

# Electrical Properties of Composites as Affected by the Degree of Mixedness of the Conductive Filler in the Polymer Matrix

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The development of the electrical properties of composites as a function of the degree of mixedness of a conductive filler distributed into an insulating polymer 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 insulating binder and the conductive particles around their mean values as a function of mixing time in an intensive batch mixer. Increasing the time and hence, the specific energy input, during the mixing process results in a more homogeneous spatial distribution of the conductive filler in the polymeric matrix, which in turn results in a decrease of the volume conductivity of the composite. The decreasing conductivity of the composite is attributed to the better coating and hence the isolation of the conductive particles from each other, thus hindering the formation of a conductive network "percolation." Overall, these results suggest that the control of the electrical properties of conductive composites could benefit from a good understanding and adequate control of the dynamics of the mixing process and the resulting degree of mixedness of the conductive particles in the polymer matrix.

## INTRODUCTION AND BACKGROUND OF THE STUDY

Electrically conductive nonmetallic materials are used in various applications including electromagnetic interference (EMI) shielding, adhesives, devices and sensors (1-6). 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 non-conductive 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 as the conductive solid particles are being compounded with the polymer matrix also affects the ultimate electrical conductivity of the composite (6, 7). However, in these earlier studies, quantitative measures that 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.

The original impetus of this work was to investigate, understand, and exploit the relationships between the

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electrical properties of conductive composites and their microstructural distributions for designing novel sensor materials. The approach involved the selection of an appropriate type of conductive filler, tailoring of the particle shape and size distribution, the optimization of the filler concentration, and the selection of a suitable binder. The volume loading levels, which were relevant to the percolation regime of the composite, at which the composite changes from an insulator to a conductor were especially focused upon.

At low conductive filler concentrations, when the conductive filler particles are isolated with "no contact" between them, the composite remains an insulator although its dielectric properties may change significantly. Upon the increase of the conductive filler concentration and the resulting "close proximity" of conductive filler particles, electrons can travel the polymeric gap in between the conductive particles, allowing current to flow i.e., "hopping or tunneling effect" (3, 4). The ability of an electron to jump a gap, under a given voltage field, increases exponentially with decreasing distance of separation between particles. As the conductive filler concentration is increased further, the conductive particles commence to "physically contact" each other, and a continuous network is established. The sharp drop in resistivity is achieved through the generation of a continuous network, which is defined as a "percolation" condition (8-11). The percolation behavior is primarily affected by the surface chemistry of the filler and its wettability by the polymer melt, the rheology of the polymer melt, the details of the solidification process and crystallinity of semicrystalline polymers, and the parameters of the mixing process (3-12).

By definition, the particle concentration at which uniformly distributed particles touch each other is the "maximum packing fraction,"  $\phi_m$ . The distance of separation between the particles decreases as the volume fraction of the filler approaches the maximum packing fraction of the filler. On the other hand, the maximum packing fraction  $\phi_m$  changes with the particle shape and size distribution. The greater the aspect ratio of the particles, the smaller the maximum packing fraction. On the other hand, the broader the particle size distribution of the solid particles, the greater the maximum packing fraction (13, 14). Therefore, the smallest concentration of particles necessary to achieve percolation occurs with high aspect ratio particles (low  $\phi_m$ ). Conversely, the highest concentration of the conductive filler at which percolation occurs is achieved with a broad size distribution of spherical particles (high  $\phi_m$ ). The critical number of contacts between particles necessary to achieve percolation depends on the maximum packing fraction.

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 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. For the first time, 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 are then related to the volume resistivity of the composite.

Initially, a limited amount of work was carried out using spherical aluminum powders and linear low-density polyethylene. However, the electrical properties of the composite specimens with the aluminum powders were plagued by stability problems, i.e., the behavior of the specimens changed from an insulator to a conductor and vice versa depending on the voltage used and time. Unlike aluminum-based composites, the volume resistivity of graphite-based composites at various concentrations remained insensitive to time, and thus the elastomer/graphite system was used as the material of the study.

