Enhancement of Electrical and Thermomechanical Properties of Silver Nanowire Composites by the Introduction of Nonconductive Nanoparticles: Experiment and Simulation

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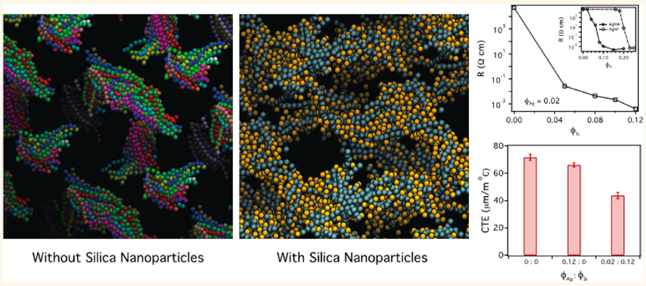

ABSTRACT Electrically conductive polymer nanocomposites have been applied extensively in many fields to develop the next generation of devices. Large amounts of conductive nanofillers in polymer matrices are, however, often required for a sufficiently high electrical conductivity, which in turn deteriorates the desired thermomechanical properties. We illustrate a novel but facile strategy to improve the electrical conductivity and the thermomechanical property of silver nanowire/polymer nanocomposites. We find that one may increase the electrical conductivity of silver nanowire/polymer nanocomposites by up to about 8 orders of magnitude by introducing silica nanoparticles with nanocomposites. The electrical percolation threshold volume fraction of silver nanowires decreases from 0.12 to 0.02. Thermomechanical properties also improve as silica nanoparticles are introduced. We carry out extensive Monte Carlo simulations to elucidate the effects of silica nanoparticles at a molecular level and find that van der Waals attractive interaction between silica nanoparticles and silver nanowires dominates over the depletion-induced interaction between silver nanowires, thus improving the dispersion of silver nanowires. Without silica nanoparticles, silver nanowires tend to aggregate, which is why additional silver nanowires are required for a desired electrical conductivity. On the other hand, with silica nanoparticles mixed, the electrical percolating network is likely to form at a smaller volume fraction of silver nanowires.

KEYWORDS: nanocomposites · silver nanowire · silica nanoparticles · Monte Carlo simulation · electrical percolating behavior

Electrically conductive polymer nanocomposites with desired mechanical and/or optical properties such as transparency,[1−4] flexibility,[5−8] and adhesive strength[9−13] are an important class of modern materials. Achieving both high electrical conductivity and good physical properties is still a challenging task because high electrical conductivity requires a large amount of conductive nanofillers in a polymer matrix, which often worsens physical properties of composites. For example, a large amount of silver nanoparticles, usually required for sufficiently high electrical conductivity, might increase the viscosity of polymer nanocomposites and would make the processing of nanocomposites a laborious task, for which the application of polymer nanocomposites has been limited in industry. Therefore, developing a strategy to prepare polymer nanocomposites with the least possible conductive nanofillers has been an issue of significant importance in applications such as transistors, sensors, displays, and actuators.

One-dimensional conductive fillers such as silver nanowires and carbon nanotubes

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are used to reduce the contact resistance, thereby decreasing the electrical percolation threshold concentration. However, more than 10 vol % of silver nanowires are necessary for a sufficiently low electrical percolation threshold concentration.[14] The electrical percolation threshold concentration can also be reduced with carbon nanotubes due to their high aspect ratio, but the electrical conductivity of these nanocomposites is only about 10^2 S/cm.[15,16] In this paper, we illustrate a novel but facile strategy to obtain high electrical conductivity for epoxy nanocomposites with a small amount of silver nanowires by introducing nonconductive silica nanoparticles. By mixing silica nanoparticles with nanocomposites, one can decrease the concentration of silver nanowires down to 2 vol % and still obtain the electrical conductivity of 10^4 S/cm. The minimum content of silver nanoparticles or nanowires reported for electrical conductivity of 10^4 S/cm was 10–25 vol %.[10,11,17–20] And thermomechanical properties such as coefficient of thermal expansion also improve with the addition of silica nanoparticles. We perform extensive Monte Carlo (MC) simulations to elucidate how one can obtain such a good electrical conductivity by mixing silica nanoparticles.

