



A simple, low-cost approach to prepare flexible highly conductive polymer composites by *in situ* reduction of silver carboxylate for flexible electronic applications

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ARTICLE INFO

Article history:

Received 17 August 2010

Received in revised form 22 December 2010

Accepted 5 January 2011

Available online 11 January 2011

Keywords:

- A. Flexible composites
- A. Adhesive joints
- B. Electrical properties
- E. Sintering
- D. Raman spectroscopy

ABSTRACT

In recent years, efforts to prepare flexible highly conductive polymer composites at low temperatures for flexible electronic applications have increased significantly. Here, we describe a novel approach for the preparation of flexible highly conductive polymer composites (resistivity: $2.5 \times 10^{-5} \Omega \text{ cm}$) at a low temperature (150 °C), enabling the wide use of low cost, flexible substrates such as paper and polyethylene terephthalate (PET). The approach involves (i) *in situ* reduction of silver carboxylate on the surface of silver flakes by a flexible epoxy (diglycidyl ether of polypropylene glycol) to form highly surface reactive nano/submicron-sized particles; (ii) the *in situ* formed nano/submicron-sized particles facilitate the sintering between silver flakes during curing. Morphology and Raman studies indicated that the improved electrical conductivity was the result of sintering and direct metal–metal contacts between silver flakes. This approach developed for the preparation of flexible highly conductive polymer composites offers significant advantages, including simple low temperature processing, low cost, low viscosity, suitability for low-cost jet dispensing technologies, flexibility while maintaining high conductivity, and tunable mechanical properties. The developed flexible highly conductive materials with these advantages are attractive for current and emerging flexible electronic applications.

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1. Introduction

The preparation of novel flexible highly conductive interconnect materials at low temperatures (preferably 150 °C or below) is essential for the future of low-cost flexible electronics [1–6]. The popularity of flexible circuits and building electronic devices on flexible substrates requires the interconnect materials to be mechanically compliant and highly conductive [6–9]. Low processing temperatures of the interconnect materials are also required to enable the wide use of low cost, flexible substrates such as paper and polyethylene terephthalate (PET). Flexible conductive polydimethylsiloxane (PDMS) composites have been developed for various microelectronic applications, owing to the unique physical and chemical properties of PDMS. These properties include superior elasticity and flexibility, optical transparency, biocompatibility and stable physical and chemical properties over a wide range of

temperatures from –50 °C to +200 °C [10]. Agar et al. reported that the resistivity of PDMS filled with 80 wt.% bimodal distribution of micron-sized silver flakes is about $7 \times 10^{-4} \Omega \text{ cm}$ [11]. Electrical resistivity of PDMS filled with 19 vol.% silver particles showed a resistivity of about $10^{-2} \Omega \text{ cm}$ and the resistivity of the PDMS-based conductive composites exhibited no significant decreases as the filler loading increased [10]. Lutz and Cole reported the lowest resistivity of $2 \times 10^{-4} \Omega \text{ cm}$ for PDMS filled with 80 wt.% silver particles and the resistivity leveled off even increasing the filler loading [12]. However, a minimum resistivity of on the order of $10^{-5} \Omega \text{ cm}$ is required to avoid severe resistive losses [13]. Another limitation of flexible conductive PDMS composites lies in the poor adhesion on metal surfaces due to the low surface energy of PDMS. This further limits their wide application as a flexible interconnect material. Therefore, new flexible interconnect materials with low electrical resistivity, good adhesion and low processing temperature must be developed for flexible electronic applications.

The resistivity of a conductive polymer composite is determined by the composite composition (such as filler loading), the surface properties of conductive fillers (such as the presence of a thin layer of lubricant or oxide film), physiochemical properties of polymer matrix (such as cure shrinkage and the interaction between the

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polymer matrix and conductive fillers), interlayer thickness, temperature, processing conditions of conductive polymer composites, etc. [3,14,15]. The resistance of conductive polymer composites is the sum of filler resistances (R_f) and inter-particle contact resistances (R_c). The contact resistance is composed of constriction resistance and tunneling resistance [16–21]. Constriction resistance occurs as the current must squeeze through the small area of contact. Tunnel resistance is due to the intermediate layer between conductive fillers. In conductive polymer composites, conductive fillers may be separated by a thin layer of polymer, oxide, and/or lubricant [3,14,20]. The thickness of the interface can vary from 10 to 100 Å, depending on the physiochemical properties of the polymer matrix, filler, filler concentration, and the conditions of composite preparation [14]. Relatively low conductivity of conductive polymer composites such as conductive PDMS composites results from the physical contact, instead of metallurgical joints between conductive fillers [22–24]. Reducing or even eliminating the contact resistance between conductive fillers is crucial for the preparation of highly conductive polymer composites.

