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Formation of Thin Transparent Conductive Composite Films from Aqueous Colloidal Dispersions

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ABSTRACT: This investigation examines the percolation and electrical resistivity behavior of films containing electrically conductive antimony-doped tin oxide particles in different polymer matrices. The polymers include gelatin, a soft polymer latex (glass transition temperature T_g < room temperature), and a hard polymer latex (T_g > room temperature). The films are formed through the evaporation of water from aqueous dispersions of conductive particles and film-forming polymers. The critical volume fraction of conductive particles for conductive network formation was found to be significantly lower when the film former was a polymer latex. This was attributed to differences in the interactions of particles in the colloidal state prior to the point where particles start to touch. In the critical transition region or slightly above the critical transition region, the hard latex provides an order of magnitude improved surface resistivity compared to that of the soft latex. This result was discussed in terms of the polymer particle deformation and flow during the film formation process.

Introduction

The electrical properties of composites containing a mixture of conductive and insulating materials are of interest in a variety of applications such as photoconductors, batteries, optical devices, sensors, conductive paints for electromagnetic shielding, and antistatic coatings. Many theoretical and experimental studies on the resistivity behavior of such composites have been reported in the literature.[1,2] Most of these studies were interested in thick films prepared by blending and compacting dry powders of inorganic or polymeric insulating binders with metal oxide or carbon black conductive particles or fibers at low temperatures or by blending conductive fillers into polymer melts. The formation of a conductive network in such systems strongly depends on parameters such as the rheologies of polymer melts during the mixing process, the wettability of the conductive particles by the polymer, the details of the solidification process after mixing, and the factors that control the mixing process.

Experimental resistivity data have been interpreted mostly in terms of either percolation theory or a general effective media approach.[1,3] Percolation theory predicts that close to the percolation threshold the concentration dependence of the resistivity obeys a power law of the form

$$\rho_m \propto (\varphi - \varphi_c)^{-t} \quad \text{for } \varphi > \varphi_c \tag{1}$$

where ρ_m is the resistivity of the composite, φ is the volume fraction of the conductive phase, φ_c is the critical volume fraction (i.e., the conductive phase volume fraction where incipient formation of a conductive network occurs (the percolation threshold)), and t is the critical exponent.

The percolation equation (1) is phenomenological and derived in the context of a regular lattice. Strictly speaking, it only applies when the conductivity of one of the phases is either infinite or zero. In many real systems, the ratio of the conductivities of the two phases may not be high enough to enable the percolation equation to be used accurately. This is especially true extremely close to the percolation threshold. The general effective media (GEM) equation, originally suggested as an effective media interpolation formula, has been shown to more accurately fit the resistivity data for a large number of binary composite media.[4] The GEM equation is

$$\frac{(1-\varphi)({\rho_m}^{1/t} - {\rho_h}^{1/t})}{{\rho_m}^{1/t} + (1/\varphi_c - 1){\rho_h}^{1/t}} + \frac{\varphi({\rho_m}^{1/t} - {\rho_l}^{1/t})}{{\rho_m}^{1/t} + (1/\varphi_c - 1){\rho_l}^{1/t}} = 0 \tag{2}$$

where ρ_h is the resistivity for the insulating phase, ρ_l is the resistivity for the conductive phase, and φ, φ_c, ρ_m, and t are the same as defined in eq 1. The GEM equation (2) reduces to the percolation equation when either $\rho_h = \infty$ or $\rho_l = 0$.

The value of φ_c should be about 0.16 for a system of conducting hard spheres that are placed at random on a regular lattice or conducting hard spheres that are randomly packed with equally, or nearly equally, sized insulating spheres.[3] However, experimentally determined values of φ_c typically range from 0.01 to 0.6.[1] Small values of φ_c can be obtained for composites in which small conducting particles are mixed with much larger insulating particles or when the conductive material has a high aspect ratio, e.g., a whisker or fiber. For a composite in which some of the nearest-neighbor conducting particles fail to make electrical contact then φ_c will be larger than 0.16.

The exponent t typically has a value in the range 1.5−2.0, although values as high as 7.0 have been reported.[5] Values of t larger than the "universal" value of $t \approx 2$ predicted by percolation theory have been reported for composites containing fibrous conductive fillers. However, it has been suggested that experimental values of $t > 2$ may result from using the percolation equation to fit data that is too far outside the critical region.[6]

In this report, we compare the percolation and resistivity behavior of ultrathin films containing electrically conductive antimony-doped tin oxide particles in different polymer matrices. The films are formed from aqueous dispersions containing the conductive particles

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and various polymeric film formers that include gelatin, a soft polymer latex (glass transition temperature $T_g <$ room temperature), and a hard polymer latex ($T_g >$ room temperature). Unlike that in thick films prepared by blending and compacting, the percolation and resistivity behavior of thin films prepared from such aqueous dispersions depend strongly not only on drying and film formation process but also on interactions between solution polymers and particles and between particles and particles in the colloidal state.