When the concentration of silver nanowires is below a percolation threshold concentration, composites are insulators with very high resistance. As the concentration increases beyond the percolation threshold concentration, an electrical percolating network of silver nanowires forms and composites become conductors. The electrical conductivity (Σ) follows a well-known scaling relation,[21,22] $\Sigma \sim (\phi_{Ag} - \phi_c)^t$, where ϕ_{Ag} and ϕ_c are the volume fraction of silver nanowires and its value at the percolation threshold, respectively. A scaling exponent (t) ranges from 1.3 to 7.[23–25]

According to the scaling relation one can obtain a high electrical conductivity even at a lower value of ϕ_{Ag} if ϕ_c decreases. To decrease ϕ_c, silver nanowires need be dispersed well in polymer matrices. Previous theoretical and experimental studies of the effect of nonconductive nanoparticles on the electrical conductivity showed that the depletion-induced attraction between conductive nanoparticles should play a role in enhancing the dispersion of conductive nanoparticles.[26–29] On the other hand, however, we find from MC simulations that when one introduces silica nanoparticles, the attractive van der Waals interaction at short length scales between silver nanowires and silica nanoparticles should dominate over the depletion-induced attraction and improve the dispersion of silver nanowires in epoxy polymer matrices.

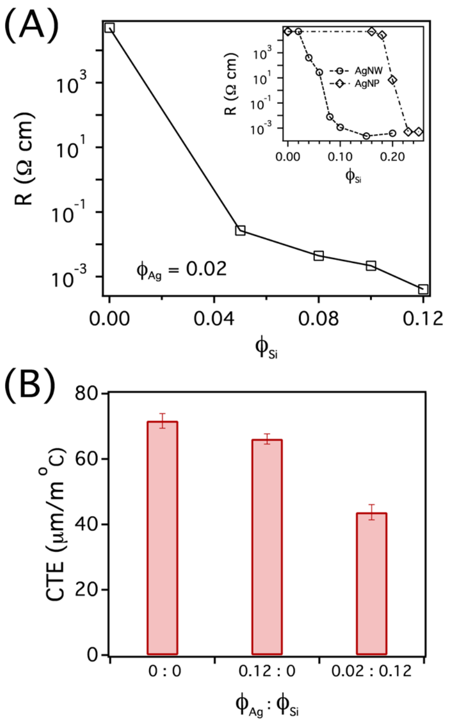

Figure 1. (A) Experimental results for the electric resistivity of epoxy/silver nanowire composites as a function of ϕ_{Si}. In the inset, the values of electric resistivity for the epoxy/silver nanowire (AgNW) composite and the epoxy/silver nanoparticle (AgNP) composites are compared. (B) The coefficients of thermal expansion (CTE) measured for different values of ϕ_{Ag} and ϕ_{Si}.

RESULTS AND DISCUSSIONS

The structure of conductive nanofillers relates closely to the electrical conductivity of polymer nanocomposites at various length scales. For example, at molecular length scales, the dimensionality of conductive nanofillers influences the percolation threshold and the electrical conductivity of polymer nanocomposites. One-dimensional silver nanowires with a high aspect ratio usually result in much higher conductivity than zero-dimensional silver nanoparticles.[23,30,31] As depicted in the inset of Figure 1A, the electrical percolation threshold volume fraction of silver nanowires is around 15 vol % while that of silver nanoparticles is more than 23 vol %. Because viscosity increases and adhesive strength worsens tremendously for 23 vol % of nanoparticles, silver nanowires are a better candidate for various applications such as electrical conductive adhesives. At a larger length scale, the structure of electrical percolating networks of conductive nanofillers, determined by intermolecular interactions of conductive nanofillers in polymer nanocomposites, affects electrical conductivity.[32,33] The intermolecular interactions are usually tuned by either modifying the surface of nanofillers or introducing dispersing agents.[34,35] Recent experiments and simulation studies[26–29] showed that one could also tune the intermolecular interactions by introducing nonconductive nanoparticles.

