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Drying-induced reduction in electrical resistivity of carbon black-polyamideimide nanocomposite films

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We provide evidence that the electrical resistivity of carbon black (CB)/polyamideimide (PAI) composites are tunable by drying below the glass transition temperature of the polymer matrix. Solution casting experiments of N-methyl-2-pyrrolidone (NMP)/CB/PAI systems reveal that with increasing drying temperature, the measured volume resistivity reduces by four orders of magnitude in an intermediate range of particle volume fractions, which is between 12% and 15%. However, no temperature-dependence was observed for particle-free polymeric films and nanocomposites with high particle volume fractions, which is above 23%. The measured values obey a single master curve, independent of the primary size and surface pH of the nanoparticles. This suggests that the desorption of PAI molecules from the nanoparticle surface enhances the evolution of conductive pathway formation in the course of drying.

Keywords: Coating; Adsorption; Composites; Drying; Films

1. Introduction

During the fabrication of nanocomposites containing conductive nanoparticles in a polymer matrix, an insulator-conductor transition emerges when the particles form an agglomerate pathway that allows electrons to travel a macroscopic distance through the composite [1]. Such an electrical transition has received significant scientific and technological attentions because the composite resistivity decreases by orders of magnitude at a certain threshold, obeying percolation theory [2-4]. Heating above the glass transition temperature (T_g) of the matrix, usually referred to as annealing, has been recognized as a critical process to assist the evolution of a conductive network in a rubbery matrix because it increases the mobility of the particles.

Polyimide-derivatives are a particular intriguing class of systems that exhibit a high T_g of ~ 300 °C owing to intermolecular attractions. When acid-treated nanoparticles are embedded in such systems, additional polymer-particle attractions evolve via hydrogen bonding between carbonyl and amino groups; these attractions strongly affect the dynamic agglomeration behavior through their complex coupling with co-existing intermolecular forces. Conductivity enhancement has been extensively examined via the application of an electric field to promote anisotropic particle alignments [5-6]; alter the particles to ellipsoidal [7], tubular [8-9], or platelet [10-11] shapes;

segregate nanoparticles into boundary regions between compacting latex particles [1,12-13]; or swell the matrix in solvent vapor [14]. Despite these attempts at improving conductivity, little attention has been paid to the polymer-particle interactions and resulting transient agglomeration of particles during solvent evaporation. Indeed, most prior studies have only researched composites annealed above T_g , or the melting temperature of polymer matrix in near equilibrium state [15-16].

In this article, we provide experimental evidence that a significant reduction in film resistivity emerges by four orders of magnitude in carbon black (CB)/N-methyl-2-pyrrolidone (NMP)/polyamideimide (PAI) solutions at temperatures 90 K below T_g of PAI matrix. The measured resistivity obeys a single master curve, independent of the primary CB particle diameters and their pH . These facts suggest that the desorption of PAI molecules from the nanoparticle surface enhances the evolution of the conductive network in drying films.

2. Material and Methods

The ternary composite solutions described here contain CB (Evonik), NMP (Kanto Chem. Ltd.), and PAI (Hitachi Chem. Ltd., Mw = 38000, T_g = 280 °C). We used surface-modified CB particles that have different primary diameters of 13 or 20 nm and surface pH values of 4.5 or 2.5 (Table 1); these values originate from the different amounts of carboxyl groups on the surface. The prepared solution with an initial solid concentration of 16.5 wt% was allowed to settle for 12 h to remove the air bubbles in the liquid and was then deposited on a 15 cm² aluminum substrate. The coated area was limited to 100 cm² by gluing a polymer shim to the substrate. The excess liquids were scraped off from the substrate by sliding a metal rod on the shim. Room-temperature air was blown at 2.0 m/s through a channel that was 1.2 m long, 0.15 m wide, and 0.10 m high. The wet coating was set in the air channel and heated at an initial heating rate of 15 K/min from below until the film surface temperature reached the final temperature (T_f), which ranged between 130 and 190 °C. The surface temperature was continuously monitored by an infrared radiation thermometer, which was calibrated with a radiation coefficient of 1.0. After 60 min drying, the as-dried film was cooled in the air for 40 min and peeled off from the substrate; next, the specific volume resistivity, $\pi d^2 R / (4t)$, was measured, where R denotes the measured resistance, d denotes the probe distance, and t denotes the dry thickness. The sample was sandwiched between a metal plate and either ring probe A (weight = 2.0 kg, d = 3.0 cm), which charged at 100 V for 5s, or ring probe B (weight = 0.5 kg, d = 5.32 cm), which was charged at 1000 V for 15 s, to measure the current across the film. To ensure reproducibility, we measured the resistivity at three different points of the sample and averaged the values.

3. Results and Discussion

We first examined how the measured volume resistivity varies for different drying temperatures.

