

# Maximum Conductivity of Packed Nanoparticles and Their Polymer Composites

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**ABSTRACT** Adding conductive fillers to nonconductive polymers is a common way to make soft conductive materials such as conductive adhesives. An important issue is how to achieve high volume conductivity with acceptable mechanical performance. Two questions pertaining to this issue were studied in this paper. One question was whether the maximum conductivity benefits from larger or smaller particle sizes. The second was what is the maximum achievable conductivity. One incentive for this work is the recent availability of nanomaterials that provide opportunities to make conductive composites using much smaller particles than in the past. We found that the conductivity of platinum, carbon black, and silver particles in their polyurethane composites did not vary greatly with particle size (from micrometer to nanometer range). What was unexpected was that in all the composite examples, the highest conductivity achieved was only on the order of 1 % of that of the pure bulk conductive materials. Further experiments to emulate these conductive composites with platinum, carbon black, copper, and nickel particles without polymer matrix showed similar results, indicating the issue is not simply dispersion homogeneity, nano versus macro particles, particle connectivity/percolation, or the presence of the matrix materials. We interpret this to mean that the composite systems are intrinsically limited by the contact between filler particles.

**KEYWORDS:** Nanocomposite • nanoparticle • conductivity • contact

## INTRODUCTION

Compounding conductive fillers into nonconductive polymers is a routine method to make polymers electrically conductive while still maintaining their polymeric characteristics. Carbon black, carbon fiber, silver, and other metallic particles have often been used as fillers. Recently, nanosized versions of these and other materials including carbon nanotubes have become available. Some of these have been studied extensively for conductive composite applications (1–13). Some research has reported that carbon nanotubes in polymer matrices can become conductive at much lower filler concentrations than if spherical fillers are employed. However, the typical conductivity of carbon nanotube composites after the percolation transition was still only about  $1 \times 10^{-5}$  to  $1 \times 10^{-1}$  S/cm (8, 9), which is in a range similar to that of carbon black. These observations lead to questions about how conductive a nanocomposite can be made, and what factors limit the ultimate conductivity of such composites.

The limiting conductivity is as critical as percolation transitions when considering conductive composites for applications. For example, the ultimate conductivity is often a central issue for conductive adhesives; loading levels high enough to produce high conductivity usually compromises the adhesive and cohesive strengths of these materials. The

same is true for conductive materials for biomedical applications in which it generally is challenging to achieve both high conductivity and high mechanical toughness at same time.

To address these issues and determine if there are optimum ways to design conductive composites, we developed simple conceptual models to clarify key principles and then used these models to guide our thinking to interpret conductivity measurements of conductive fillers and their polymer composites. We were interested in understanding the conductivity of the pure fillers because they would seem to define the ceiling of the conductivity for the composites. The fillers we chose include nanoparticles (carbon and platinum), micro particles (silver and copper), and macro-particles (nickel).

## EXPERIMENTAL SECTION

**Materials.** The conductive fillers used in the present studies include platinum (Pt), silver (Ag), carbon black (CB), copper (Cu), and nickel (Ni) particles (Table 1). Also listed are the conductivity and density of the parent bulk materials (14). The micrographs of the filler materials were obtained with scanning electron microscopy (Jeol 5900). The filler particles were immobilized by a conductive tape and were directly imaged. As shown in Figure 1, the particle sizes of the fillers range from 50 nm to a few hundred micrometers. The surface compositions of the filler particles (such as oxidation layers and organic coatings) were determined with electron spectroscopy for chemical analysis (Physical Electronics Quantum 2000 Scanning ESCA, MN). The X-ray source was monochromatic Al K $\alpha$ . The carbon 1s peak in C–C and C–H was set to 284.8 eV for charge correction. The results indicated that there were 14 at % carbon in the Pt particle surface. This amount of carbon is equivalent to about 1 atomic layer or less of organic coating in the Pt particle surface (15). No oxidation layer was detected in the Pt surface. The results also showed that there was a 3 nm thick oxidation layer