## EXPERIMENTAL

### Materials

A relatively high maximum packing fraction of the solid phase was aimed at. Thus, the particle size distribution of the conductive powder was tailored to achieve a high  $\phi_{max}$ . A bimodal size distribution of graphite was targeted and two grades of "artificial graphite" powders available from Asbury Graphite Mills, of New Jersey, i.e., "coarse" A-60 and "fine" M-450, were used. The coarse graphite consists of low-aspect-ratio particles with an average particle size of 70  $\mu\text{m}$ . The fine graphite particles are flaky and exhibit higher aspect ratios with an average particle diameter of 5  $\mu\text{m}$ . 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<sup>3</sup>.

The particle size distributions of the two powders were further characterized using computerized image analysis. NIH version 2.1 particle size analysis software was used in conjunction with the assumption of equivalent spherical particles. The results of this analysis are shown in Fig. 1. This mixture provided a relatively high theoretical maximum packing fraction of  $\sim 0.82$  upon application of 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/m<sup>3</sup>, a product of Shell Oil Company with the tradename 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/m<sup>3</sup>. The ratio of

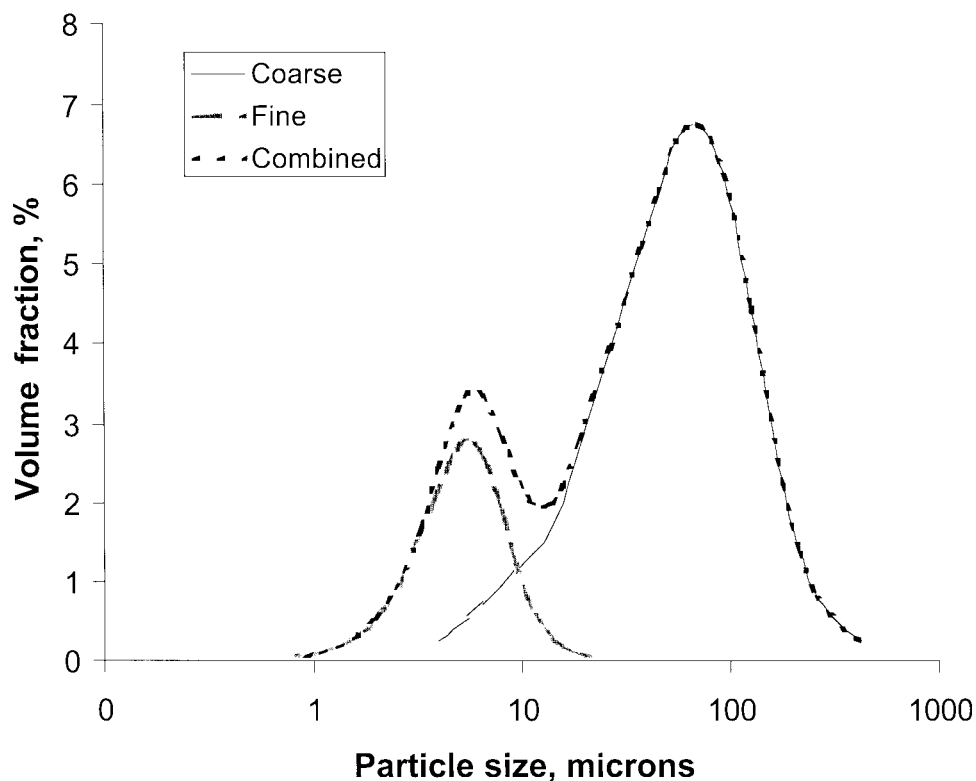


Fig. 1. Particle size distribution of coarse graphite and fine graphite and their mixture.

the oil to the elastomer was varied initially, i.e., the Kraton elastomer was plasticized with 40% and 80% by weight Tufflo oil, representing a plasticizer/elastomer ratio of 0.67 and 4, respectively. Both plasticizer to elastomer ratios were employed to generate the results reported in Fig. 2. However, the rest of the experimental results reported in Figs. 3-7 and Table 1 are obtained with the plasticizer/elastomer weight ratio of 0.67.

