Metal-Polymer Interactions in a Polymer/Metal Nanocomposite

Douglas H. Cole
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
and Department of Materials Science and Engineering, Northwestern University,
2225 North Campus Drive, Evanston, Illinois 60208

Kenneth R. Shull
Department of Materials Science and Engineering, Northwestern University,
2225 North Campus Drive, Evanston, Illinois 60208

L. E. Rehn and P. Baldo
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

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A poly(*t*-butyl acrylate)/gold nanocomposite sandwich was annealed to induce diffusion of the gold particles, which was monitored using Rutherford backscattering spectrometry. Marker motion experiments were also performed to probe particle and polymer mobilities independently. The experiments revealed that particle mobility was decreased by 2 to 3 orders of magnitude compared with the predictions by Stokes-Einstein theory. Diffusion of polymer molecules through a gold particle layer is decreased by a much smaller extent. These results are attributed to bridging between particles arising from slow exchange kinetics of polymer segments at the polymer/metal interface. [S0031-9007(97)03435-2]

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Polymers and metals come into contact in many areas of modern technology. Automobiles are increasingly assembled using adhesives rather than welds [1], metal catalysts are embedded in polymer electrolytes for fuel cells [2], and prosthetic devices frequently feature acrylic bone cement in contact with metallic implant materials. Polymers, especially polyimides, are also used as substrates in the deposition of metallization lines for integrated circuits. With such widespread technological impact, it is important to understand on a more fundamental level how the polymers interact with the metals. In this Letter, we explore the area of polymer-metal interactions by examining diffusive processes related to these interactions.

The underlying principle in this study is that by introducing metal particles into a polymer matrix, we can determine the tendency of the particles to affect the mobility of the polymer by examining the diffusive behavior of the particles themselves. A "strongly" interacting system is one that shows large deviations from theoretical predictions, while a "weakly" interacting system exhibits near-idealized behavior. A distinguishing feature of the strongly interacting systems is that exchange of polymer segments in intimate contact with the metal particles is very slow. Our qualitative picture is that the interactions are directional, in that the energy is minimized for a specific orientation of the polymer segment with respect to the particle surface. In order for one segment to be replaced with another, the segments must achieve a configuration which is energetically unfavorable. The energy of this unfavorable configuration is the activation energy, which we expect to increase as the strength of the interaction (depth of the energy minimum) increases. The reduced rate of exchange allows for polymer strands bound to the particles to act as bridges between particles. For sufficiently high particle concentrations, a network of bridges is formed, which retards particle diffusion.

This particular study involves the examination of gold nanoparticles in a poly(*t*-butyl acrylate) (PTBA) matrix. Gold was chosen for its high atomic number and relative inertness to chemical reaction. The acrylic polymer is easily spun cast into uniform films, and can also be converted to other acrylic systems, allowing for future work to probe the effects of different functional groups on the polymer-metal interactions [3]. PTBA also has a glass transition temperature (T_g) $\sim 45\,^\circ\mathrm{C}$, which is conveniently accessible. The polymer was synthesized using anionic polymerization and its polydispersity (the ratio of weight average to number average molecular weight) was less than 1.15. Previous work on poly(2-vinylpyridine) showed very strong interactions between the polymer and the gold particles [4], while initial results from PTBA have shown surprisingly weak interactions—the particles showed appreciable diffusion into a PTBA film. The relative lack of interaction is thought to be derived from the presence of the bulky *t-butyl* group, which shields the gold particles from the more interactive ester group and its delocalized π-bonded electrons. One should keep in mind that even relatively weak polymer-metal interactions of order k_BT (0.03–0.04 eV) can significantly affect the mobility of polymer segments in the vicinity of a gold particle. These interactions are much weaker than those which can be probed by direct spectroscopic methods such as x-ray

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photoemission spectroscopy [5,6]. Even the "strong" interactions to which we refer are much weaker than those which have been studied by these other methods.