As one adds nonconductive silica nanoparticles for a given volume fraction (ϕ_{Ag}) of silver nanowires, the electrical conductivity improves by up to 8 orders of magnitude. As depicted in Figure 1A, as the volume fraction (ϕ_{Si}) of silica nanoparticles increases up to 0.12 for $\phi_{Ag} = 0.02$, the resistivity decreases from 5×10^4 Ωcm to 4×10^{-4} Ωcm. This is comparable to the electrical resistivity at the percolation threshold ($\phi_{Ag} = 0.15$) of nanocomposites without silica nanoparticles. This implies that silver nanowires could form electrical percolation networks more easily in the presence of silica nanoparticles, thereby decreasing the percolation threshold volume fraction of silver nanowires. Only with $\phi_{Ag} = 0.02$, one can reach the electrical resistivity required in industry for electrical conductive adhesives.

The addition of silica particles to the epoxy/silver nanowire composites also improves thermomechanical properties by decreasing the coefficient of thermal expansion (CTE) (Figure 1B). A large CTE of conductive nanocomposites causes a serious reliability problem for electrical interconnections.[36] CTE mismatch between nanocomposites and substrates also leads to cracking and delamination at the interface during repeated thermal cycling, thus resulting in the mechanical and functional failure, which may cause significant problems in the electronic packaging. To improve the reliability of nanocomposites, the CTE of epoxy composites needs be reduced down to that of inorganic substrates. While the CTE of neat epoxy without nanofillers is high around 75 μm/(m °C), CTE of the epoxy/silver nanowire composites with $\phi_{Ag} = 0.12$ decreases to 64.9 μm/(m °C). When nonconductive silica nanoparticles are added, CTE decreases further down to 43.6 μm/(m °C) for $\phi_{Ag} = 0.02$ and $\phi_{Si} = 0.12$, which could be attributed to the low CTE of silica. Epoxy/silver nanowires composites mixed with silica nanoparticles possess lower CTE and could be more suitable for electrical interconnections than composites without silica.

Adding the silica nanoparticles modifies the local structure of silver nanowires. Without silica nanoparticles (Figure 2 A,B), silver nanowires are aggregated owing to unfavorable interactions between hydrophilic silver nanowires and hydrophobic epoxy resins.[37] Locally ordered aggregates of silver nanowires are observed. Even though such aggregated silver nanowires align parallel to each other locally, any nematic phase does not form. The measured electrical conductivity of our nanocomposites is also isotropic. And such aggregates do not show any long-range order, which implies that the local aggregates should not be caused by shear imposed during film-casting. Meanwhile, as we add more silica nanoparticles, such local aggregates disappear and the dispersion of silver nanowires improves (Figure 2D,E).

Monte Carlo simulations reproduce the structure of silver nanowire/epoxy composites in a qualitative fashion. Figure 2 panels C and F are representative snapshots of Monte Carlo simulations for $\phi_{Ag} = 0.026$. Without silica nanoparticles (Figure 2C), many small clusters of locally aggregated silver nanowires form, thus decreasing the effective aspect ratio of silver nanowires and preventing the formation of percolating networks. Therefore, additional silver nanowires are required to construct a percolating network of silver nanowires. A simulation value for the percolation threshold volume fraction (ϕ_c) without silica nanoparticles is 0.032. When $\phi_{Si} = 0.052$, silver nanowires are dispersed well, forming a percolating network even for $\phi_{Ag} = 0.026$. Figure 2F depicts a percolating network of silver nanowires and some silica nanoparticles around the percolating network. Note that silver nanowires that do not belong to the percolating network are ignored in this figure for the sake of clarity. With silica nanoparticles, a simulation value for ϕ_c decreases from 0.032 to 0.02.