The filler powders were mixed with the binder and the plasticizer using a Haake torque rheometer with a 300 ml intensive batch mixer. 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, on the spatial distribution of the conductive filler in the elastomer and the resulting electrical conductivity of the composite. The volume fraction of graphite powder in the composites was varied between 10% and 40%. 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 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

also carried out under vacuum and at 95°C, and at a rotational speed of 64 rpm. The specimens of the composite were removed and sealed in double polyethylene bags upon reaching the predetermined mixing times of 5, 10, 20, 40 minutes. These specimens were then compression molded under vacuum to provide specimens for the characterization of 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 disc-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 at a pressure of 2.75 MPa. The total duration of time during which the melt was kept under the compression molding pressure was five minutes. Sets of three samples were prepared for each concentration to investigate the reproducibility of the measurements. 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 during flow (22-26). All the specimens were sealed in

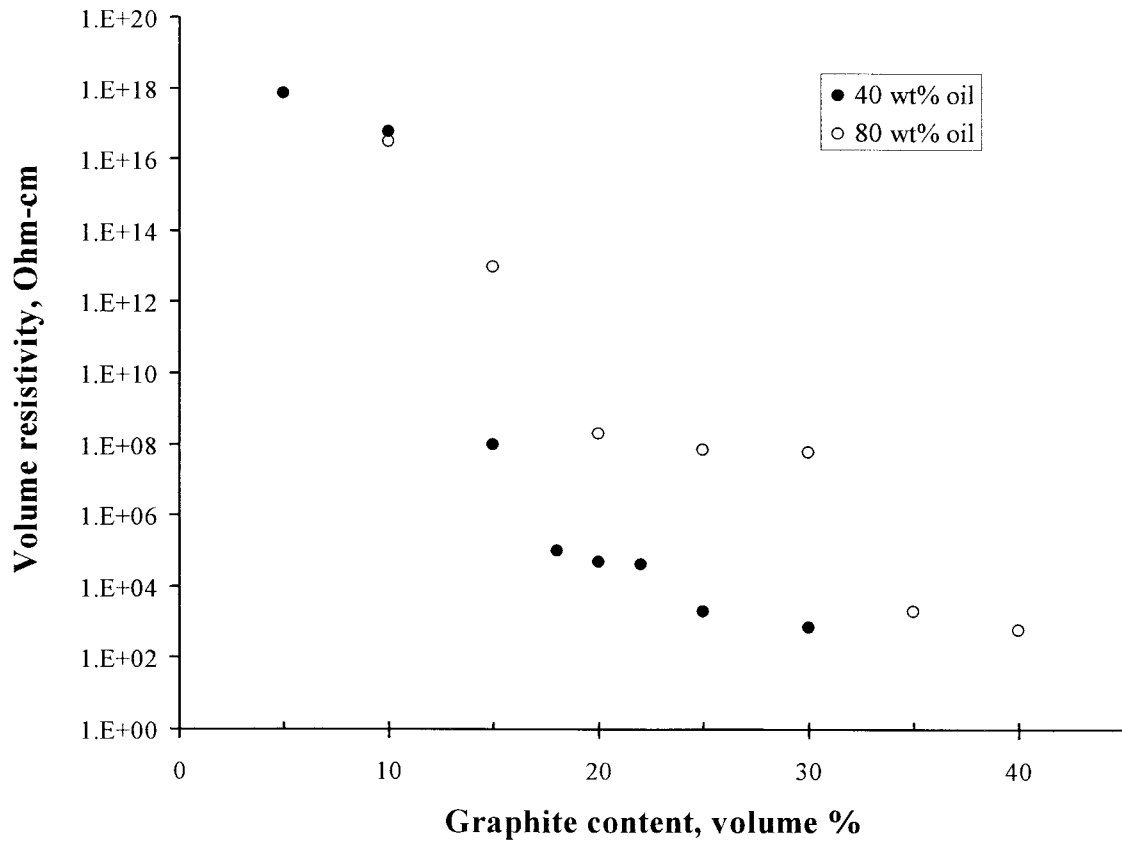


Fig. 2. Volume resistivity versus volume-fraction of graphite.