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Table 1. Conductive Fillers Used in This Work

materials	sources	average particle sizes	particle purity (%)	density of bulk material (g/cm <sup>3</sup> )	conductivity of bulk material (s/cm)
Pt	Nanophase, Romeoville, IL	50 nm		21.5	$1 \times 10^5$
Carbon black	Cabot Corp., Billerica, MA	50–100 nm	100	1.78	$1 \times 10^3$
Ag	SigmaAldrich, WI	2–3 $\mu\text{m}$	99.9	10.49	$6.3 \times 10^5$
Cu	AEE, Bergenfield, NJ	~3, 10, and 40 $\mu\text{m}$	99.9	8.94	$6.0 \times 10^5$
Ni	AEE, Bergenfield, NJ	4–8, ~44, and ~149 $\mu\text{m}$	99.9	8.91	$1.4 \times 10^5$

in the Ni particles, an atomic layer of oxidation layer in the Cu particles, and almost no oxidation in the Ag surface. There was no organic coating detected in the Ag, Cu, and Ni particle surface. All the filler samples were used as received.

Polyurethane was used as the matrix material to make composites in the present study. This polyurethane was prepared through a condensation reaction using 4,4-methylene bisphenyl diisocyanate (MDI), polytetramethylene oxide (PTMO, 1000 g/mol), and 1,4-butanediol (BDO). The hard segments are made from MDI and BDO and the soft segments made from MDI and PTMO. The molar ratio of PTMO to BDO used was 1:3.2, which is equivalent to a composition of 53 wt % soft segments and 47 wt % hard segments. The target molecular weight of this polyurethane was 56 kg/mol.

The composites were made using solvent blending. The polyurethane was dissolved in tetrahydrofuran (THF) at a 5 wt % concentration at room temperature. Various fillers were dispersed in the polyurethane solution by manual stirring, followed by mixing with a rotational mixer at 3000 rpm for 1 min (DAC150, FlackTek Inc., SC). The suspensions were cast onto polytetrafluoroethylene (PTFE) sheets and dried in a nitrogen-purged environment for at least two days.

**Measurements.** The impedance of the composite samples was measured using DC excitation with a Keithley Multimeter (2002, Cleveland, OH). The impedances of fillers were measured with both DC and AC excitation (100 Hz, and 1, 10, and 10 KHz with Quadtech 1730 LCR, Digibridge, NY). The filler samples were loaded into a cylindrical nonconductive cavity (3

mm diameter) that was placed on the surface of a silver sheet (one electrode). A silver rod (3 mm diameter, the other electrode) was inserted into the cavity from the top after the filler was added. The entire assembly, including the silver rod, filler loaded cylinder, and bottom silver sheet, was placed between two clamps of a compression testing machine (MTS, MN). Packing density and impedance were measured at the same time an increasing compression force was applied to the filler samples.

## RESULTS

The conductivity of the composites, measured using DC excitation, is summarized in Figure 2A. As expected, all the composites had nonconductive to conductive transitions or percolation transitions when the filler concentrations reached about 10–20 vol %. As filler concentrations increased, the conductivity continued to increase. But the conductivity of individual composites differs from each other. For example, the conductivity of silver composites was about 2 orders of magnitude higher than that of the carbon black composites. However, if the conductivity of each composite was normalized to the conductivity of the bulk materials (e.g., the conductivity of silver composites was normalized to the conductivity of bulk silver), all the composites followed a similar trend; the normalized conductivity approaches