Experimental Section

Materials. The conductive antimony-doped tin oxide particle is a media-milled Keeling & Walker CPM 375 which is stabilized in water with Dequest 2006 dispersant (aminotri(methylene−phosphonic acid), potassium salt). It has a mean particle size of 65 nm and a powder resistivity value of 100 Ω cm. Its size distribution in the presence and absence of gelatin was measured by the sedimentation field flow fraction (SFFF) technique using a model F-1000 Universal fractionator. Gelatin is a photographic grade and alkali-processed sample that has a nominal molecular weight of 107 000 and a polydispersity of 3 with a bimodal size distribution.[7] Both soft and hard polymer latex particles were prepared by emulsion polymerization process using potassium persulfate as initiator at 80 °C. The surfactant used is Rhodapex CO-436 (ammonium salt of sulfated poly(ethoxynonylphenol)) at 2 wt % based on the monomers. The soft polymer latex particle is made of poly(*n*-butyl acrylate-*co*-acrylamido-2-methylpropanesulfonic acid, sodium salt) (PBA-AMPS 95/5 weight ratio) and has a glass transition temperature of −45 °C and a mean size of 65 nm as measured by photocorrelation spectroscopic technique. The hard polymer latex particle is made of poly(*n*-butyl methacrylate-*co*-acrylamido-2-methylpropanesulfonic acid, sodium salt) (PBMA-AMPS 95/5 weight ratio) and has a glass transition temperature of 38 °C and a mean size of 60 nm. The polymer molecular weight was determined by gel permeation chromatography (GPC) coupled with tandem refractive index detector. The molecular weights are nominal, based upon polystyrene standards. Both polymers have a weight-average molecular weight of about 1.1×10^5. Other latex polymers used in this study are poly(*n*-butyl methacrylate) (PBMA) latex having a particle size of about 80 nm and a weight-average molecular weight of about 1.1×10^5 and poly(*n*-butyl methacrylate-*co*-methacrylic acid) (PBMA−MAA 95/5 weight ratio) having a particle size of about 100 nm and a weight-average molecular weight of about 2×10^5. All the polymer latices used have a pH of about 2.2−2.5. Effect of initial latex pH on the film surface resistivity was studied using PBMA−AMPS latex at a pH of about 5.7. The effect was found to be insignificant. Stock gelatin solutions were prepared at a pH value of about 6. All solutions used in this study were prepared using deionized water.

Film Preparation. Thin films were prepared by applying about 27 μm thick layers of aqueous dispersions at 4 wt % total solids onto a poly(ethylene terephthalate) substrate and drying the wet dispersions at 100 °C for 3 min. The thin films have a dry weight of 1.08 g/m^2 and a thickness ranging from 150 to 900 nm.

Resistivity Measurements. Surface electrical resistivity (SER) values (Ω/□) of the thin films were measured at 5% relative humidity and 22 °C by applying a 200 V potential (Keithley 247 high-voltage power supply) between two knife edges (5 mm apart and 10 cm long) in intimate contact with the film surface. The resistivity value was recorded using a Keithley 617 electrometer. Ohm's law for the thin films was found to be linear from 5 to 200 V with a correlation coefficient of 0.999. The measurement condition at 5% relative humidity ensured that there was no significant ionic conductivity contribution to the electrical resistivity readings. Four measurements were made on each sample, and the reported value was taken as the average.

For studies on composite resistivity behavior described in the literature the bulk resistivity (Ω cm) for pressed pellets or thick molded samples is typically reported. In our study we measure surface resistivity value. The bulk resistivity is calculated from the measured surface resistivity value and film thickness, where bulk resistivity ρ is related to surface electrical resistivity (SER) by $\rho = \text{SER} \times$ film thickness. At a constant dry film weight, the density and film thickness vary dramatically with the volume concentration of tin oxide since the density of tin oxide is nearly 6 times that of the polymers. The dried film thickness in this study is estimated from the weighted average of the individual component densities and the dried film weight.

Atomic Force Microscope. The instrument used is the Park M-5 (Park Scientific). The images were generated using the sample modulation mode with imaging VS tip modulation. The probe used was a gold-coated conical silicon cantilever with a radius of curvature of approximately 100 Å. The cantilever is about 0.6 μm thick and has an aspect ratio of about 4:1 and an included angle of about 10°. The force constant for the probe was about 0.24 N/m. The scanning frequency was between 0.4 and 0.5 Hz. The set point (force) was approximately 10 nN. The static noise of the instrument was <10 Å. All images and statistical information were generated from raw unfiltered data.

Results and Discussion

Resistivity Behavior in Gelatin Matrix. In Figure 1a we display the film bulk resistivity value as a function of tin oxide volume fraction φ at a constant dry film weight of 1.08 g/m^2 in a gelatin matrix. The bulk resistivity value at high tin oxide concentration approaches a value of 100 Ω cm, which essentially equals the packed powder resistivity for the pure tin oxide particles. The critical volume fraction φ_c at which the film bulk electrical resistivity shows a sharp transition (corresponding to the incipient formation of a conductive network) is about 0.14−0.16, compared to the value of 0.16 predicted for conductive spheres placed at random on a regular lattice or randomly packed with equal, or nearly equal, size insulating spheres.[3] This seems to indicate that the neighboring conductive particles in a random close packed lattice are electrically connected. If, at random, some of the nearest-neighbor conductive particles fail to make electrically contact, the critical volume fraction, φ_c, would be larger.