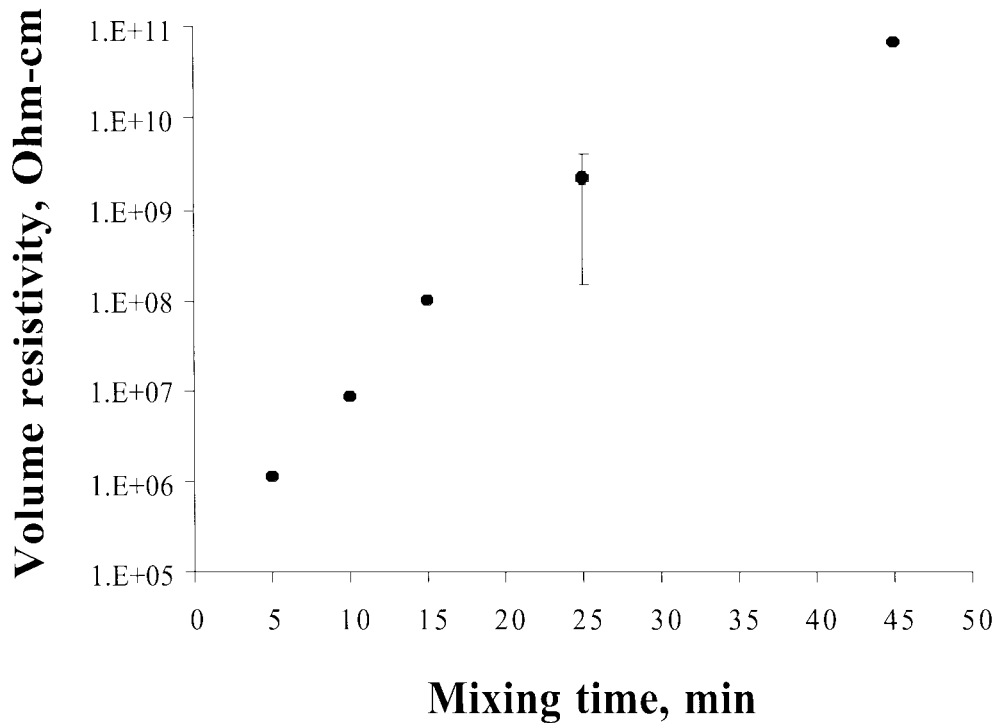


Fig. 3. Effect of mixing time on the development of the volume resistivity (50% by volume elastomer, 35% by volume plasticizer and 15% by volume graphite).

