

Effect of Graphitic Filler Characteristics and Particle Size Ratio on the Percolation Behavior, Microstructure and Electrical Properties of Segregated Network Polymer Composites

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ABSTRACT

Polymer composites can be rendered conducting via the addition of conductive fillers, such as carbon blacks and metallic pigments. Such composites can be used in a wide range of applications as in electromagnetic shielding devices, self-regulating heaters, temperature sensors, as well as in devices that can control and regulate the flow of electrical current. To achieve optimal performance, an ideal interconnected filler network needs to be maintained. Most recent work on polymer nanocomposites has been dominated by work focusing on using single wall carbon nanotubes, multiwall carbon nanotubes, graphite nanoplatelets and graphene. However, many of these filler materials are quite expensive therefore it is desirable to find a way to obtain the needed electrical response at minimal cost, while maintaining the mechanical integrity of the wanted components. A method of producing a segregated microstructure has been developed and will be described here.

Keywords: carbon black, multiwall carbon nanotubes, segregated network composites, PMMA, polystyrene

1 INTRODUCTION

For many years, research focused on creating conducting polymer composites touted the desire to create random networks of the conducting filler. This was primarily driven by the desire to obtain good mechanical properties while electrical conductivity was a secondary goal. However, if what one wishes to obtain is the formation of a continuous network that will allow electrons to have a path to travel throughout the system, such percolation networks can be obtained more easily if one considers the usage of excluded volume concepts[1]. In such systems, one can achieve dramatic decreases in the resistivity of the system (by as many as ten orders of magnitude) that are governed by the properties of the polymer matrix and the conductivity of the filler[2-6]. In previous papers, we have utilized solution mixing, melt-mixing, mechanical mixing and combinations to obtain different percolation thresholds using the same polymer matrix and the same filler type[7-9]. Most of the work has been carried out using polymethyl methacrylate (PMMA)

and polystyrene (PS) as the polymer matrix while the fillers have ranged from ITO and ATO nanoparticles to different grades of carbon black. It has been found that mechanical mixing followed by compression molding results in the best conductivity properties while still maintaining reasonable mechanical properties at the lowest volume fractions of added filler[10].

The percolation threshold is strongly influenced by the precursor materials used and the processing parameters utilized to make the composites [3,7-9]. Not only does the fabrication method used influence the percolation threshold, but the characteristics of the fillers and the size of starting polymer matrix used can also play a role[8,4,10-17]. In this paper, we present results on a series of polymethylmethacrylate (PMMA) composites made by the same exact method but utilizing carbon blacks with different characteristics such as their size and surface area (see table 1). Their response will be compared to behavior of composites made with short multiwall carbon nanotubes which have been extensively characterized as free-standing films [18,19]. At the same time, we will utilize one single carbon black type (CDX 975) and change the size and scale of the polystyrene matrix. It will be shown that the characteristics of the filler affect the speed of the percolation transition, while the size of the polymer matrix has a bigger effect on the percolation threshold as has been predicted before[20,8].

2 EXPERIMENTAL PROCEDURE

Samples were made by mechanically mixing the PMMA polymer beads with the desired amount of graphitic fillers as previously described. After mixing, the composite samples were compression molded at 170°C for 15 minutes using an applied pressure of 20kN. For the polystyrene composites, the starting pellets were broken up with a blender. It was found that a large portion of the PS when broken down to a certain size, could not be further broken down. A coarse sieve was used to separate the relative large polystyrene pieces from the more fine particles. Thus, three different average sized PS were available for making PS composites with different starting PS particles. These were mixed with CDX 975 carbon black for comparing the effect of the starting polymer size and were hot compression molded at the same times and temperatures as the PMMA composites.

3 RESULTS AND DISCUSSION

3.1 Effect of Graphitic Filler Type

Table 1 lists all of the graphitic fillers used and their main characteristics. The three carbon blacks were obtained from Columbian Chemicals Corp (Marietta, GA), Pure black was obtained from Superior Graphite (Chicago, IL) and the multiwall carbon nanotubes were obtained from Cheaptubes.com. The length of the nanotubes ranged from 0.5 to 2.0 μm .

Graphitic Filler	Oil absorption (cc/100g)	Iodine number (mg/g)	STSA (static thick surface area) (m^2/g)	Avg Size (nm)
N-550	121	43	38	50
N-772	65	30	30	50
CDX 975	169	250	131	20
Pure Black	Acetone Absorption 290	45	70	15
MWNT			233	8-15 OD

Table 1. Characteristics of graphitic fillers used

Optical micrographs and electron microscopy images were obtained to confirm the expected segregated microstructure that leads to very low percolation threshold[2]. Previous results had shown that for PMMA composites containing CDX975 carbon black, it was found that a random arrangement of the carbon black resulted in a percolation threshold of 2.7 vol% CB whereas a segregated microstructure resulted in one order of magnitude decrease in the percolation threshold.