The initial experiments were conducted by creating sandwich samples of PTBA containing a buried layer of gold nanoparticles. The samples were created by spin casting 0.3–0.4 μm PTBA films of various molecular weights onto highly polished single crystal silicon substrates. The substrates were then placed into a thermal evaporation system, and gold was deposited on the sample. The thickness of gold on the sample was monitored with a quartz crystal thickness monitor. The equivalent thickness of gold deposited was between 0.4–0.5 nm. This thickness is insufficient to achieve continuous coverage, and the film that actually forms consists of islands, approximately 3 nm in diameter, of roughly spherical shape [7].

Following the evaporation of the gold, another polymer film was spun cast onto a glass slide, and the film was floated off the slide onto a water bath. This film was then placed on the silicon substrate, on top of the evaporated layer, creating a sandwich. The excess water was evaporated in vacuum at room temperature, producing a uniform sample with a gold layer buried in the center of the film. Diffusion experiments were then performed by annealing the sandwich in vacuum, at temperatures between 50–165 °C, depending on the polymer molecular weight. Higher temperatures were avoided, since PTBA will degrade at ~180 °C, and partial conversion to poly(acrylic acid) may occur at slightly lower temperatures [8].

Upon annealing, the particles diffuse through the polymer by Brownian motion. This motion was quantified by utilizing Rutherford backscattering spectrometry (RBS) as a depth profiling technique. The polymer sandwich samples are well suited for RBS, as the sensitivity to marker atoms increases as the square of atomic number [9]. This allows extremely small fractions of a high mass element, such as gold, to be detected reliably while embedded in a low atomic mass matrix, such as the PTBA film. The separation in recoil energy of incident ions scattered from gold and from the lower atomic mass constituents allows the gold concentration profile to be isolated from the signal from the substrate to a depth of ~1 μm. The samples showed extensive mass loss due to the ion beam striking the sample, but further experimentation revealed that despite the degradation of the polymer, the distribution of particles in the sample remained unaltered, allowing quantitative analysis despite the beam damage.

To extract a diffusion coefficient from the measured depth profile, a simulated concentration profile was fit to the actual data. The simulated profile corresponds to the appropriate solution to the diffusion equation, convoluted with a Gaussian broadening function to account for the effective RBS depth resolution. Figure 1 shows the result of an experiment in which the polymer was PTBA with a molecular weight of 7000 g/mol, heated for one hour at 65 °C. The gold particle diffusion coefficient, D, in this case is 1.58×10^{-14} cm^2 s^{-1}.

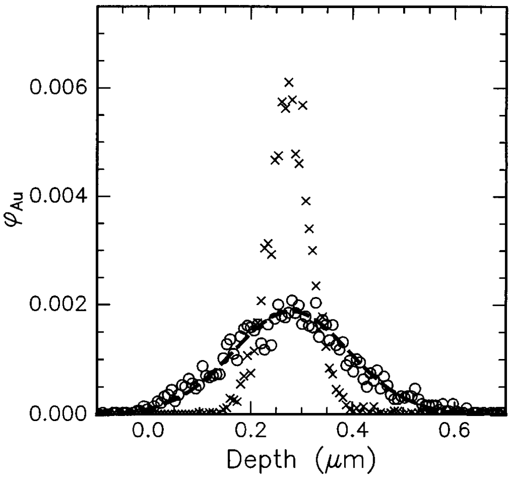

FIG. 1. Characteristic gold particle volume fraction profiles. The unannealed control sample (×) shows a sharp Gaussian peak, while the second sample (○) has been annealed for 1 h at 65 °C. The dashed line shows a simulated diffusion profile with $D = 1.58 \times 10^{-14}$ cm^2 s^{-1}.