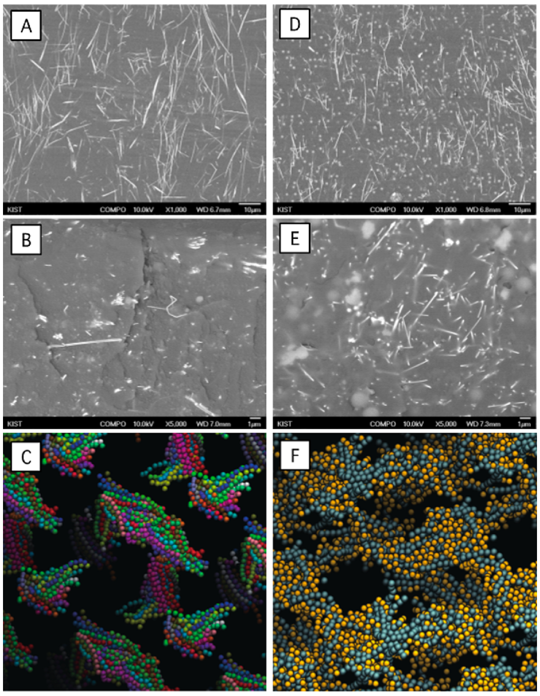

Figure 2. SEM images of epoxy/silver nanowire composites (A, B, D, E) and simulation snapshots (C, F) for $\phi_{Ag} = 0.02$ in experiments and $\phi_{Ag} = 0.026$ in simulations. $\phi_{Si} = 0$ for panels A, B, and C while $\phi_{Si} = 0.12$ for panels D and E and $\phi_{Si} = 0.052$ for panel F. Without silica nanoparticles locally ordered aggregates of the silver nanowires are observed. (A, B) Such local aggregates vanish in the presence of silica nanoparticles. (D, E) In panel C, different particles represent beads of different nanowires. Note that in panel F only silver nanowires (cyan) of a percolating network and silica nanoparticles (yellow) near the percolating network are shown for the sake of clarity.

The electrical conductivity (Σ) scales as $\Sigma \sim (\phi_{Ag} - \phi_c)^t$.[21,22] To calculate the simulation value of ϕ_c, we use equilibrated configurations obtained from MC simulations and estimate the probability (P) that equilibrated configurations would possess percolating networks.[40,41]

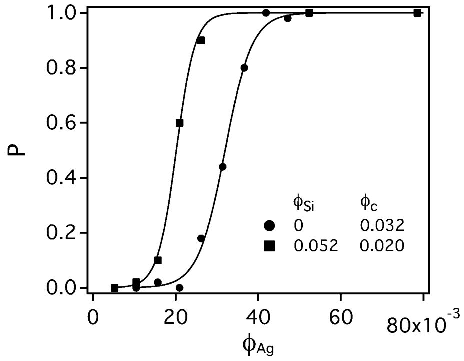

Figure 3. Simulation results for the probability (P) that configurations of composites contain percolating networks for ϕ_{Si} = 0 and 0.052. Solid lines are fits to the hyperbolic tangent functions.

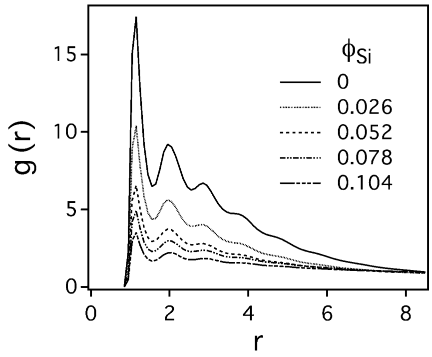

Figure 4. Simulation results for radial distribution function $g(r)$ between silver nanowires for ϕ_{Ag} = 0.026 and different values of ϕ_{Si}. As ϕ_{Si} increases, the peak heights of the first two peaks diminish, implying that silver nanowires are less likely to aggregate.