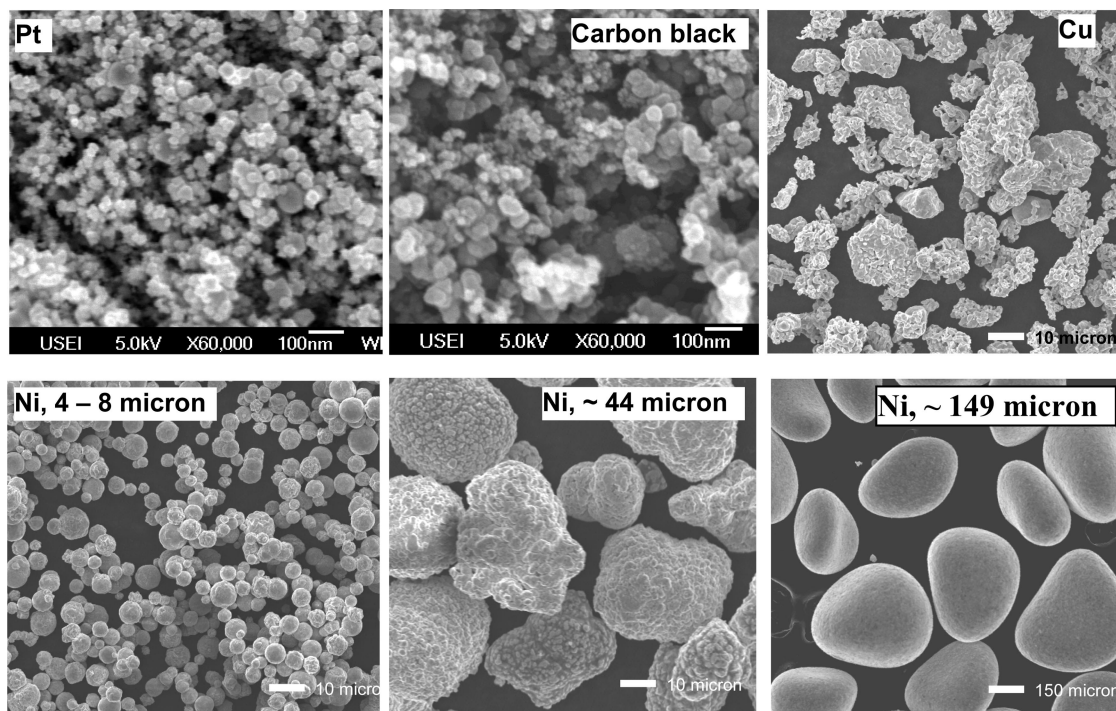
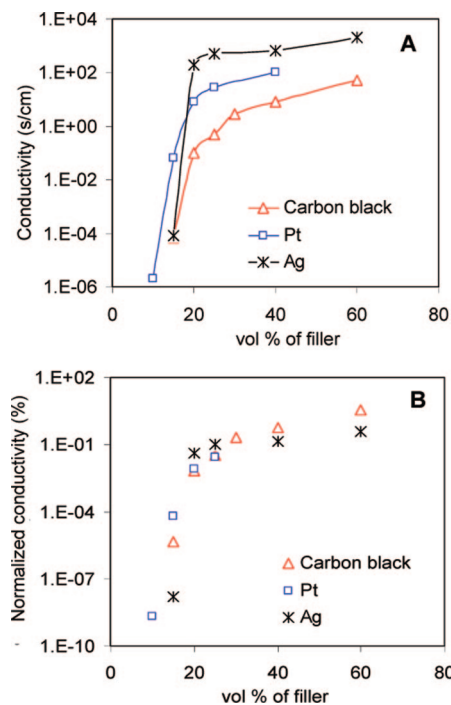


FIGURE 1. SEM of platinum (Pt), carbon black (CB), copper (Cu, about 3  $\mu\text{m}$ ), nickel (Ni with the as-received average diameters being 2–4, about 44, and about 149  $\mu\text{m}$ ). Notice that scale bar sizes are different because of the particle size differences.