A convenient way to analyze the data is by comparison to the Stokes-Einstein equation for diffusion of isolated spherical particles in a viscous medium: $D = k_B T / 6\pi\eta R$. Here k_B is Boltzmann's constant, T is the absolute temperature, η is the viscosity of the medium, and R is the particle hydrodynamic radius [10]. This theory contains the implicit assumption that the viscosity of the medium is not affected by the particles themselves. It is this assumption that leads to our definition that a system which shows particle diffusion in close accord with the Stokes-Einstein prediction should be classified as "noninteracting," a system in which diffusion is present but substantially slowed compared to Stokes-Einstein predictions is "weakly interacting," and a system where diffusion is eliminated entirely (as is the case for polyvinylpyridine) [11] is "strongly interacting."

In Fig. 2, the diffusion coefficients are plotted versus temperature in order to obtain an effective hydrodynamic radius, R, selected to force agreement with the Stokes-Einstein equation. The viscosity was determined separately for each polymer molecular weight and temperature by oscillatory shear rheometry. Our analysis here in terms of the Stokes-Einstein equation is instructive. Note that the values of the effective hydrodynamic radius determined in this way are quite large, varying from 70 nm for PTBA with a molecular weight of 7000 g/mol, up to 1000 nm for PTBA with a molecular weight of 100 000 g/mol. The highest of these values is nearly 3 orders of magnitude larger than the actual mean particle radius, measured by TEM to obtain $R_{\text{avg}} = 1.5$ nm after deposition. Even in the event of coarsening during the heat treatment, the radius would not be expected to exceed 10 nm [11]. These large effective hydrodynamic radii are compelling evidence of the formation of bridging interactions between particles.

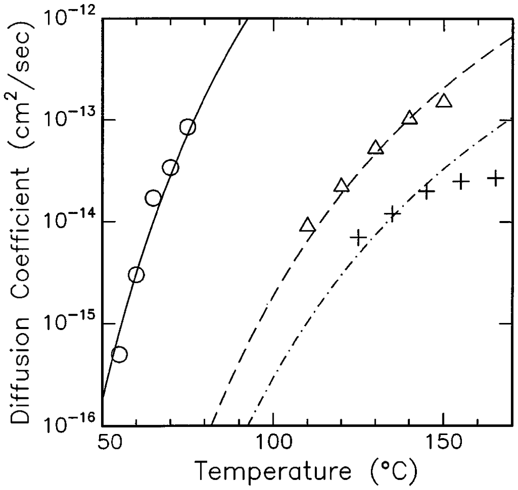

FIG. 2. Gold particle diffusion coefficient vs temperature for three polymer molecular weights. $M = 7000$ g/mol (○), $M = 77\,000$ g/mol (△), and $M = 100\,000$ g/mol (+). The Stokes-Einstein predictions are indicated for each polymer. The effective hydrodynamic radii are 70 nm (———), 400 nm (– – – –), and 1000 nm (· – · –).

A comparison of the length scales of a polymer molecule to the interparticle spacing shows that even for relatively short chains such as the 7000 g/mol PTBA, bridging interactions are likely. The statistical segment length, a, defined as the effective length of a monomer in a random walk model of polymer chain dimensions, is roughly 0.7 nm for PTBA [12]. The root-mean-square end-to-end distance, R_0, for a polymer molecule with a molecular weight of M is $R_0 = a(M/M_0)^{1/2}$, where M_0 is the repeat unit molecular weight. For PTBA, $M_0 = 128$ g/mol, from which we obtain $R_0 = 5.2$ nm for PTBA with $M = 7000$ g/mol, as compared with $R_0 = 17$ nm for $M = 77\,000$ g/mol, and $R_0 = 20$ nm for $M = 100\,000$ g/mol. The average particle separation, L, will depend on the size and distribution of the particles. For particles which reside in a two-dimensional layer, simple geometric arguments yield $L = (4\pi/3)^{1/2} r^{3/2} h^{-1/2}$, where r is the particle radius and h is the equivalent thickness of the metal particle layer. For our samples $r \sim 1.5$ nm and $h \sim 0.4$ nm, yielding $L = 5.9$ nm. If the particles are distributed through the thickness of a polymer film of thickness H, the scaling changes to $L = r(4\pi H/3h)^{1/3}$. For a 100 nm film $L = 15.2$ nm, which exceeds the end-to-end distance for only the lowest molecular weight polymer in our experiments. Clearly, at a fixed value of L, the importance of bridging interactions will increase as the polymer molecular weight increases. This effect is evident in our experiments, where the effective hydrodynamic radii of the gold particles increase dramatically as the polymer molecular weight increases. Also, we have found in recent experiments that the effective hydrodynamic radius decreases as the particles diffuse, and does not necessarily remain constant throughout a given diffusion experiment. The decrease in effective particle radius can be attributed to increase in L as the particles diffuse throughout the film. Increases in L due to particle coarsening may also play a role here. Other experiments using colloidal gold suggest that reducing the concentration of particles to the point where L far exceeds typical polymer chain dimensions leads to fewer bridging interactions and better agreement with the Stokes-Einstein predictions based on actual particle dimensions [4].

