraction (WAXD) based quantitative phase analysis method was used to characterize the variations of the concentrations of the elastomer and the graphite particles around their mean values as a function of mixing time in an intensive batch mixer. Increasing the specific energy input during the mixing process results in a more homogeneous spatial distribution of graphite in the elastomer. The increasing specific energy input alters the rheology of the composite suggesting that significant structural changes do occur. Indeed the degree of mixedness of the graphite in the matrix is quantitatively determined to be improved, generally resulting in better coating of the individual graphite particles. This improved coating effectiveness in turn results in a decrease of the volume conductivity of the composite.

Background

Electrically conductive nonmetallic materials are used in various applications including electromagnetic interference (EMI) shielding, adhesives, devices and sensors (1-12). Doping of the polymer, vacuum metallization on the surface of the polymer, implantation of metallic ions and compounding with conductive particles are employed to obtain such conductive nonmetallic materials. The mixing of an insulating polymer with conductive particles is one of the widely-used methods because compounds of polymers with conductive fillers can be easily shaped into various complicated shapes. Traditional polymer processing methods including extrusion and injection molding can be utilized. Various conductive fillers including, metal powders, i.e., Al, Au, Ag, Cu and stainless steel or carbon and graphite powders are employed (1-3).

Bigg (3,4) has reviewed the development of the electrical properties of metal filled polymers and the mechanisms involved in the formation of conductive composites of polymer/metal systems. Metallic powders generally suffer from the oxidation of the metallic particles and the corresponding deterioration of the electrical

properties of the composite due to the nonconductive nature of such oxide layers (3). It is well known that the electrical properties of the composite are dependent on the concentration, size and shape distributions of the conductive particles (1-5). Furthermore, a number of studies have revealed that the mixing time of the conductive filler into the polymer matrix also affects the ultimate electrical conductivity of the composite (6, 7). However, measures, which characterize the state of the mixedness of the composite at various stages of the mixing process, were not obtained and related to the development of the electrical properties of the composite.

This study is part of a larger study, which aims to investigate the magnetic and electrical properties of particulate filled polymers (15-21). During our earlier studies we had recognized that the mixing plays a significant role in the development of the electrical properties of conductive composites and thus we focused this study on the dynamics of the mixing process and its relation to the development of electrical conductivity. A quantitative technique involving the wide-angle x-ray diffraction, WAXD, is used to characterize the statistics of the spatial distribution of the conductive filler in the elastomeric matrix. The statistics of the degree of mixedness of the graphite in the elastomer is then related to the volume resistivity of the composite.

Experimental

Two grades of "artificial graphite" powders available from Asbury Graphite Mills, of NJ, i.e., "coarse" A-60 and "fine" M-450, were intermixed and used as the conductive phase. The coarse graphite consists of low-aspect-ratio particles with an average particle size of 70 μm . The fine graphite particles are flaky and exhibit higher aspect ratios with an average particle diameter of 5 μm . The two powders were mixed at a fine-to-coarse weight ratio of 0.25 which gives rise to a relatively high maximum packing fraction of the solid phase for bimodal size distributions (13, 14). The density of the graphite is 2500 kg/m^3 .

The particle size distributions of the two powders were characterized and are shown in Figure 1. This mixture provided a relatively high theoretical maximum packing fraction of around 0.82 upon applying the theory of Ouchiyama and Tanaka (13) for the determination of the maximum packing fraction for bimodal spherical particles.

The elastomer used in this work is a tri-block copolymer with polystyrene end blocks and poly(ethylene-butylene) mid block with a solid density of 910 kg/m³. It was purchased from Shell Oil Company under the trade name of Kraton R G1652. The plasticizer used with the Kraton elastomer was the Tufflo Process Oil, 6016 (a white mineral oil), available from Lyondell Petrochemical Company with a density of 860 kg/m³. The ratio of the oil to the elastomer was 40% by weight representing a plasticizer/elastomer ratio of 0.67. The formulation used thus involved 40% by weight Kraton, 26% by weight Tufflo oil and 33% by weight of graphite (15% by volume).

The filler powders were mixed with the binder and the plasticizer using a Haake torque rheometer with a 300 ml intensive batch mixer (Figure 2). The torque rheometer is an intensive mixer (a mini-Banbury mixer) with the capability of measuring the torque and hence the specific energy input generated during the mixing process under isothermal conditions. In our mixing experiments the total duration of the mixing process was varied systematically in order to assess the effects of the specific energy input, expanded during the mixing process, Es:

$$E_s = 2 \pi \frac{N}{M} \int T dt \quad (1)$$

where M is the mass of the composite sample in the mixer, N is the rotational speed, and T is the torque value at time t. The typical mixing procedure involved first the mixing of the elastomer with the mineral oil in the batch mixer. The mixing was done under vacuum at 51 KPa and at 95 °C for a duration of five minutes. Upon the mixing of the elastomer with the mineral oil, the conductive graphite filler was added into the mixer. The batch mixing of the graphite with the binder was carried-out under vacuum at 51 KPa and at 95 °C, using a rotational speed of 64 rpm, for the predetermined mixing times of 5, 10, 20,40 minutes.