Figure 1 displays TEM images of several of the graphitic fillers used in this study. The images presented in Figure 1 were obtained using a JEOL 100CX Transmission Electron Microscope using 100kV accelerating voltage.

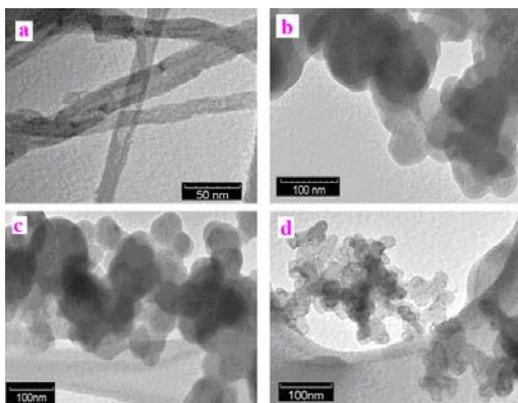


Figure 1. Transmission electron microscopy images of the various fillers used in this study. (a) multiwall carbon nanotubes, (b) N550 carbon black, (c) N772 carbon black and (d) Pure black.

After surface polishing and microstructure characterization, the samples were electroded with Ag paint and then measured using a Solartron 1260 in combination with a Solartron 1296 Impedance Analyzer. Measurements were carried out over the frequency range from 10MHz down to 0.001 Hz using an ac voltage of 500 mV. We also used a Quadtech 1910 Inductance Analyzer for specimens that were highly conducting. Specimens were approximately 2mm thick and had a diameter of 2.7 cm. These dimensions were used to convert the measured real and imaginary impedance to the corresponding resistivity or conductivity. The frequency dependence was as expected, with the samples that hadn't yet percolated showing a strong frequency dependence which slowly disappeared as the percolation threshold was reached and then exceeded[2]. The complex impedance behavior revealed many interesting trends which are related to changes in the interfaces between the contacting graphitic fillers and mirrored some of the trends described in measurements of free standing carbon nanotube films and that of other graphitic fillers[18,19] but will not be included here due to space limitations.

The calculated resistivity for the four new graphitic fillers evaluated for this study with PMMA as the matrix are shown in Figure 2. It is clear that the percolation threshold for the samples containing MWNT occurs very early, whereas the behavior for the three other graphitic materials are closer in value but are nevertheless different. For example, the Pure black filler appears to have a more ideal percolation curve, presumably because the average size of these fillers is less polydisperse than those of the N550 and N772 carbon blacks whose aggregates vary in size(see TEM images in Fig. 1). It is interesting to also notice that once percolation has taken place, the behavior of all four conducting fillers appears to converge suggesting that the fully interconnected percolated network is very similar in all cases. These results are in agreement with the trends reported in freestanding films made with graphite flakes, carbon black, single wall and multiwall carbon nanotubes [19].

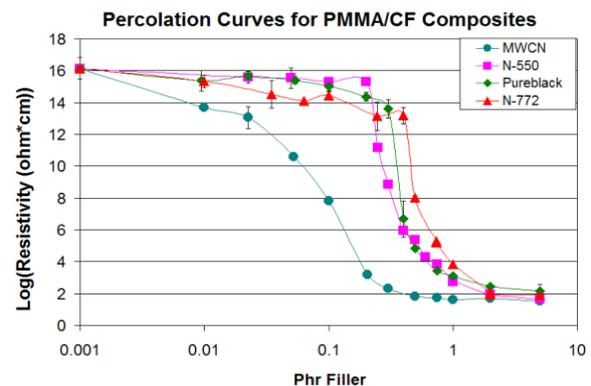


Figure 2. Log resistivity versus log of the filler content curve demonstrating that the MWNT can achieve percolation at a much lower filler content than any of the carbon black fillers used.

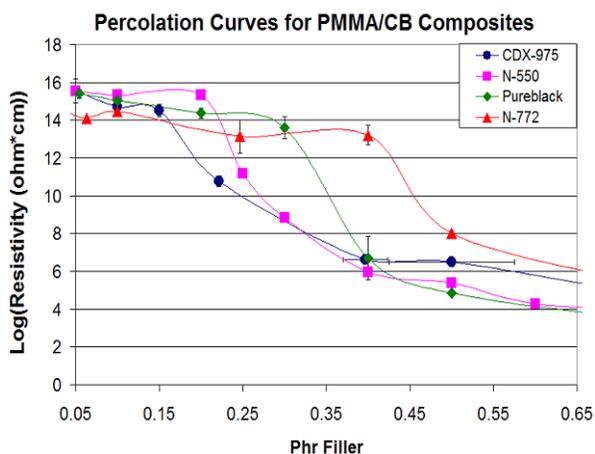


Figure 3. Expanded log resistivity vs filler content curves for all carbon black types evaluated as fillers in PMMA. The details of when they percolate appear to be related to their average size.