A log−log plot of the data in Figure 1a according to eq 1 using $\varphi_c = 0.14$ is shown in Figure 1b. A least-squares fit of each set of data yields values for the slope $t = 6.4$ and 6.8. It is unclear why the critical exponent is so high for this system. Anomalous critical exponents have been reported for composites containing particulate conductors. For example, studies on thick film resistors containing conductive RuO_2 and $BiRu_2O_7$ particles[8] or other conductive ruthenium oxide particles[9] have reported t values of 3−7. It was suggested that the critical region for these composites might be very narrow, and therefore, the data used to determine the critical exponent were outside the critical region. It was also suggested that these composites might actually exhibit anomalous or nonuniversal critical behavior as proposed in several theoretical studies.[10,11] For example, a distribution in the thickness of the barrier layer between the conductor and the insulator can lead to a distribution in conductivity. We believe that such a distribution-induced nonuniversality is at least partially responsible for the high t values determined for the gelatin/tin oxide films.

The conductive antimony-doped tin oxide particle used in the present study is a media-milled particle. The particle is at best described by a granular morphology.

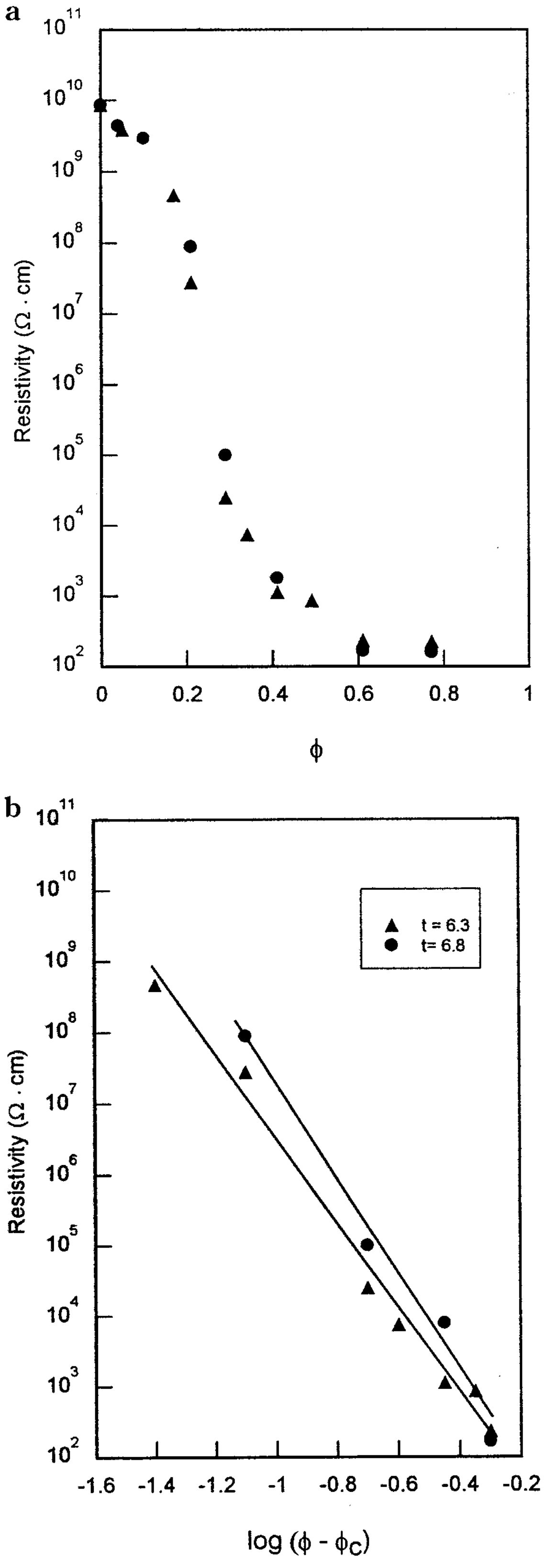

Figure 1. Electrical resistivity as a function of tin oxide volume fraction for films prepared with gelatin.

Particle size analysis by the sedimentation field flow fractionation technique on the milled tin oxide shows a rather broad size distribution with a mean size of about 60 nm (Figure 2). This mean particle size is increased to about 170 nm in the presence of gelatin. This increase in particle size is unlikely due to bridging of tin oxide particles by gelatin under our experimental conditions. Rather it is due to the adsorption of gelatin molecules onto the tin oxide particle surface. In other words, gelatin becomes adsorbed onto the conductive particle surface in the colloidal state to effectively encapsulate the particle. When such a solution dries on a substrate to form a thin film, the gelatin shell has to break to allow the tin oxide particles to form a conductive network. The trapped gelatin molecules can therefore form a barrier layer between the conductive particles, and a distribution in the thickness of the barrier layer then leads to a distribution in conductivity.