Here we describe a novel approach to enable the formation of metallurgical joints between silver flakes within a flexible polymer matrix by simply incorporating a flexible epoxy with reduction capability—diglycidyl ether of polypropylene glycol (DGEPPG), leading to flexible highly conductive polymer composites. The approach involves (i) *in situ* reduction of silver carboxylate present on the surface of silver flakes by DGEPPG, a mild reducing agent, to form nano/submicron-sized silver particles both on the surface of and at the edge of silver flakes; (ii) the *in situ* formed nano/submicron-sized silver particles, due to high surface area-to-volume ratios and lack of strong capping agents, are highly surface reactive, which results in the low temperature sintering between silver flakes during curing. Sintering enables the formation of metallurgical joints and reduces or even eliminates the contact resistance among the conductive fillers, leading to highly conductive polymer composites. We first characterized the silver flakes and verified the presence of silver carboxylate on the surface of silver flakes. Then we investigated the reduction of silver carboxylate by DGEPPG on the surface of silver flakes. The formation of silver nano/submicron-sized particles on the surface of silver flakes and the sintering between silver flakes were characterized by scanning electron microscopy (SEM). Finally, the electrical and adhesion properties of the flexible conductive polymer composites were discussed.

2. Materials and methods

2.1. Materials

Epoxy resins used were diglycidyl ether of polypropylene glycol (DGEPPG, D.E.R. 732, Dow Chemical) and diglycidyl ether of bisphenol F (DGEBF, EPON 862, Shell Chemical Co.) (Fig. 1). DGEPPG has a much lower viscosity (60–70 mPa s) than DGEBF (2500–4500 mPa s). Molecular structures of the epoxy resins were verified by Mass Spectrometry (Fig. S-1 in the Supplementary data). The curing agent was hexahydro-4-methylphthalic anhydride (HMPA) donated by Lindau Chemicals. Catalyst was 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN, Shikoku Chemicals Corp.) Two silver flakes with different sizes and surface lubricants (Ag-FA and Ag-FB, Ferro Corp.) were used to improve the packing density and adjust the viscosity of the formulated paste. All chemicals were used as received.

2.2. Reduction of silver carboxylate on the surface of silver flakes

An epoxy resin (DGEBF or DGEPPG) was mixed with silver flakes and then heated at 150 °C for 10 or 30 min. Silver flakes lost their luster and the surface appeared dull after being treated with DGEPPG, while no significant change of surface appearance was observed for silver flakes treated with DGEBF. Acetone was added to the mixture and the resulting mixture was centrifuged. After removal of the superant, the silver flakes were re-dispersed in acetone. Five cycles of dispersing and centrifugation were used in an effort to remove the residual epoxy resin. Note that the lubricant on the surface of silver flakes was hardly washed off by acetone during the process [25]. Finally, the silver flakes were dried in vacuum before the characterization.

2.3. Preparation of polymer composites

Different ratios of DGEBF and DGEPPG were mixed with 80 wt.% silver flakes (Ag-FA and Ag-FB with a mass ratio of 1:1), HMPA and the catalyst. Two strips of a Kapton tape (Dupont) were applied onto a pre-cleaned glass slide. The formulated pastes were printed on the glass slide. Then the pastes were thermally cured at 150 °C in air for 1 h. To show flexibility of conductive polymer composites, the formulated pastes were printed on the surface of polyethylene terephthalate. After curing, the samples were bended conformally