Figure 1a depicts the resistivity of the as-dried films under 190 °C (open symbols) and the post-annealed films at 230-320 °C after being dried at $T_f = 190$ °C (closed symbols). The resistivity was normalized by that of the particle-free PAI films dried at the same temperatures. For the CB-A samples (circle), the resistivity decreases by four orders of magnitude as the temperature increases from 130 to 230 °C, below the glass transition temperature of the PAI matrix of 280 °C. Furthermore, more variation in resistivity was observed for the CB-B particles (triangle), which exhibited a lower surface pH . This strongly suggests that the interfacial interactions between polymer-particle surfaces, rather than the thermal properties in bulk polymer matrix, play a crucial role in the evolution of the conductive network in the composites.

Because NMP is known as a solvent that has a high affinity for water, dissolved water molecules in solutions may enhance the electron transport and thus reduce the film resistivity. However, the residual solvent mass measurements revealed that the solvent content monotonically decreased with increasing temperature and was less than 0.9 wt% at $T_f > 150$ °C (Figure 1b). Additionally, the dried film thickness remained at 52 ± 3 μm for any temperature. These observations imply that variations in neither the residual solvents nor the film thickness stem the temperature-dependent reduction in resistivity. The resistivity measurements also revealed that an increase in the initial heating rate from 15 to 20 K/s resulted in a monotonic decrease for a given T_f , indicating that the conductive pathway formation is process dependent for the CB/PAI composites.

Figure 2 illustrates a typical example of cross-sectional field emission scanning electron microscopy (FE-SEM) images of the film center at 130 °C. Nanoparticles are in contact with each other with agglomerates 100 nm in average size, but no distinct network was observed in the 2D plane. Similar agglomerations were observed in the vicinity of the top and bottom surfaces of the composite. Such agglomeration behavior is qualitatively consistent with the prior images from transmission electron microscopy combined with computerized tomography (3D-TEM), which show that the polymer matrix wets the surfaces of the CB aggregates, whereas the particles in an aggregate are in direct contact [17].

To explore the critical conditions for reduction in resistivity, we conducted resistivity measurements of the as-dried films for different CB particle loading values. As shown in Figure 3a, the measured resistivity showed no temperature dependence for particle-free polymeric films of $\phi = 0$ and for a high particle loading of $\phi = 27.5\%$, where ϕ denotes the CB volume fraction in dried films. However, a significant temperature dependence emerges in an intermediate range of particle volume fractions. We calculated the resistivity ratios at two different temperatures of 130 and 190 °C, and replotted them against the particle volume fraction in Figure 3b. The maximum resistivity reduction was obtained at a ϕ_m of 14–15 vol%. Our preliminary resistivity measurements (not shown) revealed that the percolation threshold (ϕ_c), at which an insulator-conductor transition emerged, was $\phi_c = 10.5 \pm 1.3$ vol% at $T_f = 130$ °C. This indicates that a drastic change in the

conductive network pathways, and thus the resistivity, occurs in a narrow range of $\phi_c < \phi < \phi_m$. It is worth noting that classical percolation theories have predicted $\phi_c = 15$ vol% when spherical particles exhibit 3D random packing [2]. The threshold in our sample was lower than the theory, implying that the particles agglomerate and show non-isotropic distributions in the film. This is consistent with the cross-sectional image in Figure 2.

Interestingly, the resistivity of the CB-PAI composites exhibited a thickness-dependence at ϕ_m . As shown in Figure 4, the resistivity monotonically decreases with increasing temperature for the 112- μm -thick dried film, whereas it remains constant in a specific range of $T_f < 175$ °C for the composite with 30 μm thickness, despite the temperature profile with respect to the drying time being the same in these series of experiments.

To understand the temperature/thickness-dependent reduction in electrical resistivity, the physical desorption of PAI molecules from CB particle surfaces, and the resulting increases in particle mobility must be considered. As mentioned, the CB particle surfaces were modified to contain a certain amount of carboxyl groups. These groups interact with the -NH groups from the PAI backbones when the particles are suspended in the polymer solutions, resulting in a polymer adsorption onto the particle surface via hydrogen bonding. As the CB-suspended solutions are heated for solvent drying, the growing thermal fluctuations overcome the bonding energy and some of the PAI molecules detach from the surface below the T_g of the PAI matrix. Consequently, the Brownian motion of the CB particles is enhanced, assisting their agglomerations and, giving rise to the evolution of conductive pathways in composites. This physical description is supported by the observation that the nanocomposite shows an increasing resistivity with decreasing surface pH, i.e., larger amounts of -COOH groups on the nanoparticle surface (see Figure 1a). In contrast, for high particle loadings, the nanoparticles agglomerate and are in contact with each other without the aid of desorption-assisted motions, leading to a negligible temperature dependence on the nanocomposite resistivity. This is consistent with our observations that the resistivity reduction is observed in a particular intermediate range of particle volume fractions (Figure 3b). Although it is not immediately clear how fast the PAI molecules desorb from the CB surface, the thickness-dependent variations in resistivity strongly suggest that the time scale for solvent drying is shorter than or comparable to the time scale required for the polymer chains to detach from the particles. The agglomerate structures are readily locked in before the polymers desorb, and the polymer-particle hydrogen bonds that remain on the surface hinder the mobility of the particle agglomerates, leading to the retention of the electrical resistivity regardless of the drying temperature. This is consistent with the negligible temperature dependence of thinner composites in low temperature regimes, as shown in Figure 4. In contrast, the probability that the desorption of the polymer chains proceeds before the drying completes increases with increasing temperature or composite thickness, demonstrates the significant resistivity reduction. To the best of our knowledge, the existing percolation theories for