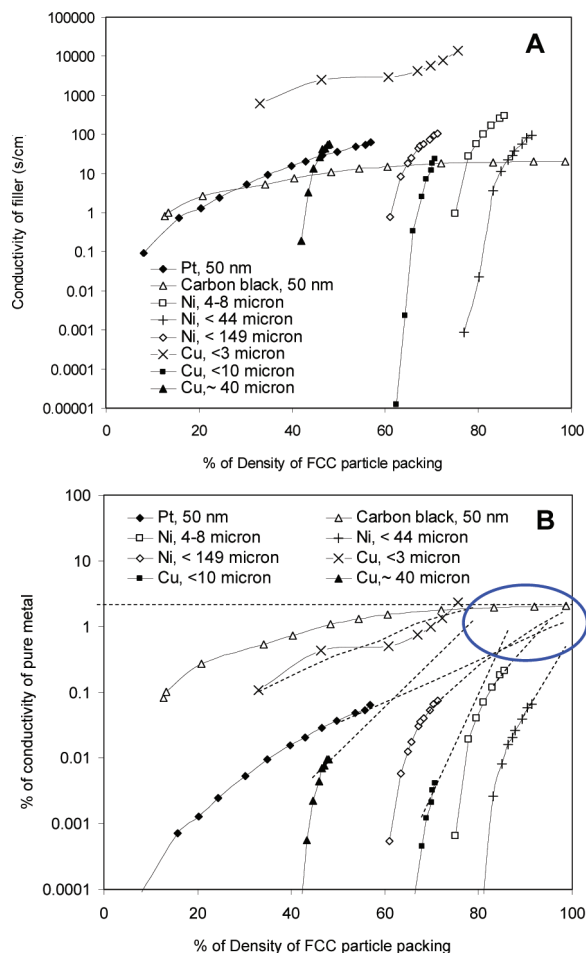


**FIGURE 2.** (A) Conductivity of polymer/filler composites as functions of volume fraction of fillers. (B) Composite conductivity normalized to that of the bulk fillers as functions of volume fraction of fillers.

0.1–1 % of the bulk conductivity regardless of the fillers (carbon black, silver, or platinum), filler particle sizes (50 nm to 1  $\mu\text{m}$ ), or surface coatings (a thin organic coating in Pt particles but no coating in Ag and CB). This suggests a question: why is only 0.1–1 % of the bulk conductivity achieved even when the filler concentration approaches 60 vol %?

To help address this question, we measured the conductivities of the pure fillers. It was assumed that the packed fillers would set the ceiling conductivity for their composites. The fillers are powders and have very low packing densities. Hence, a compressing force was applied to these samples to increase their packing densities. The particle packing in these studies is probably not regular; however, it is useful to reference what would be expected if they packed in FCC or hexagonal lattices. Because such lattices have a maximum density (74 % of bulk), one might expect the pure fillers to have conductivities about same fraction of the bulk solid materials.

Figure 3A shows the conductivity of packed fillers as function of packing density that was normalized to their FCC packing density (74 % of bulk density). As shown, the measured conductivity of individual fillers varied greatly with their packing density. For example, the conductivity of copper at high packing densities differs by almost 3 orders of magnitude from that of carbon black. However, when the conductivity of the packed fillers was normalized to that of the bulk materials (Figure 3B), one finds some interesting results. First, even though individual fillers are morphologically significantly different, the normalized conductivity approaches a similar range of values as packing density reaches 100 % of the FCC density (Figure 3B). Second, the “highest” normalized conductivities of all the fillers are on

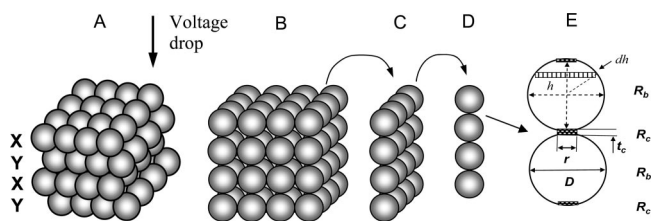


**FIGURE 3.** (A) Conductivity of individual fillers as functions of packing density that was normalized to the bulk density. (B) Conductivities of fillers normalized to that of the bulk materials as functions of normalized packing density. Note that all plots tend to converge on the normalized value of 0.1–1 % of bulk conductivity.

the order of 0.1–1 % of that of the bulk materials regardless of filler types, particle sizes, and surface oxidation layers. This ultimate value was much lower than can be explained on the basis of packing inefficiency. However, this trend and the ultimate value for pure filler particles were consistent with the observations in the composites shown in Figure 2, where the highest conductivity approaches 0.1–1 % of that of the bulk materials. The Ag particles were also tested but not included in Figure 3. The Ag particles were too soft and sintered under the applied forces.