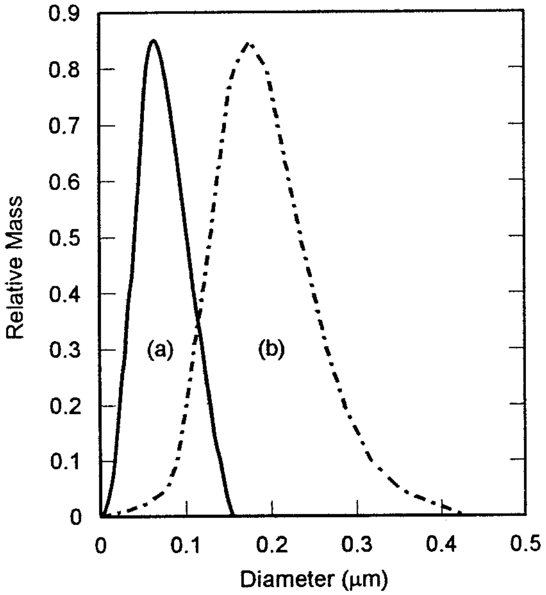

Figure 2. Tin oxide particle size as measured by SFFF (a) in the absence and (b) in the presence of gelatin.

To test this hypothesis, we measured the humidity dependence of the film bulk resistivity value as a function of tin oxide volume fraction φ in gelatin matrix. Figure 3 shows the results. There is a significant increase in the film bulk resistivity value at 75% relative humidity (RH) compared to that at 5% RH at tin oxide volume fractions $0.15 < \varphi < 0.6$, and this increase can be attributed to the increase in the thickness of the gelatin barrier layer between the conductive particles. Gelatin is a water-soluble polymer, and it absorbs about 5 times more moisture at 75% RH than at 5% RH.[7] This increase in moisture content will increase the gelatin barrier layer thickness between conductive particles and therefore the film bulk electrical resistivity values. One expects to see very little variation in the film bulk resistivity value at high volume fractions (e.g., $\varphi > 0.6$) since there may not be enough gelatin molecules available to be trapped between the conductive particles.

Resistivity Behavior in Polymer Latex Matrices. Figure 4 compares the electrical resistivity as a function of tin oxide volume fraction for films prepared with gelatin, poly(*n*-butyl acrylate-*co*-acrylamido-2-methylpropanesulfonic acid, sodium salt) latex, and poly(*n*-butyl methacrylate-*co*-acrylamido-2-methylpropanesulfonic acid, sodium salt) latex. Several interesting features in the resistivity data can be observed for the three different polymer matrices:

(1) The critical volume fraction φ_c of tin oxide particles necessary for conductive network formation is significantly lower when a polymer latex is used as the matrix.

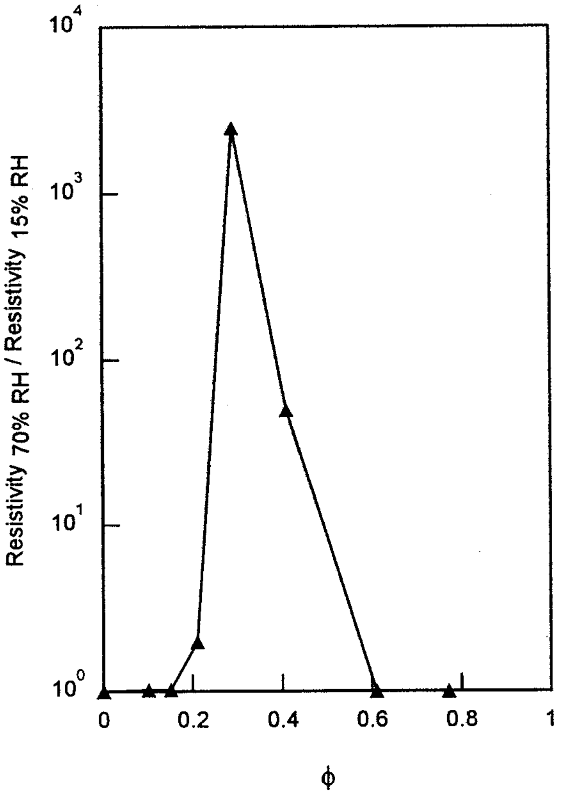

Figure 3. Dependence of electrical resistivity on relative humidity as a function of tin oxide volume fraction for films prepared with gelatin.

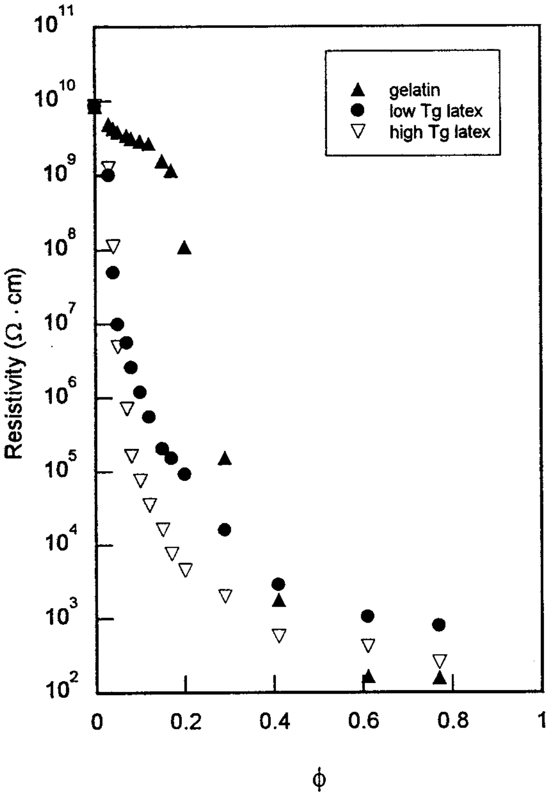

Figure 4. Electrical resistivity as a function of tin oxide volume fraction for films prepared with gelatin, poly(*n*-butyl acrylate-*co*-acrylamido-2-methylpropanesulfonic acid, sodium salt) latex, and poly(*n*-butyl methacrylate-*co*-acrylamido-2-methylpropanesulfonic acid, sodium salt) latex.