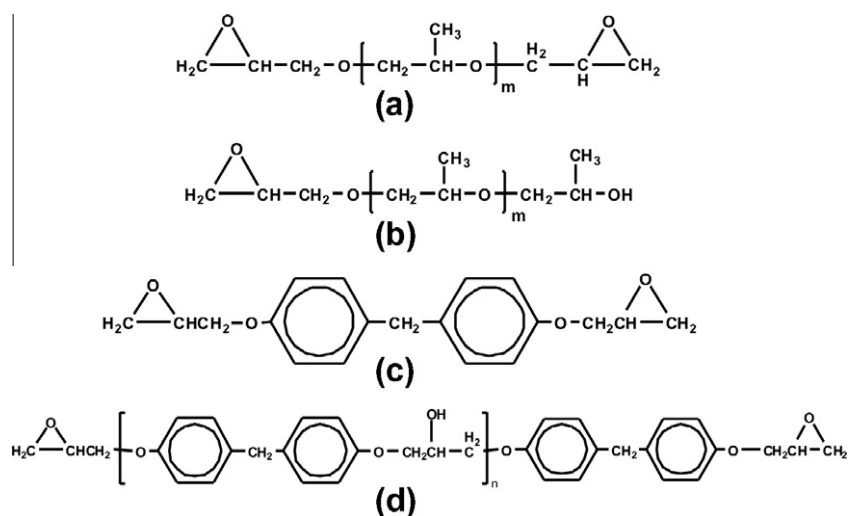


Fig. 1. Molecular structures of DGEPPG (a) mainly $m = 5, 6, 7, 8, 9$ and 10 and (b) mainly $m = 7, 8, 9$ and 10, and DGEBF (c) and (d) ($n = 1$).

to the surface of cylinders with different radii to measure the resistivity change under bending condition.

2.4. Characterization

After curing, bulk resistances (R) of polymer composite strips were measured by a Keithley 2000 multimeter. The widths and lengths of the specimens were measured by digital caliber (VWR). The thickness of the specimen was measured by Heidenhain (thickness measuring equipment, ND 281B, Germany). Bulk resistivity, ρ , was calculated using $\rho = Rtw/l$, where l , w , t are the length, width and thickness of the sample, respectively.

Weight loss of silver flakes during heating in air was studied using thermogravimetric analyzer (TGA, TA Instruments, model 2050). The heating rate was 20 °C/min.

Morphologies of the treated silver flakes and the polymer composites were studied by field emission scanning electron microscopy (SEM, LEO 1530).

Decomposition of the lubricants on the surface of silver flakes was studied by differential scanning calorimetry (DSC, TA Instruments, Q100). The heating rate was 10 °C/min.

Raman spectra were obtained by using a LabRAM ARAMIS Raman confocal microscope (HORIBA Jobin Yvon) equipped with a 532 nm diode pumped solid state (DPSS) laser. Si wafer was used as a substrate for Raman measurements.

3. Results and discussion

3.1. Characterization of silver flakes

It is well known that a thin layer of lubricant is present on the surface of commercial silver flakes to prevent the aggregation of silver flakes during production. This layer of lubricant affects the interaction of silver flake with other silver flakes and with the polymer system and thus affects the dispersion of silver flakes, the rheology of formulated pastes and the electrical conductivity of the resulting polymer composites [25–27]. Fig. 2 shows Raman spectra of the lubricant on the surface of silver flakes. The presence of carboxylate groups on the surface of silver flakes was verified by the symmetric ($\nu_s(\text{COO}^-)$) stretching at 1432 cm^{-1} (or 1438 cm^{-1}) and asymmetric ($\nu_{as}(\text{COO}^-)$) stretching at 1591 cm^{-1} (or 1587 cm^{-1}) [27–29]. This result is consistent with previous studies that the lubricant layer is indeed silver carboxylate [25–27]. The distinct differences between the two spectra were (i) the intensity of the peaks at 930 and 664 cm^{-1} in Fig. 2a, assigned to the C–

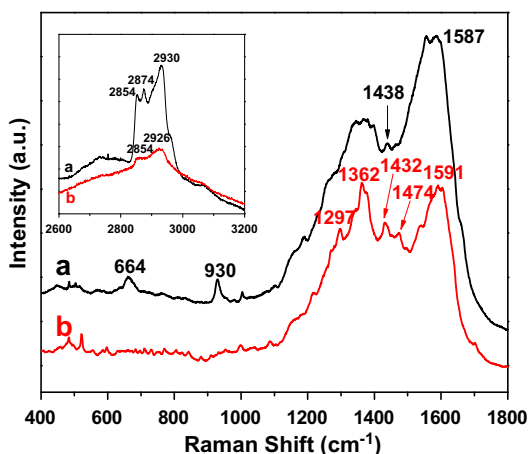


Fig. 2. Raman spectra of the lubricant on the surface of (a) Ag-FA and (b) Ag-FB. Inset is the spectra in the range of 2800–3200 cm^{-1} .

