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Surface Functionalized Silver Nanoparticles for Ultrahigh Conductive Polymer Composites

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Silver nanoparticles were surface functionalized with diacids and then incorporated into the polymer matrix with silver flakes as conductive fillers. By using appropriate diacids, the resistivity of the silver flakes and nanoparticles (molar ratio of silver flakes to nanoparticles is equal to 6:4) incorporated polymer composites was dramatically reduced to as low as $5 \times 10^{-6} \Omega \cdot \text{cm}$. Morphology studies showed that the decreased resistivity resulted from the sintering of silver nanoparticles. The contact resistance of the polymer composites under 85 °C and 85% relative humidity was significantly stable with respect to aging time as a result of the further sintering of silver nanoparticles.

Introduction

Polymer nanocomposites have been paid much attention because of their unique electrical, thermal, mechanical, and optical properties.¹ However, the dispersion of nanoparticles into a polymer matrix has been a bottleneck for nanocomposite fabrication. One of the best ways to uniformly disperse nanoparticles in a polymer matrix is to functionalize the particle surface with organic surfactants. The polymer matrix and inorganic particles often possess different polarities. Simple blending of particles with polymer will result in the aggregates of particles.² If the particles are surface functionalized with organic surfactants, they will become more compatible with the polymer matrix, resulting in a homogeneous dispersion of nanoparticles.³ In the current research, the silver nanoparticles were synthesized and then surface functionalized for the nanocomposite applications.

Many types of organic compounds were used as surfactants to functionalize the silver nanoparticle surface, such as thiol,⁴ pyridine,⁵ carboxylic acids,⁶ and so forth. Moskovits and Suh has characterized dicarboxylic acids adsorbed on silver particle surfaces by surface-enhanced Raman spectroscopy.⁶ It was found that the dicarboxylate group was responsible for the surface bond, probably chelating to silver surface sites. The molecule gains sufficient stability by bonding two carboxylate groups to the surface, and the molecule is able to adopt less favorable chain conformation. The polymethylene groups can, therefore, be arranged in a way best to accomplish the chelating of both carboxylate groups.

Polymer composite materials have versatile applications in electronic packaging because of their low-temperature processability and various functionalities endowed by other ingredients in the composites. Since silver filled polymer composites were first patented as conductive adhesives (ECAs) in 1956,⁷ the conductive adhesives have been proposed as one of the alternatives of tin/lead (Sn/Pb) solders.^{8–12} Lead, one of components in the commonly used eutectic solder, has long been known as a hazard to human beings. Thus, worldwide regulations against the use of lead in electronics have become more apparent. Therefore, the elimination of lead from interconnected materials¹³ has been an urgent research project in the electronics industry.

Comparing to the eutectic Sn/Pb solders, one of the main disadvantages of polymer composites is the lower conductivity resulting in poor current carrying capability. The overall electrical resistance of polymer composites is the sum of the resistance of fillers, the contact resistance between fillers, and the contact resistance between filler and pads. To decrease the overall contact resistance, reducing the number of contact points between fillers could be effective.

In the composites with both silver flakes and nanoparticles as conductive fillers, if the finer particles are fused or sintered together, the number of contact points between fillers will be reduced (Figure 1c). This will lead to lower contact resistance. To improve the electrical properties of the polymer composites, low-temperature sintering of nanoparticles in the polymer matrix has been reported.¹⁴

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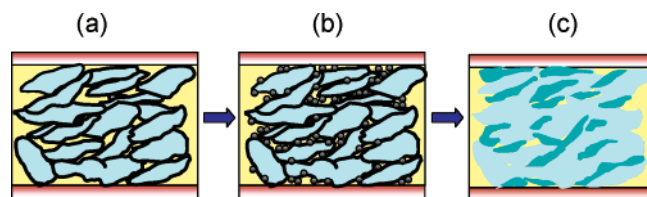


Figure 1. Schematic of particles and flakes between the metal pads: (a) polymer composite with silver flakes as fillers; (b) polymer composite with both flakes and nanoparticles as fillers; and (c) polymer composite with sintered particles among flakes as fillers.