In order to relate the mobility of the gold particles to the mobility of the polymer molecules themselves, marker motion experiments similar to those performed by Green *et al.* with polystyrene were performed [13]. Two samples similar to the earlier sandwiches were prepared, but with two different molecular weights for the polymer top and bottom layers. For one sample, the higher molecular weight (~420 000 g/mol) was spun cast on the silicon substrate. Gold was then evaporated on this sample, and a low molecular weight (~7000 g/mol) film was floated on top of the higher M film. The second sample had the reverse of this geometry, with the lower molecular weight film directly against the substrate. Both samples were annealed for 30 min at 85 °C. In both cases, the interface moved toward the low molecular weight layer, as would be expected from the different self-diffusion coefficients that two polymers of such disparate molecular weights possess.

Analysis of the marker motion experiments was straightforward, and followed precisely that of Green *et al.* The distance, Δx_m, traversed by the marker layer is equal to $C(D^* t)^{1/2}$, where C is a constant related to the ratio of diffusion coefficients of the two polymer layers, D^* is the tracer-diffusion coefficient of the lower molecular weight polymer, and t is the annealing time. In our case, the diffusion constants of the two polymers are very different, and C can be assumed to be equal to the limiting value of 0.48 for a divergent ratio of diffusion coefficients. In this manner we obtain $D^* = 8 \times 10^{-12}$ cm^2 s^{-1} for sample 1, and $D^* = 9 \times 10^{-12}$ cm^2 s^{-1} for sample 2. This comparison indicates that there is no preference for the markers to move toward the substrate or toward the free surface. Evaluating the marker motion as a function of time reveals that the marker displacement scales as $t^{1/2}$. Figure 3 shows the data from a series of marker motion experiments carried out at 60 °C. A best fit to the data produces $D^* = 2.52 \times 10^{-14}$ cm^2 s^{-1}.

The central quantity relating diffusive and rheological behavior of polymer melts is the monomeric friction factor, ζ_0. The tracer diffusion coefficient of a relatively low molecular weight polymer molecule is given by $D^* = k_B T M_0 / M \zeta_0$, provided that it does not form entanglements with the surrounding molecules in the polymer matrix. The monomeric friction factor can also be related to the viscosity of an unentangled polymer melt through the Rouse theory of polymer dynamics [14]. In this context, $\zeta_0 = 36\eta M_0^2 / M N_{\mathrm{Av}} \rho a^2$, where ρ is the bulk density of PTBA and N_{Av} is Avogadro's number. Previous comparisons of polymer diffusion coefficients and melt viscosities in the unentangled