## DISCUSSION

To get a better understanding of the issues involved in interpreting the results described above, we present very simple conceptual models to help sort out what is important about these systems. As shown in Figure 4A, we assume particles in an FCC lattice to approximate the above filler particles that were packed by compression force. However, a FCC lattice is complicated to use to estimate impedance. A simple cubic (SC) lattice is relatively simple; for this reason, we first calculated impedance with a SC lattice (Figure 4B), then later return to the FCC lattice. We assume voltage is



**FIGURE 4.** Conceptual model of packed filler particles for estimating impedance. A, face centered cubic (FCC) packing of spheres. The packing is composed by alternatively stacking layer X and Y. (B) Simple cubic packing (SC). (C) Layer of packed spheres from SC packing. (D) Chain of spheres from the layer (C). (E) Impedance of two contact spheres (in D). A slice of sphere ( $dh$ ) is indicated in the upper one.

applied from top to bottom of the lattice (as indicated in Figure 4). This SC packing of particles can be separated into layers (Figure 4C), which can be further separated into chains of stacking particles (Figure 4D). The impedance of an individual particle was approximated in the following way.

As shown in Figure 4E, two spheres in contact are modeled as two spheres with a contacting layer between them. The impedance from one sphere to the other is the sum of the volume resistance of the spheres ( $R_b$ ) and the contact impedance ( $R_c$ ). The volume resistance of spheres can be calculated on the basis of the bulk resistance. The resistance of the contact layer can be due to a few reasons. One reason can be electron tunneling from one sphere surface to the other. Other reasons include organic coating, oxidation layers in surface, and surface roughness induced inefficient contact. In this paper, we use the contact layer to represent the sum of all these possible reasons. Let the contact area between two spheres be  $\pi r^2$  ( $r$  being the diameter of the contact area). This diameter approximately is

$$r^2 = Dt_c \quad (1)$$

where  $D$  is the sphere diameter and  $t_c$  is the contact layer thickness. Typically, tunneling distance ranges up to 5 nm (16–19). In the present paper, the thickness of organic coating or oxidation layers in the Pt, C, Cu, or Ni is less than 3 nm. Then, we take  $t_c \approx 5$  nm. It should be noted that eq 1 requires that  $D > t_c$ .  $D$  for most of the fillers used here was 50 nm or greater; hence this condition was met. The impedance of the contact is reciprocal to the contact area, or

$$R_c = \rho_c / (\pi Dt_c) \quad (2)$$

Where,  $\rho_c$  is a constant characterizing the impedance of contact. The unit of  $\rho_c$  is Ohm  $\text{cm}^2$ .

The impedance of the particle volume can be calculated by integrating the impedance of a slice over a whole particle (a slice,  $dh$ , is indicated in the top particle in Figure 4E). The impedance of the slice is  $\rho dh / (D^2 - h^2)$ , where  $\rho$  is resistivity of the bulk material (its unit is Ohm cm). The impedance of the whole particle is

$$2 \int_0^{D/2-t_c} \rho dh / (D^2 - h^2) = 2\rho / (\pi D) \ln(D/t_c) \quad (3)$$

Then, the total impedance of the contacting sphere is the following.

$$R_s = (2\rho/D\pi) \ln(D/t_c) + \rho_c / (\pi Dt_c) \quad (4)$$

The impedance of the entire chain of particles is proportional to the number of particles, or  $R_s(L/D)$ , where  $L$  is the chain length. The impedance of the whole SC particle pack is equal to that of all the chains arranged in parallel;  $R_s(L/D)/(L/D)^2 = R_s(D/L)$ . Substituting  $R_s$ , we have the impedance ( $\rho_p$ ) of particles packed in SC lattice

$$\rho_p = R_s(D/L)(L^2/L) = (2\rho/\pi) \ln(D/t_c) + \rho_c/\pi t_c \quad (5)$$

The first part of the impedance of packed particles (eq 5) is the contribution from particle volumes or the bulk impedance. It indicates that impedance decreases (or conductivity increases) very slowly (logarithmically) with decreasing filler size. For example, if the particle size is 0.15 mm (Ni particles, Table 1), the normalized impedance of the SC packed particles is about  $7\rho$  ( $t_c = 5$  nm). If the particle size is reduced to 50 nm (Pt and carbon black, Table 1), this value is about  $1.5\rho$ . This suggests that with decreasing particle size, the impedance of packed particles should decrease very slowly, getting close to the bulk material at the nano scale. If this volume (or bulk) impedance were the only contribution, the conductivity of packed filler particles would increase from about 15% to 67% of the bulk material when particle sizes decrease from 0.15 mm to 50 nm. Comparing this to the above measurements, where the maximum conductivity of the packed fillers is only 1–2% that of the bulk materials regardless of particle size, makes us believe that the volume impedance is even not a major contribution to the impedance of the packed fillers.