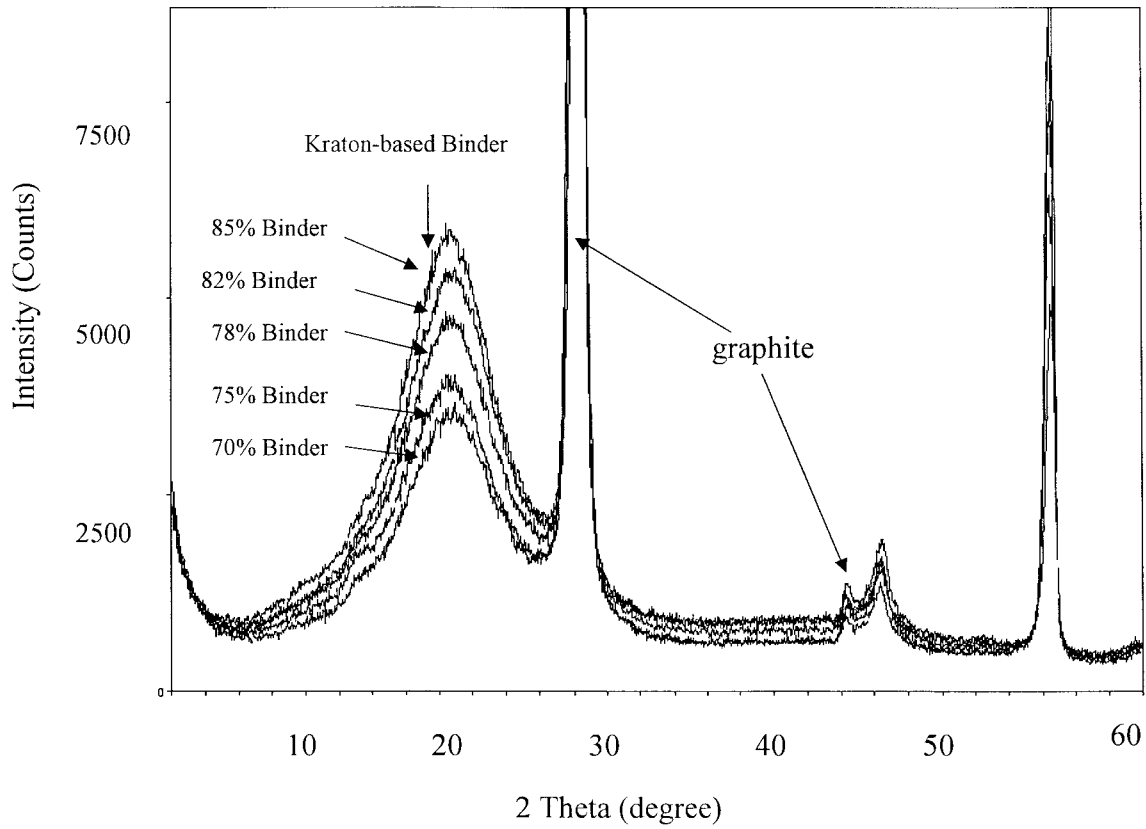


Fig. 4. WAXD patterns of calibration samples with 70, 75, 80, 82, 85 volume percent of graphite.

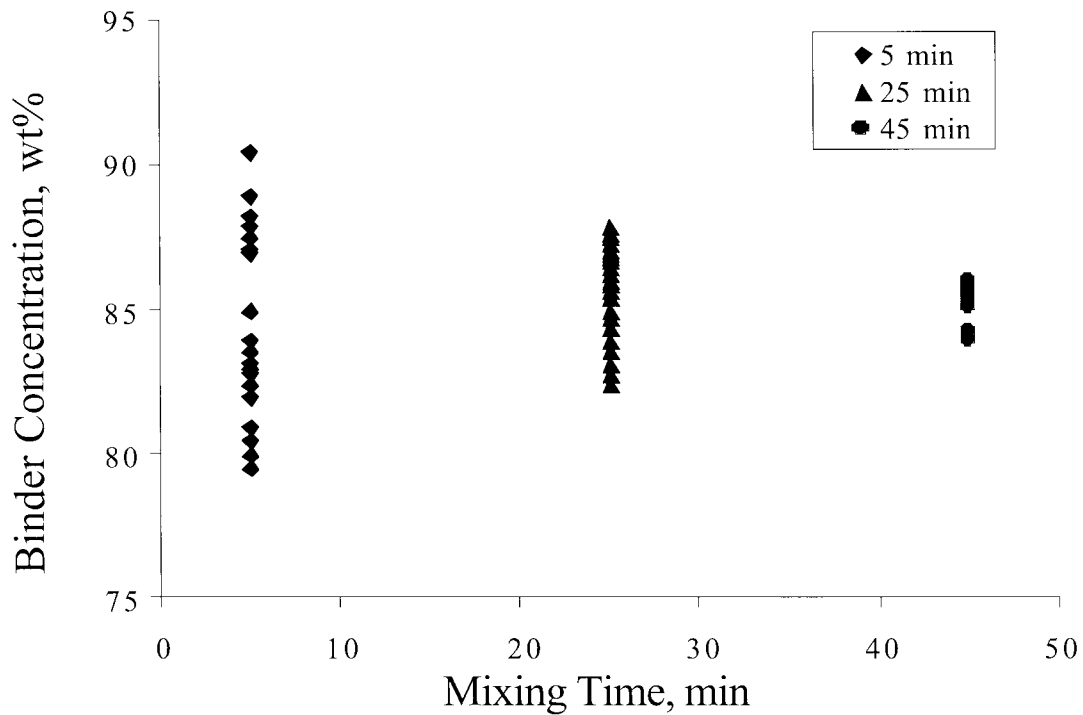


Fig. 5. Scatter of the concentrations of the conductive particles found at various locations in the mixture as a function of mixing time (50% by volume elastomer, 35% by volume plasticizer and 15% by volume graphite).