Previous researchers have reported that the nano-silver filled composites showed higher bulk resistivity than the micrometer sized silver flake filled ones, with resistivities of $10^{-2} \Omega \cdot \text{cm}$ and $10^{-4} \Omega \cdot \text{cm}$ from 60 wt % nano-silver and 70 wt % silver flake loadings, respectively.¹⁵ In some cases, nano-silver filled composites showed unmeasurable resistivity and nonconductive behavior.¹⁶ This increased bulk resistivity of nano-silver filled polymer composites is due to the increased number of contact points between nanoparticles comparing to the same weight percent of silver flakes.

In this paper, both silver flakes and surface functionalized silver nanoparticles were incorporated into the polymer matrix, and their electrical properties were studied. The interfacial properties between the surfactants, flakes, and nanoparticles and the electrical properties of the composites as well as their morphologies are discussed.

Experimental Section

Materials. The epoxy resin and hardener used were diglycidyl ether of bisphenol A (Epon 828, Resolution Performance Products) and hexahydro-4-methylphthalic anhydride (HMPA, Lindau Chemicals), respectively. The weight ratio of epoxy to hardener was 1:0.75. The catalyst was 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN, Shikoku Chemicals Crop.) Silver nanoparticles used in this study were synthesized by the combustion chemical vapor condensation¹⁷ method. A diacid¹⁸ was used as the surfactant to treat the silver nanoparticle surface. All the chemicals were used as received.

Silver Nanoparticles Treated by Surfactants. The molar ratio of silver nanoparticles to surfactants was set to 1:1. The solution of the nanoparticles, surfactants, and ethanol was sonicated for 2 h. From the transmission electron microscopy studies, there are no changes for the average size and size distribution of silver nanoparticles after sonication for 2 h because of the existence of surfactants. The surfactants coated on the particle surface can prevent the nanoparticles from growing. The solution was centrifuged to remove the solvent and unreacted surfactant molecules. These particles were rinsed three times by solvent. Finally the particles were dried in a vacuum chamber for 24 h at room temperature.

Polymer Composites. Different molar ratios of surface functionalized silver nanoparticles and silver flakes were incorporated into the mixture of bisphenol A and HMPA. The polymer composite

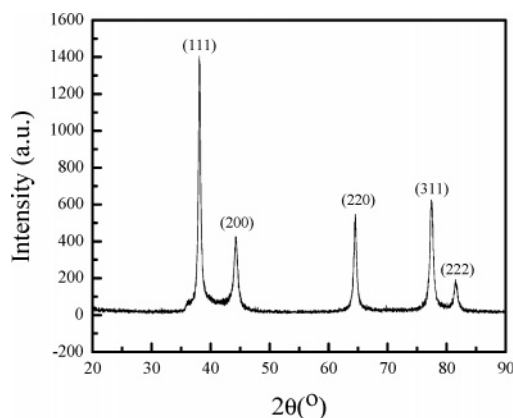


Figure 2. XRD patterns of the synthesized silver nanoparticles.

was sonicated for 1 h. Then the catalyst was incorporated, and the mixture was sonicated again for 5 min.

Characterization Method. Thermogravimetric analysis (TGA, 2050 from Thermal Advantages, Inc.) was used to investigate the weight loss of the surfactant functionalized silver nanoparticles. The debonding temperature between the surfactant and the silver nanoparticles was determined by a standard differential scanning calorimeter (DSC, TA Instruments, model 2970). A sample of about 10 mg was placed into a hermetically sealed DSC sample pan and placed in the DSC cell under a 40 mL/min nitrogen purge. Nonisothermal scans were made at a heating rate of 5 °C/min. After the nonisothermal scan, the sample was cooled to room temperature and then re-scanned under the same condition. For morphology studies, field emission scanning electron microscopy (SEM, JEOL 1530) was used.

Measurement of the Resistivity of Polymer Composites. Resistivity of the polymer composites was determined from the bulk resistance of the specimen with the specific dimensions. Two strips of a Kapton tape (Dupont) were applied onto a pre-cleaned glass slide. The formulated pastes were doctor-bladed between the two strips and cured at 150 °C for 90 min. The Kapton tapes were then removed. The thickness of the cured film was determined by Heidenhain (thickness measuring equipment, ND 281 B, Germany).

Results and Discussion

Synthesis and Surface Functionalization of Silver Nanoparticles. Figure 2 shows the X-ray diffraction (XRD) patterns of the silver nanoparticles used. The average size of the synthesized silver nanoparticles calculated from XRD patterns by the Scherrer equation¹⁹ is around 16 nm.