The typical specific energy versus time observed during the mixing process is shown in Figure 3. The specific energy input increases monotonically as a function of mixing time, but the rate of the increase decreases as time elapses. These specific energy input data were used in the analysis of the specimens, which were also characterized for their rheology, degree of mixedness and their electrical conductivity.

Upon mixing, the specimens of the composite were removed and sealed in double polyethylene bags. These specimens were then compression molded under vacuum to provide the specimens for the characterization of the

electrical properties and for the characterization of their degree of mixedness using the WAXD technique.

Compression Molding of the Specimens and Measurements of Volume Conductivity

A Carver compression molder was used to prepare disk shaped specimens of diameter 7.62 cm (3”) and thickness 0.64 cm (0.25”) for the determination of the volume resistivity. The molding was carried out at 150°C and using a pressure of 2.75 MPa. The surfaces of the specimens were polished with sandpaper to remove the resin-rich surface layer and to eliminate surface irregularities. Such resin-rich layers invariably form because during flow and the subsequent solidification, the particles cannot occupy the space adjacent to the mold wall as effectively as the volume away from the wall, thus generating a resin-rich layer designated as the "apparent" slip layer (22-26). All of the specimens were sealed in polyethylene bags using dry argon gas prior to testing in order to eliminate atmospheric and humidity effects that induce substantial changes of the surface conductivity of the samples. The copper electrodes used for resistivity measurements were bonded to samples with SEM-grade conductive silver paint (DY 350 from Zymet in East Hanover, NJ) and sealed inside the bag.

For the measurement of the volume resistivity, ASTM standard D257 (d.c. Resistance or Conductance of Insulating Materials) was followed. A d.c. voltage is applied to the sample, which is placed inside a Keithley resistivity chamber, model 6105 under ambient temperature. A 10V voltage is applied to the sample (as also verified with a Fluke 37 digital multimeter) and the current flowing through the sample is measured with a Keithley picoammeter, model 485. The picoammeter is equipped with an IEEE 488 interface. The collection and statistical analysis of the data are automated (16-21).

The resistivity adapter has disc-shaped electrodes. The top electrode applies a 4.4 N constant normal force to the sample. The bottom electrode is spring-loaded. Maintaining a constant pressure from run to run is important since the resistivity is known to be affected by pressure, below a critical pressure value during the testing (27). In our experiments the bottom electrode included a guard ring, which eliminates edge effects. The metal enclosure around the electrodes shields against stray pick-up (17).

WAXD Experiments

For x-ray diffractometry a 0.6 degree receiving slit was used in all runs. The x-ray probe size was varied by using 2 degree and 0.4 degree primary beam slits and a 8 mm high window. The x-ray probe size used was 5 mm x 2 mm (10 mm²) at a Bragg angle, 2θ, of 90 degrees.

Statistics of Mixing Homogeneity “Degree of Mixedness”

If one makes N measurements of the concentration, c_i , of one of the components, the variance s^2 , provides an index to quantitatively assess the degree of mixedness. The variance is given by:

$$s^2 = \frac{1}{(N-1)} \sum_{i=1}^N (c_i - \bar{c})^2 \quad (2)$$

where \bar{c} is the mean concentration. The maximum variance s_0^2 occurs if the components are completely segregated. The maximum variance is given by (28, 31)

$$s_0^2 = \bar{c}(1 - \bar{c}) \quad (3)$$

If the variance is normalized to its maximum value, the resulting parameter can be defined as the Mixing Index (32):

$$\text{Mixing Index, MI} = 1 - s/s_0 \quad (4)$$

Rheological Analysis:

The shear viscosity of the composite was characterized as a function of the shear rate employing an Instron capillary rheometer using a capillary with a diameter of 3.3 mm and a length over diameter ratio of 40 at a temperature of 95 °C. The use of the relatively large capillary diameter minimized the wall slip effect which was not characterized and not corrected. The dynamic properties of the suspension were characterized using a Rheometric Scientific ARES unit in conjunction with 8 mm parallel plate fixtures in the frequency range of 0.1 to 100 rps, 95 °C and at a strain amplitude of 1%.