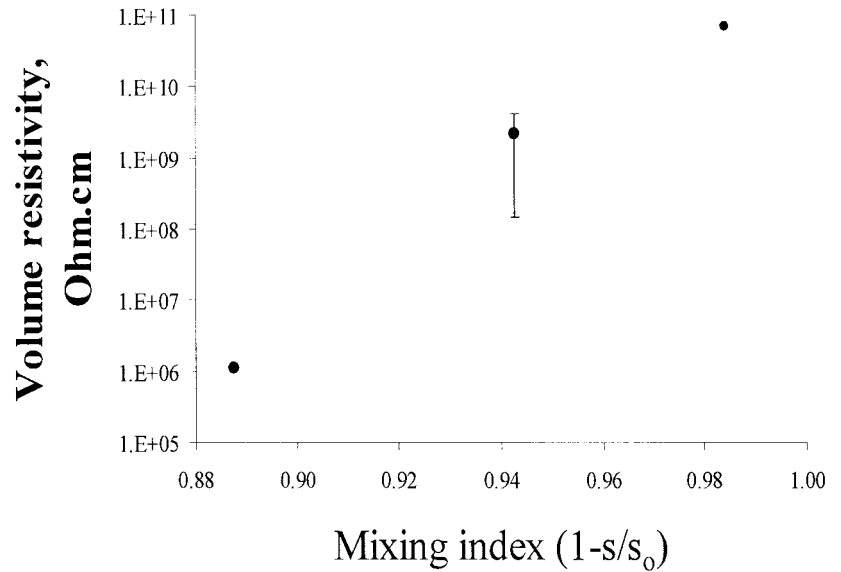


Fig. 6. Volume resistivity vs. the mixing index,  $ML$ .

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 polyethylene bags.

For the measurement of the volume resistivity, ASTM standard D257 (d.c. Resistance or Conductance of Insulating Materials) was followed. A 10V d.c. voltage (as also verified with a Fluke 37 digital multimeter) was applied to the sample, which was placed inside a Keithley resistivity chamber, model 6105, under ambient temperature. The current flowing through the sample was measured with a Keithley picoammeter, model 485. The picoammeter was 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 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 the pressure below a critical 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).

**Sample Preparation and Wide-Angle X-ray analysis of the Specimens for Their Degree of Mixedness**

A disc-shaped mold cavity was used for the preparation of the specimens for their degree of mixedness measurements. The disc-shaped specimens had a diameter of 1" (25.4 mm) and a thickness of 0.078" (2.0 mm). The weight of the specimens was kept constant at 1.1 g. A Carver compression molder was used for

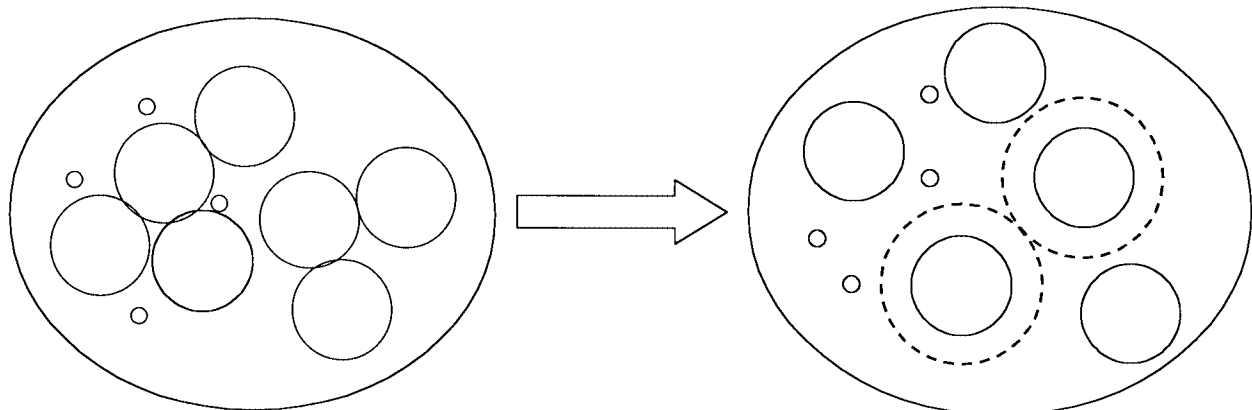


Fig. 7. Schematic representation of the conductive particles being more homogeneously coated with increased mixing time.