The synthesized silver nanoparticles and silver flakes were both incorporated into epoxy resin as conductive fillers. There are still challenges to fabricate the nanocomposites, one of which is the dispersion of the nanofillers in the polymer matrix. This is due to their large surface area that increases the viscosity of the formulation dramatically. For this reason, it is relatively challenging to formulate highly filled nanocomposites. Thus, to enhance the dispersion and to increase nanofiller loadings in the epoxy resin, organic surfactants were used to functionalize silver nanoparticles.

According to Moskovits's work,⁶ one of the diacids was selected to functionalize the silver nanoparticle surface in this study. The DSC and TGA curves of the silver nanoparticles treated by diacids are shown in Figure 3. In the

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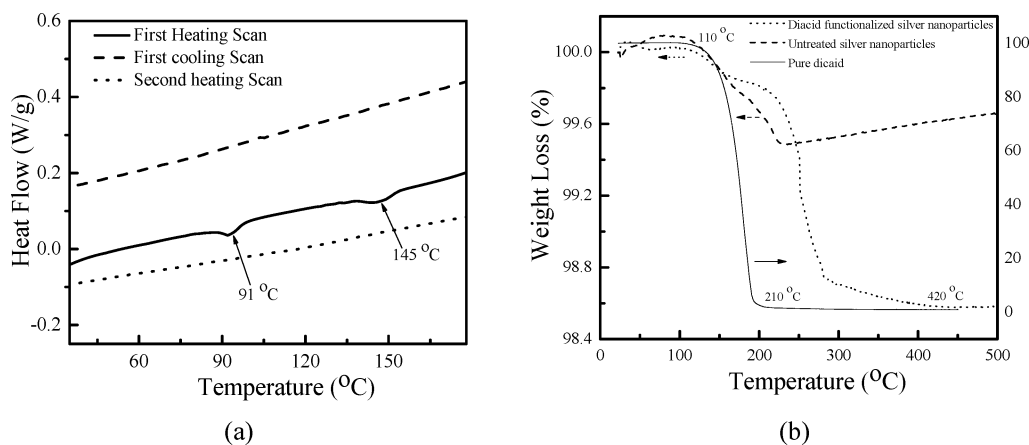


Figure 3. DSC (a) and TGA (b) curves of silver nanoparticles treated by diacids.