rubbery polymers do not sufficiently explain such the complex temperature/thickness dependence for nanocomposites.

On the basis of this hypothesis, the hydrogen bonds on the CB particle surfaces influence their agglomeration, and thus the conductive pathway formation in the composite. However, it is not easy to quantify the amount of bonds at the particle-polymer interfaces because intra- and/or inter-molecular carbonyl-amino bonds co-exist in PAI molecules, and some of these bonds can be replaced by the bonds on CB surfaces in the course of drying. We characterize the composite resistivity by assuming that the hydrogen bonds are retained at a drying temperature of T , which is determined by a standard temperature T_0 ($< T$). The resultant difference in resistivity (R) is expressed by the function $\Delta R = \log R(T) - \log R(T_0) = f(R(T_0))$. In other words, the reduction in resistivity depends on the amount of detached PAI molecules as the temperature is increased from T_0 to T . To prove this, we replotted the resistivity ratios at two different temperatures against the resistivity at $T_0 = 130$ °C for different primary diameters and surface pH values of nanoparticles (Figure 5). The measured values were found to obey a single master curve, independent of the size or the amount of carboxyl groups at the particle surface. No simple correlation was obtained with respect to the particle volume fraction. For instance, at $\phi = 25.1$ vol%, the CB-A and CB-B samples exhibit $\Delta R = -0.19$ and 3.0 , respectively, showing distinct resistivity differences at the same volume fraction. Further studies are needed to derive a theoretical expression for the reduction in resistivity of PAI/CB composites as the function of the operating parameters. Nevertheless, the master curve in Figure 5 allows the prediction of the resistivity once the resistivity for a given temperature T_0 is known.

4. Conclusions

In this paper, we describe the significant reduction in electrical resistivity of carbon black(CB)/polyamideimide (PAI) composites at temperatures 90 K below T_g of PAI matrix. N-Methyl-2- pyrrolidone(NMP)/CB/PAI thin liquid films were cast on a heated substrate and dried under airflow. With an increase in drying temperature, the measured volume resistivity exhibited a reduction of four orders of magnitude for an intermediate range of particle volume fractions, while no temperature dependence was observed for particle-free polymeric films and nanocomposites with high particle volume fractions, which is above 23%. The measured values were found to obey a single master curve, independent of the primary CB particle diameters and their pH , i.e., the amount of carboxyl groups, at the particle surface. These results imply that the desorption of PAI molecules from the nanoparticle surface enhances the evolution of conductive pathway formation in the course of drying.

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FIGURE CAPTIONS

Figure 1 Variations in the specific volume resistivity of the as-dried films under 190 °C (open symbols) and the post- annealed films at 230-320 °C after being dried at $T_f = 190$ °C (closed symbols). The resistivity for CB-A samples (circle) decreases by four orders of magnitude as the temperature increases, while more variation in resistivity was observed for the CB-B particles (triangle), which exhibited a lower surface pH .

Figure 2 Cross-sectional field emission scanning electron microscopy (FE-SEM) image of the CB-A film center at 130 °C. Nanoparticles are in contact with each other with agglomerates 100 nm in average size. The particle volume fraction was 15.3 vol%, and the dried film thickness was 52 μm .

Figure 3 Variations in resistivity of the as-dried films for different particle loading values of the CB-A particle. The measured resistivity showed no temperature dependence for particle-free polymeric films of $\phi = 0$ and for a high particle loading of $\phi = 27.5\%$. However, a significant temperature dependence emerges in an intermediate range of particle volume fractions. The maximum resistivity reduction was obtained at a ϕ_m of 14–15 vol%.

Figure 4 Variations in the resistivity with dried composite thickness at ϕ_m . The resistivity monotonically decreases with increasing temperature for the 112- μm -thick dried film, whereas it remains constant in a specific range of $T_f < 175$ °C for the composite with 30 μm thickness.

Figure 5 The resistivity ratios at two different temperatures against the resistivity at $T_0 = 130$ °C for different primary diameters and surface pH values of CB nanoparticles. The measured values were found to obey a single master curve, independent of the size or the amount of carboxyl groups at the particle surface.

Table 1 Primary diameter and surface pH of carbon black particles