This presumably reflects a difference in the way tin oxide particles pack in the presence of the polymer latex.

(2) φ_c appears to be similar for both soft and hard latex polymers. However, in the critical transition region or slightly above the critical transition region, the bulk resistivity value is about an order of magnitude lower for films prepared with the hard latex particles than those with the soft latex particles. There are apparently more contacts between tin oxide particles for films containing hard latex polymer.

(3) The critical exponent t values determined for the hard and soft latex polymer matrices also appear to be different. The t values estimated using eq 1 are about 3.6 for the soft latex polymer and about 3 for the hard latex polymer. The low t values obtained for the latex polymers compared to that for gelatin perhaps indicate that latex polymers are less likely to form a barrier layer on the tin oxide particle surface. This is also understandable purely on the basis of the excluded-volume effect.

We would also like to point out here that a 150 °C annealing treatment had no effect on the film bulk resistivity behavior for samples originally dried at 100 °C.

The higher film bulk resistivity values observed for the soft latex polymer matrix above the critical transition point are likely due to the excessive polymer particle deformation and polymer flow during the film formation process. To form a transparent film containing conductive tin oxide particles, latex particles have to deform and coalesce, flowing around conductive particles. If the T_g of the latex polymer is reduced, the viscosity of the polymer at the same drying temperature is lowered, and the distance that the latex polymer can penetrate into the clusters of conductive particles can increase. It also follows that the reduction of polymer viscosity by coalescing aids or drying at higher temperatures can increase the degree of latex polymer penetration. Also, since polymers are viscoelastic in nature, longer drying times may lead to more polymer penetration into the clusters of conductive particles.

In paint films, many properties change abruptly at the so-called critical pigment volume concentration (CPVC). Below CPVC, the pigment particles are not close packed, and film-forming polymers occupy the excess volume in the film. Above CPVC, all pigment particles are close packed, but there is not enough film-forming polymer to occupy all the voids between the particles. The CPVC value is lower in latex paint than in solvent-based paint.[12] It is believed that the viscosity of the coalesced latex particle is sufficiently high that it is difficult for the polymer to penetrate the center of clusters of pigment particles. It is important to point out that CPVC values for paint films are much higher than the critical volume fraction values for conductive network formation.[12] However, film resistivity above the critical transition is apparently effected by the ability of polymers to flow and penetrate into the clusters of conductive particles.

Resistivity Behavior and Film Morphologies. It is quite intriguing that φ_c is significantly lower with polymer latices as the matrices. According to percolation theory, the critical volume fraction is 0.16 for conductive spheres placed at random on a regular lattice or randomly packed with equal, or nearly equal, size insulating spheres.[3] For φ_c lower than 0.16, two models have been proposed. The first model is the grain consolidation model by Roberts and Schwartz[13] which starts with the nucleation of a random array of small insulating spheres embedded in a diphasic composite. The insulating spheres then grow to form a random close packed lattice with point contacts on the surfaces. As the radius of the insulating spheres increases, the areas of interfacial contacts grow, creating an ever-decreasing volume of pores and throats. Finally, when the volume fraction of the insulating spheres is about 0.97, the throats no longer form a percolation path. This gives φ_c of approximately 0.03 if the material remaining in the pores and throats is the pure conductive phase. The second model[14] assumes that both conductive and insulating components are initially granular. If their starting radii are approximately the same, the values of φ_c obtained tend to be in the region of 0.16. However, as the radii of the conductive particles decrease below those of the insulating particles, the value of φ_c begins to drop and reaches about 0.05 when the radii of conductive particles is about 30 times smaller than that of the insulating particles. The two models become virtually indistinguishable if in the second model the conductive particles reside in the interstitial spaces between the insulating particles.

The hard and soft latex particles used in this study have a mean size of about 60 and 65 nm, respectively. The conductive tin oxide particles have a broad size distribution with a mean size of about 60 nm. Therefore, the very low φ_c values obtained with latex polymer particles as the insulating spheres cannot be attributed to differences in particle sizes. The broad size distribution may play a role here, but it alone cannot account for the very low φ_c values. We believe that the only way to have such low φ_c values is to allow latex particles to undergo microphase separation during film formation into domains that subsequently form larger insulating spheres.

Figure 5a shows our view of a microstructure for films containing conductive tin oxide particles and latex polymer particles. It is a 2-D representation along the film plane. The microstructure shows that the conductive spheres form a chainlike structure that separates the latex polymer phase into domains. Each domain contains a number of latex particles and has a mean size (δ) which is much larger than the diameter of an individual latex particle. In our view the mean size δ changes in proportion to the volume fraction of latex polymer particles. The domain size is smaller along the direction perpendicular to the film plane.