Figure 3 demonstrates that expanding the region where the various carbon black composite responses are located can be more clearly distinguished from one another. Data for composites containing CDX 975 carbon black has been added for additional comparison. The three Columbian Chemicals carbon blacks show that their percolation threshold is a function of their average particle size. In contrast, the behavior of the Pure black does not seem to follow the same pattern. However, since Pure Black is expected to have more perfect graphitic structures, it is not surprising that composites made with them achieve the lowest resistivities earlier. Please note that in Figure 3, we are not showing the lowest achievable resistivities, which were displayed in Figure 2.

3.2 Effect of Polymer Matrix Size

As described earlier, we used polystyrene to conduct this portion of the experiment because it was found that PS is easy to break up and separate into PS particles of different sizes. In this case, only CDX 975 was used as the filler. The approximate size for the three different PS sizes used to make the composites are displayed in Figure 4. The percolation curves shown in Figure 5 clearly demonstrate that for the same filler type and processing procedure, it is the size of the polymer matrix that controls the percolation behavior, with the largest PS matrix giving the lowest percolation threshold and the smallest PS matrix particles giving the largest percolation threshold.



Figure 4. Optical pictures of the PS polymer matrix sizes used to make the composites with CDX 975 CB.

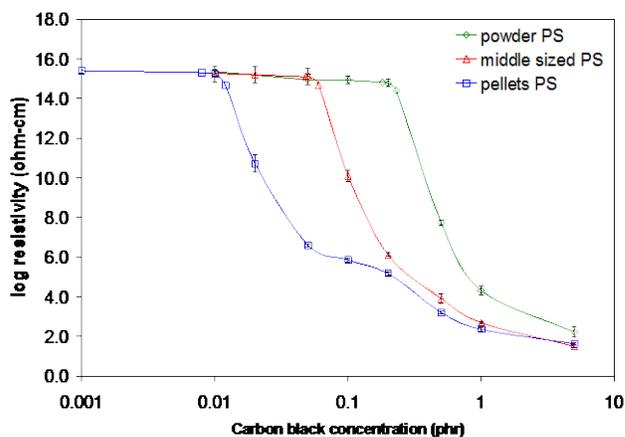


Figure 5. Log resistivity vs carbon black content for PS matrix composites containing the amounts of CDX 975 CB indicated.

To help understand the process, we present Figure 6 where images displaying the PMMA precursor materials(a) and their characteristic fracture surfaces are shown in (b) when they are compression molded by themselves. Part (c) demonstrates an optical transmission image displaying the location of the conducting fillers and part (d) illustrates the fractured surfaces of the segregated network composites which can achieve conductivities as high as 10^{-2} S/m. These properties can be obtained with most nanofillers evaluated. The expected percolation threshold can be estimated by taking the ratio of the nanofiller size to the polymer precursor particle[8,20] and provides a simple method for obtaining nanocomposites with controlled electrical behavior that may be useful for a wide variety of applications such as electromagnetic interference shielding, temperature sensors and many others.

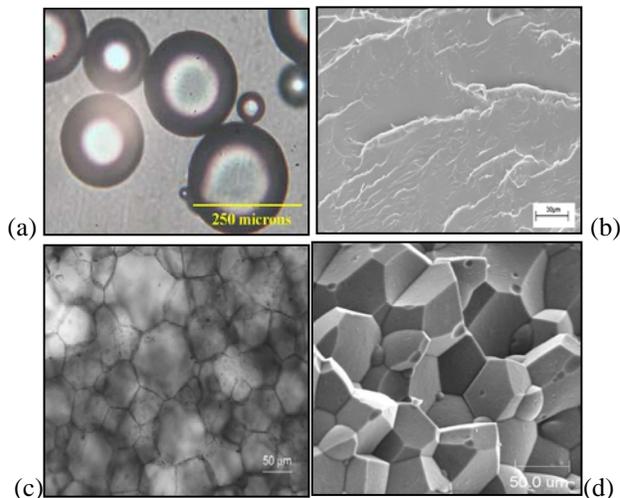


Figure 6. Spherical free standing PMMA particles (a), Fracture surface of compressed neat PMMA particles(b), Optical transmission image of nanofiller segregated network in PMMA(c), Fracture surface of a nanofiller segregated network composite.

4 CONCLUSIONS

The results described in this article are in agreement with the prediction that as the size of the excluded volume provided by the polymer matrix increases, the percolation threshold decreases when the filler used is the same[8]. If the filler characteristics change, then the expected response also changes accordingly. It should be remembered that looking at the dc percolation properties only provides part of the story and that for multicomponent materials such as polymer composites, it is important to also investigate the effect of frequency on the resultant responses[21,2]. The behavior as a function of frequency is controlled by the distribution of the conducting fillers and their quality of contact between them[21, 22].

5 Acknowledgements

This work was funded by NSF under DMR-0604211. E.A. Lucas was funded by the Fort Valley State University Summer REU program and K. Alston was supported by a GIFT Summer Experiences for Teachers in the State of Georgia. Ms. Yolande Berta is acknowledged for acquiring the TEM images displayed in Figure 1.

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