Results and Discussion

The typical shear viscosity and the magnitude of complex viscosity data collected at a specific energy input of 1.2 MJ/kg is shown in Figure 4. The values of the shear viscosity approach the values of the magnitude of complex viscosity as the frequency and the shear rate both approach zero, upholding the Cox-Merz rule. The shear thinning behavior is characteristic of such suspensions with multi-modal particle size distributions.

The dependence of the magnitude of the complex viscosity as a function of specific energy input is shown at a frequency of 1 rps in Figure 5. The same trend is observed for the entire frequency range and indicates that the resistance of the suspension to deformation decreases as the specific energy input increases. This behavior is generally a result of a more homogeneous distribution of the solid particles in the melt and the better coating of the particles (33).

The quantitative results of the degree of mixing analysis as a function of specific energy input of the composite samples with a nominal 15 % by volume graphite are shown in Figure 6. The variability of the concentrations of the plasticized elastomer binder around the mean is substantially greater at smaller durations of mixing in the batch mixer and decreases with increasing specific energy input. The variance or the standard deviation of the binder concentration decreases substantially as the mixing time is progressively increased from 5 to 45 minutes. The “Coefficient of Variation” decreased from 0.047 to 0.007 and the “Mixing Index” increased from 0.89 to 0.98, as the mixing time was increased from 5 to 45 minutes, respectively.

The typical results summarizing the effects of the specific energy input during the mixing process on the development of the volume resistivity of the composite is shown in Figure 7. The volume resistivity of the composite increases exponentially with increasing mixing time. The volume resistivity increases from $10^6 \Omega \cdot \text{cm}$ at a specific energy input of 1.2 MJ/kg to $10^{11} \Omega \cdot \text{cm}$ at a specific energy input of 3.5 MJ/kg. Figure 8 schematically illustrates our hypothesis to explain these findings. Upon increasing the mixing time and hence the specific energy input incorporated during the mixing process, the homogeneity of the spatial distribution of the conductive graphite particles in the binder is improved and the conductive particles are better coated with the binder. The improved homogeneity of the spatial distribution of the conductive particles and their more uniform coating thickness, δ , leads to the insulation of the conductive particles from each other. Thus, the formation of a conductive network, i.e., the percolation, is hindered and the resistivity of the composite increases.

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References:

1. J. M. Margolis, "*Conductive Polymers and Plastics*," Chapman & Hall, New York (1989)
2. J. Delmonte, "*Metal/Polymer Composites*," Van Nostrand, New York (1990).
3. D. M. Bigg in "*Metal Filled Polymers*," S. Bhattacharya, ed., 165-226, Marcel Dekker, New York (1986).
4. D. M. Bigg, "*Adv. Polym. Techn.*," 3/4, 255 (1984).
5. G. Yu, Q. Zhang and H. Zeng, "*J. Appl. Polym.*"

- Sci.*, 70, 559-566 (1998).
6. M. Narkis, S. Srivastava, R. Tchoudako and O. Breuer, *Synthetic Metals* 113, 29-34 (2000).
 7. K. Cheah, M. Forsyth and G. Simon, *Synthetic Metals*, 102, 1232-1233 (1999).
 8. S. Kirkpatrick, *Rev. Mod. Phys.*, 45, 574 (1973).
 9. P. Ewen and J. M. Robertson, *J. Phys. D: Appl. Phys.*, 14, 2253 (1981).
 10. F. Lux, *J. Mater. Sci.*, 28, 265 (1993).
 11. M. Weber and M. Kamal, *Polymer Composites*, 18, 6, 711-725 (1997)
 12. P. J. Mather and K. Thomas, *J. of Materials Sci.*, 32, 401-407, (1997)
 13. N. Ouchiyaama and T. Tanaka, *Ind. Eng. Chem. Fundam.*, 23, 490 (1988).
 14. T. Fiske, S. Railkar and D. Kalyon, *Powder Tech.*, 81, 57 (1994).
 15. H. Gokturk, T. Fiske and D. Kalyon, *IEEE Transactions on Magnetics*, 29, 6, 4170-4176 (1993).
 16. H. Gokturk, T. Fiske and D. Kalyon, *J. Appl. Polymer Science*, 50, 1891-1901 (1993).
 17. J. S. Sun, H. Gokturk and D. Kalyon, *J. Materials Science*, 28, 364-366 (1993).
 18. H. Gokturk, T. Fiske and D. Kalyon, *J. Appl. Physics*, 73, 5598-5600 (1993).
 19. H. Gokturk, T. Fiske and D. Kalyon, *J. Appl. Polymer Science*, 65, 1371-1377 (1997).
 20. T. Fiske, H. Gokturk and D. Kalyon, *J. Materials Science*, 32, 5551-5560 (1997).
 21. T. Fiske, H. Gokturk, R. Yazici and D. Kalyon, *Polym. Eng. Sci.*, 37, 826-837 (1997).
 22. V. Vand, *J. Phys. Colloid Chem.*, 52, 277 (1948)
 23. Y. Cohen and A. Metzner, *J. Rheol.*, 29, 67 (1985).
 24. U. Yilmazer and D. Kalyon, *J. Rheol.*, 33, 1197-1212 (1989).
 25. D. Kalyon, P. Yaras, B. Aral and U. Yilmazer, *J. Rheol.*, 37, 35-53 (1993).
 26. B. Aral and D. Kalyon, *J. Rheol.*, 38, 957-972 (1994).
 27. K. Sau, D. Khastgir and T.K. Chaki, *Synthetic Metals*, 102, 1232-1233 (1998).
 28. W. Mohr, "Processing of Thermoplastic Materials," E. Bernhardt, ed., Krieger Publishing Company, Malabar (1959).
 29. S. Middleman, "Fundamentals of Polymer Processing," McGraw-Hill Book Company, New York (1977).
 30. D. Kalyon,, "Encyclopedia of Fluid Mechanics, 7, Ch. 28, 887-926, Gulf Publishing Company, Houston, (1988).
 31. R. Yazici and D. Kalyon, *Rubber Chemistry and Techn.*, 66, 4, 527-537 (1993).
 32. D. Kalyon, A. Lawal, R. Yazici, P. Yaras and S. Railkar, *Polym. Eng. Sci.*, 39, 1139-1151 (1999)
 33. D. Kalyon, A. Gotsis, U. Yilmazer, C. Gogos, H.