To confirm our view, some of the film surfaces were examined by the atomic force microscopic technique. Detailed results will be presented in our future report. Figure 5b shows an AFM image for a film containing about 15 vol % of the conductive tin oxide particles. We see the presence of particulate-like features which have a size very similar to that of the tin oxide particle used. The most striking feature of the image is the appearance of clustering and chaining of these particulate features. It is worth pointing out that AFM images for films containing the conductive tin oxide in a gelatin matrix do not show different material domains due to particle chaining and clustering.

Resistivity Behavior and Particle Interactions in the Colloidal State. To offer a rational explanation for the formation of the microstructure described above, one needs information about the distribution of particles in the colloidal state and during the film formation process. We are clearly dealing with a dispersion containing mixtures (of conductive tin oxide particles and latex polymer particles) of particles having different chemical composition, surface structure, and hardness. When we apply such a dispersion onto a substrate, all particles move about through Brownian motion during water evaporation until they form contacts with each other. Such Brownian motion allows particles to arrange themselves to have microstructures in accordance with the evolution of repulsion and attraction forces during the drying process. It is generally agreed upon in the literature that particle packing occurs when particles come into irreversible contact with one another, and regardless of the subsequent coalescence between particles, the morphology of the dried film is derived from the particle packing stage. It is also generally agreed upon that the distribution of particles in a concentrated binary mixture should relate primarily to the particle size ratio, particle size distribution, and the colloidal properties (for example, surface characteristics) of the particles.

Several groups have recently reported their studies on the effect of particle size ratio on the particle distribution in a concentrated binary mixture. Biben and Hansen[15] demonstrated using various self-consistent integral approximations that a binary colloidal system may phase separate when the size ratio of small to large particles is less than 0.2. Feng and Winnik[16] argued that the results of their studies on the morphology of latex blend films are consistent with the phase separation picture. We have not seen any evidence of a macroscopic fluid phase separation in our systems. This is partly because the size ratio in our systems is close to unity. Bartlett and Ottewill[17] used small-angle neutron scattering measurements to examine concentrated binary dispersions of sterically stabilized poly(methyl methacrylate) particles of size ratio of about 0.31 in decalin. They demonstrated the clustering of small particles in the presence of large particles and attributed it to the long-range attractive force between small particles resulting from the depletion of large particles from between the surface of small particles. Their colloidal systems are clearly different from our systems in both the types of particles and medium. Therefore, it is possible that the clustering of the conductive tin oxide particles during the film drying process observed in our systems is due to a different mechanism.

We were initially concerned about the types of latex particles used in this study. Both the hard and soft latex particles are made of copolymers containing about 5 wt % of acrylamido-2-methylpropanesulfonic acid, sodium salt. In other words, these latices are highly charged. These charges could modify the electrostatic repulsion forces throughout the drying process and therefore the final film morphology. One way to resolve such a concern is to study the film bulk resistivity as a function of conductive tin oxide particle concentration for latex polymer particles having similar T_g values, molecular weights, and particle sizes, but, different surface compositions. The observed differences in the resistivity behavior for these polymer binders should relate primarily to differences in the interactions between the conductive particles and the polymer particles in the colloidal state. Figure 6 compares the film bulk resistivity as a function of tin oxide volume fraction for the