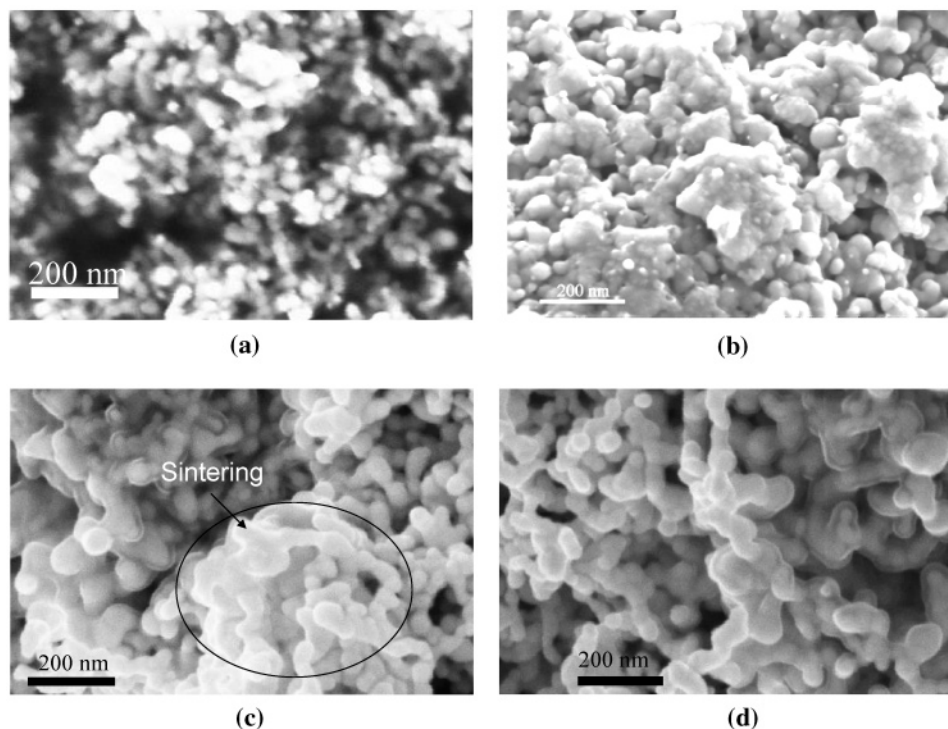


Figure 4. Comparison of the morphologies of surface functionalized silver nanoparticle powders before and after annealing at 100 and 150 °C for 30 min: (a) non-annealed surface functionalized silver nanoparticles; (b) surface functionalized silver nanoparticles annealed at 150 °C for 30 min; (c) untreated silver nanoparticles annealed at 100 °C for 30 min; and (d) surface functionalized silver nanoparticles annealed at 100 °C for 30 min.

first heating scan of DSC, there was an endothermic peak at 91 °C which corresponded to the melting point of the diacids. Another endothermic peak at 145 °C was the possible temperature at which diacids were debonded from silver nanoparticles. This peak disappeared from the second heating scan. The TGA showed that the amount of diacids bonded to silver nanoparticles was around 1.2 wt %. For the pure diacid, more than 95 wt % decomposition happened between 110 and 210 °C. For the functionalized silver nanoparticles, the decomposition between 110 and 210 °C may come from the contaminants on the silver particle surface and some pure diacids, while the rest (with chelating bonds between silver and acid groups) gradually decomposed from 210 to 420 °C. Lee et al. also found this kind of decomposition behavior from their mercaptosuccinic acid coated silver nanoparticles.²⁰ Both the DSC and the TGA results confirmed the existence of diacids bonded to silver nanoparticles.

To further prove the debonding behaviors between surfactants and nanoparticles, the morphologies of silver nanoparticles functionalized by diacids in the powder form after annealing at 100 and 150 °C for 30 min were studied, respectively. Compared with the images of Figure 4a,b, it can be seen that, after annealing at 150 °C for 30 min, the silver nanoparticles functionalized by diacids showed sintered morphologies. During the annealing process, the surfactants will be debonded from the particles according to the DSC results and then sintered together at 150 °C. At the same time, the diacids functionalized, and untreated silver nanoparticles in the powder form were annealed at 100 °C for 30 min, respectively. Morphology studies (Figure 4c,d) showed that the untreated silver nanoparticles were obviously sintered and the color of the powder changed to white, while

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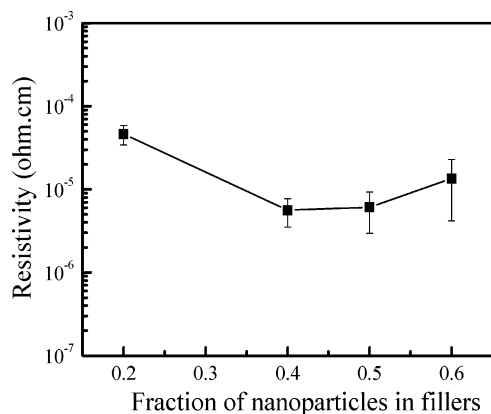


Figure 5. Bulk resistivity of the polymer composites with silver flakes and surface functionalized silver nanoparticles as conductive fillers.

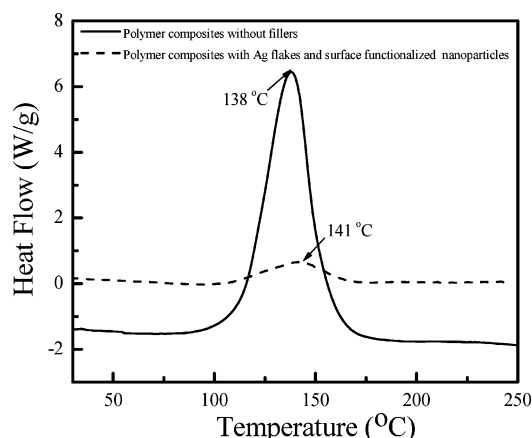


Figure 6. Curing behavior of polymer composites without fillers and with silver flakes and surface functionalized silver nanoparticles (6:4) as fillers.

the functionalized silver nanoparticles were almost not sintered and the color of the powder was still black. This is because at 100 °C the surfactants were still bonded to the nanoparticle surfaces, which prohibited the nanoparticle sintering.