On the basis of eq 5, the alternative explanation for the low conductivity of the fillers would seem to be that the impedance of contacts between particles makes up the major contribution to the increased impedance of packed fillers. By considering only the contact impedance of eq 5, the normalized conductivity is

$$\bar{\sigma}_p \approx \frac{\pi \rho t_c}{\rho_c} \quad (6)$$

This equation suggests that the normalized conductivity of packed particles is independent of their size regardless of whether they are nanoparticles or microparticles. Such a model suggests that the impedance of packed particles is mainly due to the contact resistance between adjacent particles. It explains the experimental observations that the highest conductivity of packed fillers was independent of particle sizes. A similar conclusion has been discussed in the literature on the basis of silver and other materials (20–22).

The impedance of an FCC lattice can be estimated similarly to the simple SC model above. In the FCC lattice, each particle contacts 12 other particles, six in the same layer (Figure 4A), three in the layer above, and three below. If voltage is applied as indicated in Figure 4, there is no current driven within the same layer; the current flows from the three upper particles to lower ones in parallel. Then, the impedance of each particle would be just one-third of that as in the SC lattice. If a voltage is applied in a different orientation, the impedance is different. For experimentally packed fillers, the orientation most likely is random. Equations 5 and 6 are still applicable but will have a prefactor that is an average over all the possible directions. This

prefactor should be between 1 and 1/6 because the minimum number of conducting path is 1 and the maximum is 6 (by 12 contacting particles) for particles in an FCC lattice. Mont Carlo simulation could be used to determine this prefactor. Indeed, White et al. have performed such a simulation study on conductivity near the percolation transition of carbon nanotubes (23). This method could be extended to high packing density cases, like in this study.

A question that has not been discussed is why the ratio of contact conductivity to bulk conductivity of different materials seems to be similar. As mentioned above, the contact conductivity of particles is a sum of contributions from electron tunneling, organic coatings, oxidation layers, and surface roughness. It is known that effects of oxidation layers on electric conductivity can be reduced by microdeformation or cold microwelding (due to mechanical compression). The effects of surface organic coatings and surface roughness can be reduced similarly. If these cold deformation and welding mechanisms work in the present filler examples, we would speculate that when the packing densities of the fillers are increased by applying compression force the effects of organic coatings, oxidation layers, and surface roughness on contact conductivities are reduced. When the fillers reach their maximum packing densities, the contact conductivities of the filler particles are mainly due to the tunneling effects. The ratio of tunneling conductivity ( $\sigma_t$ ) to bulk conductivity ( $\sigma_b$ ) is a function of tunneling energy barrier ( $E$ ) and applied voltage ( $V$ ) (24)

$$\sigma_t / \sigma_b \approx e^{-E/V} \quad (7)$$

The tunneling energy barrier is related to the work functions of filler materials. Interestingly, the work functions of Pt, carbon, Cu, Ag, and Ni are within a narrow range from 4.5 to 6 eV (25). The applied voltage ( $V$ ) is set to a constant. Therefore, the ratios of contact conductivity to bulk conductivity of different materials might approach a similar range of values when they reach their maximum packing densities. The observations in Figure 3B seem to support this speculation. However, to fully understand this issue, more detailed and controlled experiments have to be designed. For example, one may measure contact conductivity as a function of compression force with macroscopic specimen that have well-controlled oxidation layer and organic coating to understand how the tunneling, oxidation layer, and coating contribute to the conductivity.

The ratio of maximum contact conductivity to bulk conductivity of Pt, C, and Ag seems to be similar in their composites as well (Figure 2B) though the Pt particles have a thin layer of organic coating but the C and Ag particles do not. Polymer coating may increase the tunneling energy barrier and cause increase of contact impedance. But the

organic coating in the Pt particles is thin (one atomic layer) compared to a typical tunneling distance (<5 nm). The effects of this coating may be insignificant.