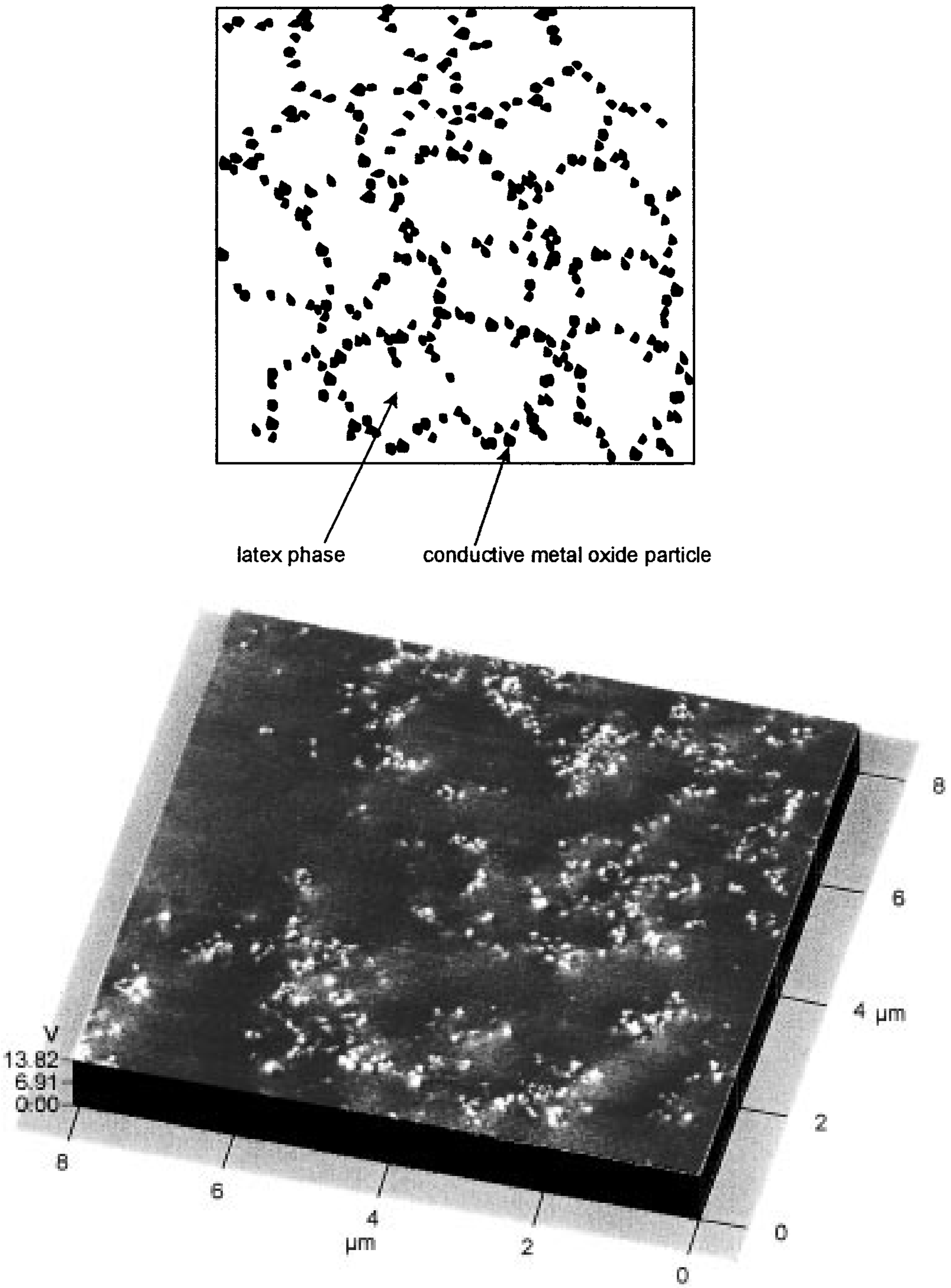

Figure 5. (a) A simple 2-D representation of the microstructure for films prepared from aqueous dispersions containing conductive tin oxide particles and latex polymer particles. (b) A surface image by AFM for a film containing about 15 vol % of conductive tin oxide particles in a latex polymer matrix.

PBMA, PBMA−MAA, and PBMA−AMPS latex particles. The critical volume fraction φ_c for PBMA−AMPS is only slightly lower than for either PBMA or PBMA−MAA. Clearly, the types of latex particle surface structures used in this study have very little to do with the very low critical volume fraction values obtained.

We offer an alternative mechanism on the formation of the microstructures observed in this study. If during water evaporation the Coulombic repulsion forces or steric repulsion forces between particles of the same or different species dominate, a binary colloidal dispersion will be stable up to very high solids and before the irreversible particle contact occurs. Such systems will generate a random close packed microstructure upon drying. On the other hand, if the repulsion forces are being modified during the drying process due to the increased electrolyte concentration and therefore ionic strength of the medium, the binary colloidal dispersion will have a tendency to segregate if there exists an imbalance in the attraction force between particles of the same species and those of different species. The magnitude of the attraction force depends on the type of materials present. For example, the conductive tin oxide particles used in this study have a high density and a high refractive index. One would expect that the Hamaker constant value for tin oxide particles be high compared to that for latex polymer particles. In other words, the tin oxide particles may attract each other

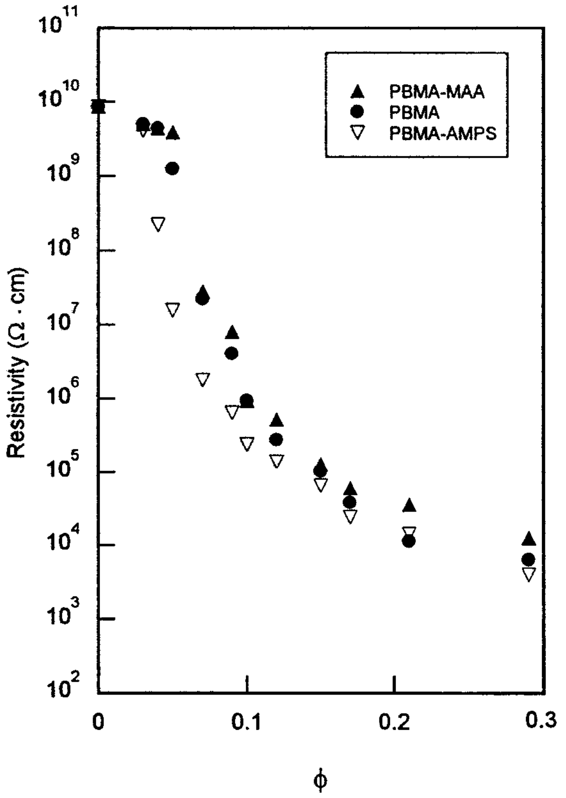

Figure 6. Electrical resistivity as a function of tin oxide volume fraction for film prepared with poly(butyl methacrylate) latex, poly(butyl methacrylate-*co*-methacrylic acid) (95/5) latex, and poly(butyl methacrylate-*co*-acrylamido-2-methylpropanesulfonic acid, sodium salt) (95/5) latex.

more strongly and preferentially when dispersed among latex particles of similar sizes and when the electrostatic repulsion forces become less effective. This can lead to clustering of the conductive tin oxide particles. The type of film microstructure observed in this study seems to suggest that this clustering occurs before the irreversible particle contact takes place and carries through to final dry films.