COO^- stretching and the deformation of $-\text{COO}^-$ [29], was much stronger than that of the corresponding peaks in Fig. 2b; (ii) The SERS peaks of C–H stretching of the lubricant on Ag-FA were well resolved, compared with those of the lubricant on Ag-FB (Fig. 2, inset); (iii) the methylene twisting, wagging and scissor appeared at 1297, 1362 and 1474 cm^{-1} [28], respectively in Fig. 2b. The intensity of these peaks was much stronger than that of the corresponding peaks in Fig. 2a. These distinct differences are related to the chain length of lubricants and their surface orientation and conformation [29]. Fig. 3 shows TGA results of the silver flakes. Ag-FA and Ag-FB showed significant weight losses at 188 °C and 218 °C, respectively (Fig. 3, inset). This clearly indicates the presence of lubricants on the surface of silver flakes. Weight losses of Ag-FA and Ag-FB at 450 °C were 0.09% and 0.23%, respectively. Both Ag-FA and Ag-FB showed endothermic peaks at 232 and 247 °C, respectively (Fig. 4). Lu et al. found that silver flakes lubricated with fatty acids of a longer chain showed exothermic DSC peaks at higher temperatures [30]. These exothermic DSC peaks in air of lubricated silver flakes are due to the oxidation of the lubricant layer [26,30]. These results indicated that the lubricant on the surface of Ag-FB may have a longer chain than that on Ag-FA.

3.2. Reduction of silver carboxylate on the surface of silver flakes

To investigate the reduction of silver carboxylate and the formation of silver particles on the surface of silver flakes, Ag-FA

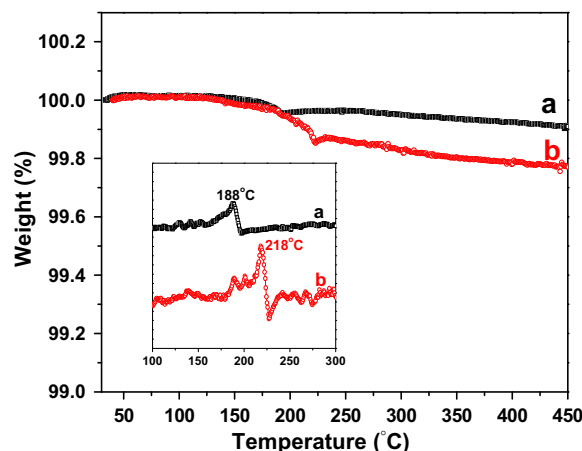


Fig. 3. TGA of (a) Ag-FA and (b) Ag-FB. Inset is the first derivative of curve a and b in the temperature range of 100–300 °C.

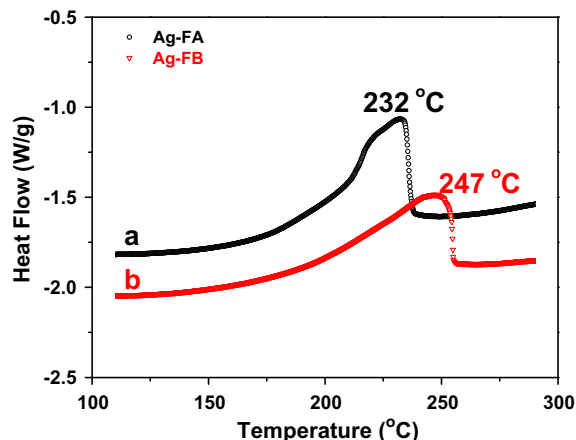


Fig. 4. DSC of (a) Ag-FA and (b) Ag-FB.