**Table 1. Degree of Mixing of the Binder Parameters for the Conductive Composite as a Function of Mixing Time in the Batch Mixer. The Mean Refers to the Mean of the Volume Percentage Values of the Binder (Elastomer and the Plasticizer Oil).**

Degree of Mixing Parameters versus Mixing Time			
	5 min	25 min	45 min
Mean	85.2	84.7	85.1
Standard Deviation	4.0	2.1	0.6
Coefficient of Variation	0.047	0.024	0.007
Mixing Index	0.89	0.94	0.98

the molding of the specimens. The molding was carried out at 100°C. Twenty different samples were prepared for each concentration.

### WAXD Experiments

For X-ray diffractometry, the disc-shaped specimen was placed into a sample holder, which fits into the goniometer of the X-ray diffractometer (a Rigaku wide-angle diffractometer with  $\text{CuK}\alpha$  radiation.) The X-ray generator was operated at 40 KV and 30 mA. The diffractometer scanning speed was one degree per minute. 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 sizes used were 20 mm  $\times$  8 mm (160 mm<sup>2</sup>) and 1 mm  $\times$  8 mm (8 mm<sup>2</sup>) at a Bragg angle,  $2\theta$ , of 90 degrees. It should be noted that the probing area changed during the scan. However, the procedures were kept similar for a fair determination of the relative behavior of the specimens.

### Statistics of Mixing Homogeneity "Degree of Mixedness"

In general, the quantitative description of the mixing quality or goodness of mixing of a given mixture can be obtained by the comparison of the state of the mixture to the most complete mixing state attainable. This complete mixing corresponds to statistical randomness of the ultimate particles of the ingredients being mixed.

If one makes  $N$  measurements of the concentration,  $c_i$ , of one of the components, then the mean concentration is given as:

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

where the mean  $\bar{c}$  should not differ significantly from  $\phi$ , the overall concentration of the components, unless a faulty sampling technique is used. The difference between  $\bar{c}$  and  $\phi$  decreases as the finite number of the characterized samples,  $N$ , is increased. The principal concentration that we have followed in our experiments is the volume fraction of the binder.

A basic measure of the homogeneity of a mixture is the extent to which the concentration values at various points within the volume of the mixture differ from the mean concentration (28–30). The variance  $s^2$ , arising from the individual concentration  $c_i$  measurements, provides such an index to quantitatively assess the degree of mixedness. The variance is given by:

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

A relatively small variance value indicates that most of the samples have concentration  $c_i$  values, which are close to the mean concentration,  $\bar{c}$ , of all samples, thus suggesting a relatively more homogeneous system. The coefficient of variation represents the relative variability of the concentration of the minor component at various locations in the mixture:

$$\text{Coefficient of variation} = s/\bar{c} \quad (3)$$

The maximum variance occurs if the components are completely segregated. The maximum variance is given by (28, 31)

$$s_0^2 = \bar{c}(1 - \bar{c}) \quad (4)$$

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

$$\text{Mixing Index, MI} = 1 - s/s_0 \quad (5)$$

The mixing index thus ranges from zero, for a completely segregated system, i.e., "worst possible degree of mixedness," to one, for a perfectly homogeneous system.

In this study, the mean, variance and the mixing index associated with the values of the volume fraction of the binder were used to characterize quantitatively the goodness of mixing of the conductive composite specimens.