From the above discussion we propose that film formation from an aqueous dispersion containing conductive tin oxide particles and film forming latex particles of similar size may involve the following steps (Figure 7): At low concentration the distribution of the two particles is random due to the strong Coulombic repulsion interactions (Figure 7a). As water evaporates, the concentration of ionic species present in the system increases and the magnitude of electrostatic repulsion is progressively reduced. The particle distribution will no longer remain random. Since particles are still quite mobile before irreversible particle contact occurs, the system may undergo microphase separation into domains of particles of the same species, and the conductive tin oxide particles start to cluster if the attraction forces between them become sufficiently strong (in the extreme case macroscopic phase separation may occur) (Figure 7b). Depending on the magnitude of the attractive force, this microphase separation and particle clustering may continue and survive throughout the rest of the drying process until the particles come into irreversible contact (Figure 7c). Finally, upon complete removal of water the film-forming polymer particle will deform to form a clear film having a microstructure as shown in Figure 7d.

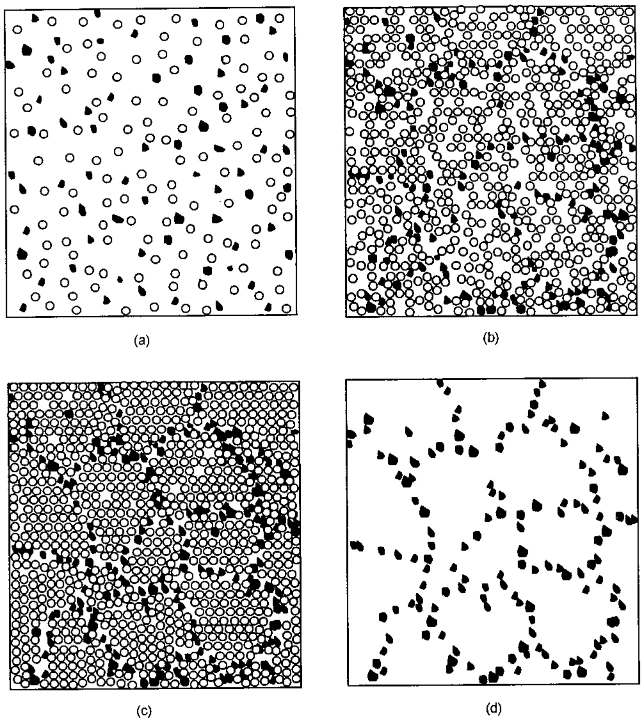
(a) (b) (c) (d)

Figure 7. A simple representation of the film formation from an aqueous dispersion containing conductive tin oxide particles and film forming latex particles of similar size: (a) particle distribution at low concentrations (less than 20−30 vol %); (b) particle distribution at high concentrations; (from about 30 to 50 vol %); (c) particle distribution at close irreversible contact (above 50−55 vol %); (d) microstructure of a completely coalesced film. The conductive particles are black particles.

Concluding Remarks

In this report we have described in detail our preliminary studies on the percolation and resistivity behavior of thin transparent films containing conductive tin oxide particles in various polymer matrices including gelatin and various polymer latices. The films are formed through the evaporation of water from aqueous dispersions of conductive particles and film-forming polymers. With gelatin matrix the critical volume fraction of conductive particles for conductive network formation was found to be 0.14−0.16, compared to the value of 0.16 predicted for conducting hard spheres placed at random on a regular lattice or randomly packed with equally or near equally sized insulating spheres. With latex particles as the film former the φ_c is about 0.04 or lower. The surface resistivity value just above the threshold can be approximately described by the power law $\rho_m \propto (\varphi - \varphi_c)^{-t}$. The t value is found to be about 6.3 for gelatin binder, about 3.6 for soft latex particles, and about 3.0 for hard latex particles. These values are significantly higher than the "universal" value of 1.9−2 reported in the literature for various polymer/carbon composites.

Above the critical transition region the hard latex provides an order of magnitude improved bulk resistivity compared to that of the soft latex. This result was discussed in terms of the ability of polymers to flow and penetrate into the clusters of conductive particles.

The low percolation threshold value observed with latex particles as the film former was discussed in terms of particle interactions in the colloidal state and during film formation. It appears necessary for the conductive tin oxide particles to cluster and the latex polymer phase to separate into domains having a mean size much greater than the diameter of an individual latex particle. This picture is in agreement with a surface image obtained by AFM.

The present report, although directed primarily at the resistivity behavior for thin composite films, also provides very useful information on the general mechanisms of film formation for water-based coating compositions containing mixtures of hard particles and soft particles, e.g., mixtures of hard and soft polymer particles and mixtures of soft polymer particles and inorganic oxide particles. In future publications we will extend these studies in the context of JKR[18] theory to provide additional information on particle elastic deformation and viscous flow during film formation in a binary mixture containing both conductive metal oxide and polymer particles. In addition, we hope to provide more detailed information on the microstructures of these composite films.

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