At a thermodynamic limit with infinite simulation cell size, P undergoes a discontinuous transition at $\phi_{Ag} = \phi_c$.[21,22] For finite systems, P changes quickly from 0 to 1 near the percolation threshold and $P \approx 0.5$ when $\phi_{Ag} \approx \phi_c$. In our study, P is obtained by calculating the ratio of the number of configurations with percolating networks to the total number of equilibrated configurations. Then, P is fitted to a hyperbolic tangent function $P(\phi,L) = {}^1/_2(1 + \tanh[(\phi - \phi_c)/\Delta\phi])$, where ϕ_c and $\Delta\phi$ are fitting parameters.[38] As depicted in Figure 3, more configurations contain percolating networks with larger P when silica nanoparticles are mixed. Even when ϕ_{Si} is only 0.052, ϕ_c decreases by about 37% compared to when ϕ_{Si} = 0. According to the scaling relation, such a decrease in ϕ_c would enhance the electrical conductivity, which is consistent with our experiments.

As silica nanoparticles are added, the local aggregates of silver nanowires dwindle. We calculate the radial distribution functions ($g(r)$) of silver nanowires as follows:

$$g(r) = \frac{1}{\rho_{Ag}}\left\langle \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \delta(r - |r_i - r_j|)\right\rangle \qquad (1)$$

where N is the total number of beads in silver nanowires, ρ_{Ag} is number density of total beads of the silver nanowires, r_i denotes the position vector of the ith bead, and the prime on summation excludes terms for pairs of beads of the same silver nanowire. As depicted in Figure 4, the first two peaks for $r \leq 3$ are significantly high without silica nanoparticles, indicating that silver nanowires are aggregated. As ϕ_{Si} increases, those peaks diminish rapidly. This clearly shows that silica nanoparticles should prevent silver nanowires from forming aggregates and enhance the formation of percolating network and the electrical conductivity.

Silica nanoparticles in our simulations and experiments play a totally different role compared to nonconductive spheres in previous studies.[26−29] Schilling *et al.*[29] proposed that depletion-induced interaction caused by nonconductive hard spheres made hard spherocylinders align locally and also decreased the percolation threshold volume fraction of hard spherocylinders significantly, which is against our observations. In experiments and simulations, silver nanowires align locally without nonconductive nanoparticles. When nonconductive nanoparticles are introduced, silver nanowires are dispersed better and the percolation threshold volume fraction is decreased. While any attractive interactions were ignored in their study and the depletion-induced interaction was purely entropic, silica nanoparticles in our model interact with silver nanowires *via* attractive van der Waals interactions at short lengths. This shows that a different type of intermolecular interactions bring about a different effect on the structure of silver nanowire clusters. The attractive van der Waals interaction between silver nanowires and silica nanoparticles dominates over the entropic depletion-induced interaction and results in a totally different trend for the local cluster structure of silver nanowires.

CONCLUSIONS

We show that the structure of silver nanowires in epoxy composites can be tuned readily by introducing nonconductive silica nanoparticles. As more silica nanoparticles are inserted into composites, silver nanowires are dispersed better and percolating networks are likely to form at a smaller volume fraction of silver nanowires. For given silver nanowires of ϕ_{Ag} = 0.02, the electrical conductivity increases by up to about 8 orders of magnitude as one adds silica nanoparticles. Such a drastic increase in the electrical conductivity allows one to use only a small amount of silver nanoparticles for a desired electrical conductivity and to also enhance thermomechanical properties, such as CTE. Monte Carlo simulations reproduce experiments in a qualitative fashion and suggest that the attractive interaction between silica nanoparticles and silver nanowires at short lengths hinders local aggregates of silver nanowires, which makes electrical percolating networks form easily.