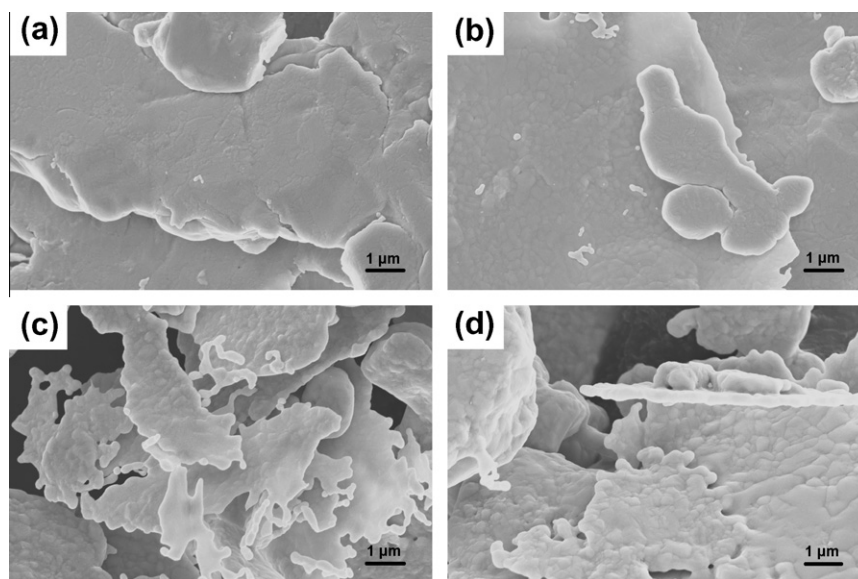


Fig. 5. Ag-FA treated with DGEBF for (a) 10 min, (b) 30 min and with DGEPG for (c) 10 min, (d) 30 min at 150 °C.

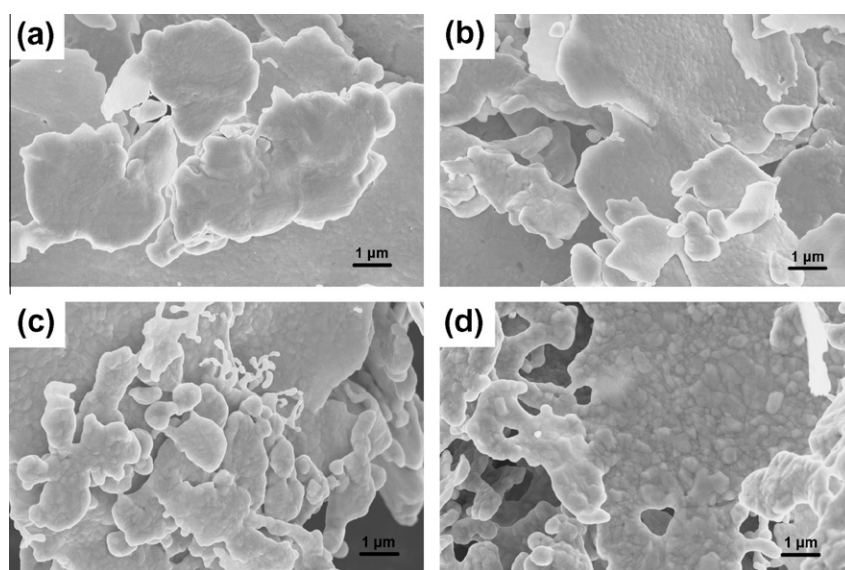


Fig. 6. Ag-FB treated with DGEBF for (a) 10 min, (b) 30 min and with DGEPG for (c) 10 min, (d) 30 min at 150 °C.

and Ag-FB were treated with DGEBF and DGEPG at the curing temperature (150 °C). Figs. 5 and 6 show the surface morphology changes of silver flakes after isothermal treatment. When treated with DGEBF at 150 °C for 10 min, the surface of silver flakes remained relatively smooth (Figs. 5a and 6a). Compared with silver flakes treated with DGEBF, silver flakes treated with DGEPG showed clearly the growth of silver nano/submicron-sized particles on their surfaces and at their edges (Figs. 5c and 6c). As the time for treatment increased, silver flakes treated with DGEBF became rough (Figs. 5b and 6b). The relatively rough surface was the result of the reduction of silver carboxylate and the formation of highly surface reactive silver nano/submicron-sized particles. These particles then sintered with the silver flakes. The growth of silver nano/submicron-sized particles was more prominent when silver flakes were treated with DGEPG for 30 min (Figs. 5d and 6d). Moreover, neckings between silver flakes were observed. The neckings between silver flakes are indicative of effective sintering

between silver flakes. This may result from the relatively stronger reduction capability of the primary –OH group in DGEPG than secondary –OH group in DGEBF at 150 °C.