It also seems fairly clear that the direct use of nanosized materials does not provide a way to improve the making of conductive composite materials. However, if filler contact density can be reduced by sintering or using high-aspect-ratio fillers, high conductivity can be accomplished. (20–22)

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## REFERENCES AND NOTES

- (1) Barrau, S.; Demont, P.; Peigney, A.; Laurent, C.; Lacabanne, C. *Macromolecules* **2003**, *36*, 5187.
- (2) Sandler, J.; Shaffer, S. P.; Prasse, T.; Bauhofer, W.; Shulte, K.; Windle, A. H. *Polymer* **1999**, *40*, 5967.
- (3) Allaoui, A.; Bai, S.; Cheng, H. M.; Bai, J. B. *Compos. Sci. Technol.* **2002**, *62*, 1995.
- (4) Shaffer, M. S. P.; Windle, A. H. *Adv. Mater.* **1999**, *11*, 937.
- (5) Kotaki, M.; Wang, K.; Toh, M. L.; Chen, L.; Wang, S. Y.; He, C. B. *Macromolecules* **2006**, *39*, 908.
- (6) Nogales, A.; Broza, G.; Schulte, R.; Sics, S.; Hsiao, B.; Sanz, A.; Garcia-Gutierrez, M.; Rueda, D.; Domingo, C.; Ezquerro, T. *Macromolecules* **2004**, *37*, 7669.
- (7) Potschke, P.; Abdel-Goad, M.; Alig, I.; Dudkin, S.; Lellinger, D. *Polymer* **2004**, *45*, 8865.
- (8) Du, F.; Scogna, R. D.; Zhou, W.; Brand, S.; Fischer, J.; Winey, K. *Macromolecules* **2004**, *37*, 9048.
- (9) Winey, K. I.; Kashiwagi, T.; Mu, M. F. *MRS Bull.* **2007**, *32*, 348.
- (10) Bryning, M. B.; Islam, M. F.; Kikkawa, J. M.; Yodh, A. G. *Adv. Mater.* **2005**, *17*, 1186.
- (11) Sandler, J. K. W. *Polymer* **2003**, *44*, 5893.
- (12) Callister, W. D. *Materials Science and Engineering. An Introduction*, 5th ed.; John Wiley & Sons: New York, 2000.
- (13) Harris, P. F. *Carbon Nanotubes and Related Structures. New Materials for the Twenty-First Century*; Cambridge University Press: Cambridge, U.K., 1999; p 130.
- (14) Lu, Q.; Keskar, G.; Ciocan, R.; Rao, R.; Mathur, R.; Rao, A.; Larcum, L. J. *Phys. Chem. B* **2006**, *110*, 24371.
- (15) Stickle, W.; Sobol, P.; Bomben, K.; Moulder, J. *Physical Electronics Handbook of X-Ray Photoelectron Spectroscopy*; Physical Electronics Inc.: Chanhassen, MN, 1992.
- (16) Simmons, J. G. *J. Appl. Phys.* **1963**, *34*, 1793.
- (17) Beebe, J. M.; Engelkes, V. B.; Miller, L. L.; Frisbie, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 11268.
- (18) Wold, D. J.; Haag, R.; Rampi, M. A.; Frisbie, C. D. *J. Phys. Chem. B* **2002**, *106*, 2815.
- (19) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541.
- (20) Jiang, H.; Moon, K.; Li, Y.; Wong, C. P. *Chem. Mater.* **2006**, *18*, 2969.
- (21) Reich, S.; Mazur, S.; Avakian, P.; Wilson, F. C. *J. Appl. Phys.* **1987**, *62*, 287.
- (22) Mdarhri, A.; Carmona, F.; Brosseau, C.; Delhaes, P. *J. Appl. Phys.* **2008**, *103*, 054303.
- (23) White, S. I.; DiDonna, B. A.; Mu, M. F.; Lubensky, T. C.; Winey, K. I. **2008**, submitted.
- (24) Strümpfer, R.; Glatz-Reichenbach, J. *J. Electroceram.* **1999**, *29*, 346.
- (25) Lide, D. R. *CRC Handbook on Chemistry and Physics*, 89th ed.; CRC Publisher: Boca Raton, FL, 2008; p 12.

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