METHODS

Fabrication of Epoxy/Silver Nanowires Composites with Silica Nanoparticles. Silver nanowires (Blue Nano Co., diameter, 90−150 nm; length, < 20 μm) and silica nanoparticles (Alfa Aesar Co., diameter 1.5 μm) were dispersed in cosolvents (ethanol and *n*-hexane) and then were precipitated for one day. Cosolvents were removed after silver nanowires and silica nanoparticles were precipitated. Inorganic fillers were mixed with an epoxy resin (YD128, bisphenol A type, EEW 182, Kukdo Chemical Co., LTD), maleic anhydride (HN2200, Kukdo Chemical Co., LTD) as a curing agent, and 2-ethyl-4-methyl imidazole (Aldrich Co.) as a catalyst. The mixture was film-casted onto glass substrates by doctor blading with a thickness of 40 μm, cured at 130 °C for 1 h, and then submitted to the second heat treatment at 160 °C for 2 h.

The electrical resistivity of the nanocomposites was measured using a Jandel 4-point probe apparatus (cylindrical type, Jandel Ltd., UK) with 1 mA current at room temperature. Field emission scanning electron microscopy (FESEM, JSM610A, JEOL) was used to identify the morphology of silver nanowires and silica nanoparticles in the epoxy matrices at an acceleration voltage of 10−15 kV using the composition mode. The CTEs of the nanocomposites were measured using a thermomechanical analyzer (TMA 7, Perkin-Elmer) over the temperature range from 30 to 250 °C at a heating rate of 10 °C/min and statistic force of 50 mN.

Monte Carlo Simulations. Monte Carlo simulations are carried out with a standard Metropolis algorithm to obtain equilibrium configurations of composites.[39] In our simulations, a silver nanowire is modeled as a rod that consists of 10 spherical particles. A silica nanoparticle is modeled as a spherical particle of the same size because the diameter of silica nanoparticles in experiments is about one tenth of the length of silver nanowires. Nonbonded interactions between any pair of particles is treated *via* Lennard-Jones (LJ) potential with an r_c of 2.5 σ and $\varepsilon = k_BT$ as follows:

$$U_{LJ}(r) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12} - \left(\dfrac{\sigma}{r_{ij}}\right)^{6}\right], & r_{ij} \le r_c \\ 0, & r_{ij} > r_c \end{cases} \tag{2}$$

where σ is the unit length in our simulations; k_B is the Boltzmann constant, T denotes temperature, and k_BT is the energy unit in our simulations. For silver nanowires, chemically bonded pairs of spherical particles interact *via* $U_{\text{bond}}(r) = k_r(r - r_0)^2$ and $U_{\text{bend}}(r) = k_\theta(\cos\theta + 1)$, where $r_0 = \sigma$, and $k_r = 20\ k_BT$, $k_\theta = 10\ k_BT$ and θ is the angle between two adjacent chemical bonds.

Initial configurations are obtained by inserting silver nanowires and silver nanoparticles sequentially at random positions in a cubic simulation cell of side $L = 30\ \sigma$ with periodic boundary conditions in all directions. The volume fractions of silver nanowires ($\phi_{Ag} \equiv 5\pi N_{Ag}\sigma^3/3L^3$) and silica nanoparticles ($\phi_{Si} \equiv \pi N_{Si}\sigma^3/6L^3$) range from 0.01 to 0.1 and from 0.025 to 0.1, respectively, where N_{Ag} and N_{Si} are the numbers of silver nanowires and silica nanoparticles. We equilibrate the system by performing millions of Monte Carlo random moves such as translation, rotation, and single-bead moves.[39]

For given ϕ_{Ag} and ϕ_{Si}, we obtain hundreds of equilibrated configurations to locate percolating networks of silver nanowires. Electrons can flow between two silver nanowires *via* a quantum mechanical tunneling process, if a distance between those two silver nanowires is smaller than a critical value R_c.[42] Two silver nanowires, then, are considered to form a connected bond. We search for a percolating cluster of connected bonds *via* a recursive algorithm. R_c should depend on system variables including the polymer matrix type. And accurate values of R_c have not yet been determined either theoretically or experimentally. However, the qualitative behavior of percolating networks should not be sensitive to values of R_c.[42] Therefore, in this simulation we set R_c equal to 0.3 σ.

Conflict of Interest: The authors declare no competing financial interest.

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