## RESULTS AND DISCUSSION

The volume resistivity versus graphite volume-fraction behavior of the graphite-based conductive composites at ambient temperature is shown in Fig. 2. Here, two binder formulations with weight ratios of plasticizer oil over the elastomer of 0.67 (40 weight% of oil in the binder) and 4.0 (80 weight % of oil in the binder) were mixed at 95°C for 15 minutes with various quantities of graphite to generate a series of formulations with 5 to 40 percent by volume graphite. It is seen that the onset of the transformation from electrically insulating to conductive behavior occurs at a smaller concentration of the graphite when the ratio of the plasticizer oil to the elastomer is smaller, i.e., 0.67.

It can be hypothesized that the reduction in the plasticizer content increases the shear viscosity of the binder during mixing (and hence increases the shear

stress at constant temperature and the dispersive mixing occurring in the mixer, which in turn reduces the agglomerate size of the graphite particles) and gives rise to the onset of conductive behavior at a smaller graphite concentration. This observation of the achievement of substantially different volume resistivity vs. the concentration of the graphite filler behavior with the amount of plasticizer in the binder provided a further impetus for our systematic investigation of the effect of degree of mixedness on the volume resistivity of the conductive composites, which was carried out using the Kraton elastomer plasticized at an oil to elastomer weight ratio of 0.67 and filled with 15% by volume graphite powder (the formulation in volume percentages involves 50% by volume elastomer, 35% by volume plasticizer, and 15% by volume graphite).

The results summarizing the effect of mixing time on the development of the volume resistivity are shown in Fig. 3 with the typical 95% confidence intervals indicated. The volume resistivity of the composite with the incorporated 15% by volume graphite increases exponentially with increasing mixing time. The volume resistivity increases from  $10^6 \Omega \cdot \text{cm}$  at 5 minutes of mixing time to  $10^{11} \Omega \cdot \text{cm}$  at 45 minutes of mixing. How did the degree of mixedness change during the course of 45 minutes of mixing?

Control samples with varying binder concentrations of 70, 75, 80, 82, 85 volume percent were prepared in order to calibrate the X-ray measurements. The typical WAXD patterns of intensity vs. the Bragg angle, obtained from the composite samples (with different concentrations of the binder) are shown in Fig. 4. The diffraction pattern consists of convoluted intensities that emanate from the diffraction signals of the plasticized Kraton binder and the graphite filler. The X-ray measurements of the control samples exhibited an increase in the relative peak intensity of the binder with the relative increase in the binder content. These quantitative phase analysis data from the control samples were used to generate a calibration curve. With this calibration procedure it was possible to quantitatively determine the content of each ingredient, i.e., the concentrations of the binder and the filler in every test sample. The variance of the volume fraction of the ingredient in a given mixture was used as the measure of the "degree of mixedness" of that lot.

The quantitative results of the degree of mixing analysis as a function of mixing time of the composite samples with a nominal 15% by volume graphite are shown in Fig. 5, and the statistical analyses of the results are summarized in Table 1. 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 mixing time. 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 (Table 1).

Since the variation of the volume resistivity as a function of mixing time was also measured a further correlation could be established between the volume resistivity and the degree of mixedness. The relationship between the mixing index and the volume resistivity is shown in Fig. 6 with the typical 95% confidence intervals indicated. The volume resistivity increases with increasing mixing index and decreasing coefficient of variation. To our knowledge this is the first time such a relationship has been generated between the quantitative measures of degree of mixedness of the ingredients of conductive filler/polymer composites and their electrical properties. It is anticipated that such measures can be used in the future to compare and contrast different mixing methods and different sets of operating conditions to improve the consistency and the reproducibility of conductive composites with various shapes.

Figure 7 schematically illustrates our hypothesis to explain these findings. With an increase in 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 lead 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.

## CONCLUSIONS

This study has attempted to link the degree of mixedness of conductive particles compounded into a polymeric matrix with the development of the electrical properties of the composite. The degree of mixedness values of the conductive composite samples were determined as a function of the mixing time in a batch mixer using wide-angle X-ray diffraction, WAXD, and were related to the volume resistivity values of the graphite/plasticized Kraton elastomer. With increased mixing time, the homogeneity of the spatial distribution of the conductive filler in the elastomer is improved and insulating-binder layers around the conductive particles are established, thus resulting in the increase of the volume resistivity of the composite.

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