Electrical Properties of Polymer Composites. The silver flakes and surface functionalized silver nanoparticles were incorporated into the epoxy resin, and the electrical resistivity of the composites was measured. The surface treatments enabled the filler loading to be increased up to 80 wt %.

Figure 5 shows the bulk resistivity of the polymer composites with various ratios of micrometer sized silver flakes to surface functionalized silver nanoparticles. The resistivity that could be achieved was as low as $5 \times 10^{-6} \Omega \cdot \text{cm}$, which is close to that of bulk silver ($2 \times 10^{-6} \Omega \cdot \text{cm}$) and lower than that of the eutectic Sn/Pb solder ($1.7 \times 10^{-5} \Omega \cdot \text{cm}$). The small standard deviations of each formulation in Figure 5 show the good reproducibility of this process. However, when the same amount of untreated silver nanoparticles and silver flakes were used as conductive fillers, the resistivity would be $2 \times 10^6 \Omega \cdot \text{cm}$, 12 orders of magnitude higher than that of the surface functionalized silver nanoparticles and silver flakes incorporated one.

The curing profiles of the polymer composites without fillers and with silver flakes and surface functionalized silver nanoparticles as conductive fillers are shown in Figure 6. The peak temperatures in the curing profiles for the two formulations were 138 and 141 °C, respectively. The total

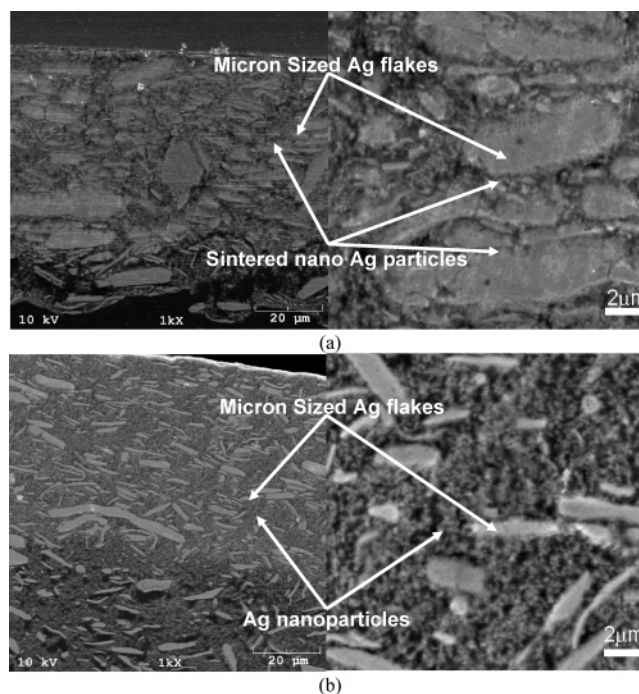


Figure 7. SEM images of polymer composites with (a) silver flakes and surface functionalized silver nanoparticles (6:4) and (b) silver flakes and untreated silver nanoparticles (6:4) as fillers, respectively.

heat of reaction of the unfilled epoxy formulation was 316 J/g, while that of the silver flakes and surface functionalized silver nanoparticle incorporated polymer composites was 162 J/g which was normalized with respect to the epoxy weight in the formulations. It can be seen that the formulation with silver flakes and surface functionalized silver nanoparticles has a lower heat of fusion during curing. This is due to the lower cross-linking density of the epoxy resin. The mechanism of the epoxy resin curing in this study is that the active imidazole group of the catalyst used reacts with epoxy molecules at the 1-N position to form an adduct which contains a highly reactive alkoxide ion. This alkoxide ion will continue to initiate the rapid anionic polymerization of the epoxy resin and form a cross-linked structure. But as a result of the existence of diacids, it will react with an imidazole group to create a salt form, which may result in the loss of the catalyzing ability of the imidazole group. In addition, the carboxylic acid can also initiate the epoxy curing reaction, but its catalyzing ability is much weaker, which may lead to the lower cross-linking density of epoxy resins. To verify the influence of the diacid on the curing behavior of the epoxy resin, the diacid was incorporated into the unfilled epoxy formulation. It was found that the total heat of reaction of this formulation was 179.8 J/g. This is very close to that of the formulation with surface functionalized silver nanoparticle and silver flakes.