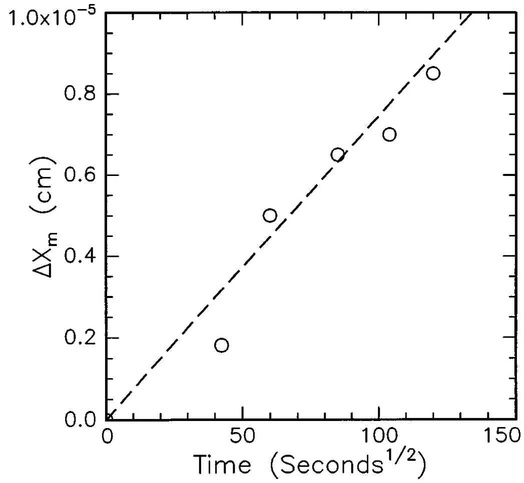

FIG. 3. Displacement, Δx_m, of solid gold particles as a function of annealing time at 60 °C, for a gold particle layer between polymer with molecular weight of 7000 g/mol and 420 000 g/mol. The dashed line represents $\Delta x_m = 0.48(D^* t)^{1/2}$, with $D^* = 2.52 \times 10^{-14}$ cm^2 s^{-1}. Here D^* is the tracer diffusion coefficient of the lower molecular weight polymer.

regime have confirmed that friction factors determined from these two types of experiments are quite consistent with each other [13,15,16]. The friction factor obtained from rheological data between 60 °C and 160 °C is given by $\log_{10} \zeta_0 = A + B/(T - T_{\mathrm{ref}})$. The reference temperature depends on the glass transition temperature of the polymer, which was found by differential scanning calorimetry to differ by 11 °C between the 7000 g/mol sample ($T_g = 40$ °C) and the 420 000 g/mol sample ($T_g = 51$ °C). For the lower molecular weight $A = -11.16$, $B = 706$, and $T_{\mathrm{ref}} = -21.3$ °C. The $M = 420\,000$ g/mol polymer has $A = -12.4$, $B = 706$, and $T_{\mathrm{ref}} = -10.3$ °C. At 60 °C, we obtain $\zeta_0 = 4.7 \times 10^{-3}$ g s^{-1} using the Rouse theory and the bulk viscosity of the polymer. The calculated friction factor at 60 °C from the marker motion experiments is $\zeta_0 = 3.34 \times 10^{-2}$ g s^{-1}. The value of the effective friction factor obtained from the marker motion experiments is 7 times larger than the value obtained from the viscosity measurements. This increase in the friction factor may indicate that the gold particles are not necessarily acting as "inert" markers, but that they somehow hinder the diffusion of the low molecular weight PTBA molecules. However, this idea is called into question by several factors. The difference in glass transition temperature between the high and low molecular weight polymers implies that the D^* measured via marker motion is not a true self-diffusion coefficient. The diffusion coefficient will be dependent on composition due to the disparity in T_g, and therefore so will be the friction factor. This fact alone can account for much of the observed difference between friction factors obtained from the viscosity and marker motion measurements. Further complications arise from our assumption that osmotic stresses in the high molecular weight polymer, associated with the swelling of the polymer by the smaller polymer molecules, are quickly relaxed. Those stresses oppose further penetration of the short polymer molecules, reducing the marker motion. In fact, our estimation of the relaxation time for the polymer with $M = 420\,000$ g/mol at 60 °C is slightly longer than the longest annealing time used in our marker motion experiments. Given these complications, our conclusion from the marker motion experiments is that the polymer molecules are relatively free to diffuse through the gold particle network.

The results obtained from both the gold diffusion and marker motion experiments are consistent with our picture of a system dominated by bridging interactions between particles. The transient network formed by the bridges slows down particle diffusion dramatically, while allowing molecules not in contact with the particles to diffuse relatively freely through the system. One must remember that the gold/PTBA system is a more weakly interacting system than any other system we have examined, in that measurable diffusion coefficients for the gold particles are still obtained. Our experiments show that the dynamics in concentrated metal particle dispersions in polymeric matrices can be reduced dramatically, even in situations where the polymer metal interactions are comparatively weak.

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