Sangani, B. Aral, and C. Tsenoglou, *Adv. Polym. Tech.*, 8, 4, 337-353 (1988).

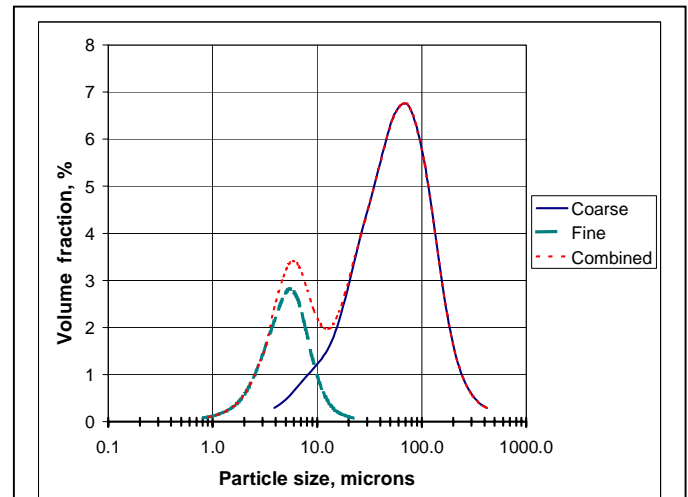


Figure 1.

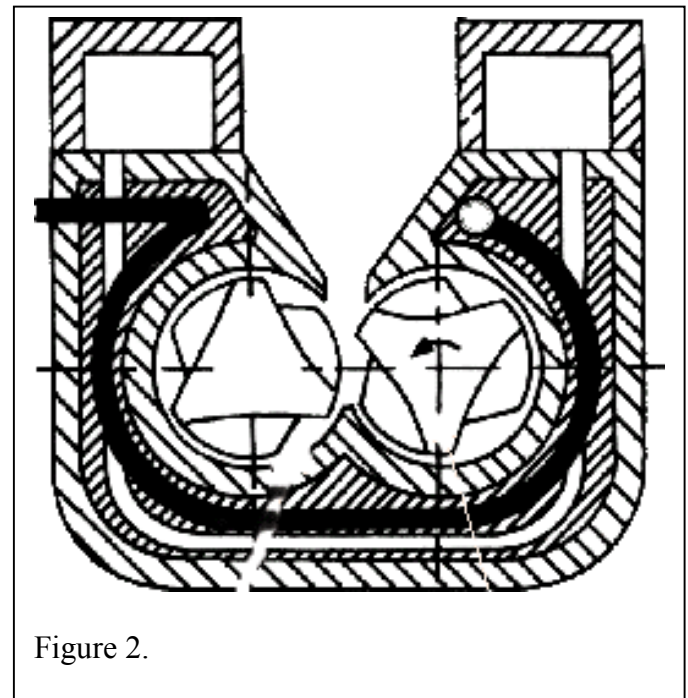


Figure 2.