Figure 7a shows the morphologies of the polymer composites filled with silver flakes and surface functionalized silver nanoparticles (6:4). It can be seen that the silver nanoparticles obviously sintered between the silver flakes and formed a significantly condensed structure. This sintered structure results in reducing the number of the interfaces between fillers and lowering the electrical resistivity. The mechanism for silver nanoparticle sintering with the aid of

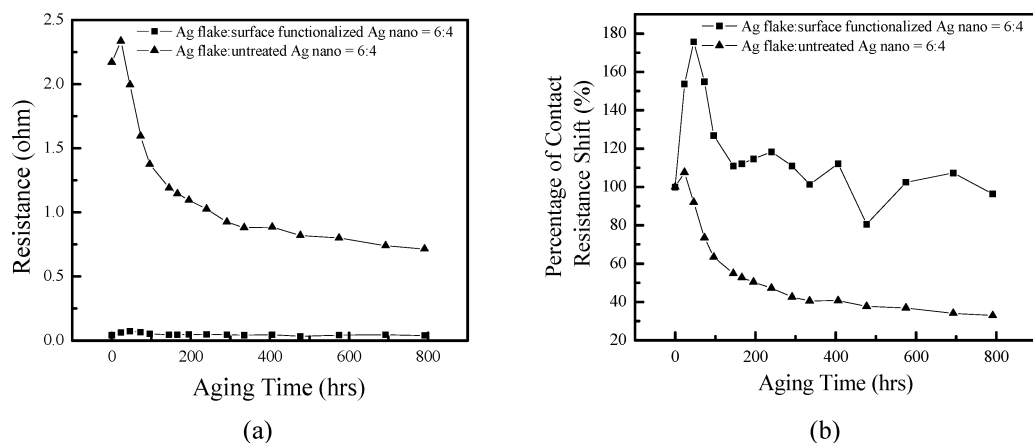


Figure 8. Contact resistances (a) and contact resistance shift (b) of polymer composites with different kinds of fillers.

diacids could be that the diacid is first adsorbed onto the silver nanoparticle surfaces. This will help the dispersion of the nanoparticles in the epoxy resin which enables a higher filler loaded formulation. During the curing process, the diacid is debonded from the silver nanoparticles at a certain temperature. The debonded diacid may act as a flux to reduce the silver oxide layer covered on the silver nanoparticles due to the reaction between the carboxylic acid and silver oxide. This fluxing process aids the sintering process of silver nanoparticles, which decreases the number of contact points between the particles resulting in lower electrical resistivity. Figure 7b shows the morphologies of the polymer composites with silver flakes and untreated silver nanoparticles as conductive fillers, where the nanoparticles are not sintered very well. Significant amounts of nonsintered silver nanoparticles and the separation between silver flakes and silver nanoparticles are observed, which is attributed to the high electrical resistivity.

Figure 8a shows the contact resistance of polymer composites with different kinds of fillers on Ni/Au surfaces during 85 °C and 85% relative humidity (RH) aging. The Ni/Au surface is relatively inert and noncorrosive under high humidity. The contact resistance of the polymer composites with silver flakes and surface functionalized silver nanoparticles is much lower than that with silver flakes and untreated silver nanoparticles. Figure 8b shows the percentage of contact resistance shift with the increase of aging time. In the first several hours, the contact resistance increased because of moisture from 85 °C and 85% RH, while the contact resistance decreased with increasing aging time. This

may be due to the fact that the nanoparticle sintering proceeded further and polar water molecules were absorbed into the composite materials. The sintering process is dependent upon various parameters such as temperature, pressure, time, surface status of the powder, and powder size. Further studies on the effects of these parameters on the sintering behavior of silver nanoparticles in the polymer resins are needed.

Conclusion

Polymer composites with ultralow electrical resistivity ($\sim 5 \times 10^{-6} \Omega \cdot \text{cm}$) were successfully created by using the combination of micrometer sized silver flakes and surface functionalized silver nanoparticles. The morphology studies revealed that this low resistivity was accomplished by dramatic reduction of the number of interfaces between conductive fillers due to low-temperature sintering of silver nanoparticles. In addition, the thermal analysis showed that the surfactant aided the sintering process by means of maintaining nanoparticle surfaces clean in the polymer resin and debonding before the gelation of the epoxy resin. The contact resistance of the formulation on Ni/Au surfaces decreased with aging time under 85 °C and 85% RH. This may be because of further sintering of the nanoparticles under the elevated temperature and humidity.

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