Fig. 7 shows DSC of silver flakes (Ag-FB) treated with DGEBF or DGEPG at 150 °C. Ag-FB shows clearly an exothermic peak and a mild broad peak at 276 °C after isothermal treatment with DGEBF for 10 and 30 min, respectively. The shift of the exothermic peak from 247 °C (Fig. 4) to 276 °C may result from the physical absorption of DGEBF onto the surface of silver flakes that delays the oxidation of the lubricant. The physical absorption was verified by the peak at 915 cm^{-1} (Fig. 8b), the characteristic vibration of epoxy rings, in the Raman spectrum of silver flakes treated with DGEBF at 150 °C (Fig. 8c). After treatment with DGEPG, the exothermic DSC peak disappeared (Fig. 7) and Raman peaks of the lubricant on the surface of silver flakes almost disappeared (Fig. 8a and d). Both DSC and Raman results indicated that silver carboxylate on the surface of silver flakes were reduced and removed. This was

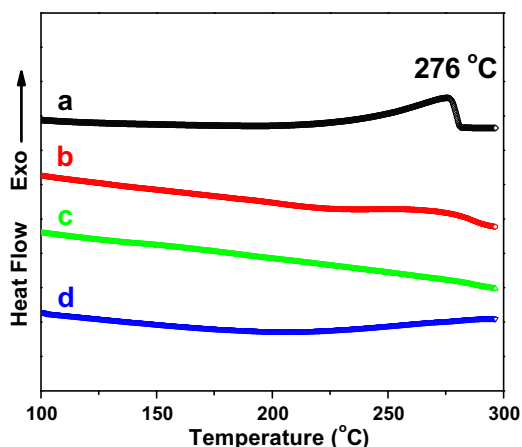


Fig. 7. DSC of Ag-FB treated with DGEBF (a) 10 min, (b) 30 min and with DGEPG (c) 10 min, (d) 30 min at 150 °C.

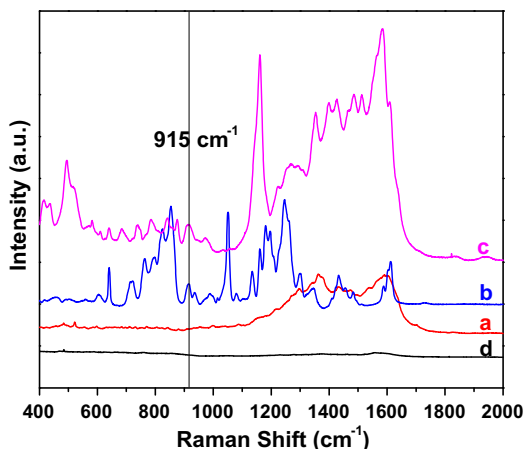


Fig. 8. Raman spectra of (a) the lubricant on the surface of Ag flakes (Ag-FB), (b) DGEBF, (c) DGEBF-treated Ag flakes, (d) DGEPG-treated Ag flakes.

consistent with the lack of luster on the surface of DGEPG treated silver flakes. It is well-documented that organic molecules on the surface of silver particles play an important role in the sintering onsets, the extent of densification and final grain sizes [31]. These organic molecules provide an energy barrier to sintering. The particles sinter if the thermal energy is sufficient to overcome the activation energy provided by the organic molecules [32]. The nearly complete removal of the lubricant from the surface of silver flakes facilitated the sintering between silver flakes for DGEPG treated silver flakes and thus the electron transport.

3.3. Properties of flexible highly conductive polymer composites

Electrical conduction of a metal-filled epoxy-based polymer composite is established through the cure shrinkage of the polymer matrix, which brings metal fillers into intimate contacts to form 3-D conductive networks within the polymer matrix. Fig. 9 shows bulk resistivity of the composites filled with 80 wt.% silver flakes using different ratios of DGEBF and DGEPG as polymer matrices. DGEBF filled with 80 wt.% silver flakes shows an averaged resistivity of $2.3 \times 10^{-4} \Omega \text{ cm}$, which is comparable to that of commercially available electrically conductive adhesives. The averaged resistivity decreased to $1.4 \times 10^{-4} \Omega \text{ cm}$ and the lowest resistivity was $6.5 \times 10^{-5} \Omega \text{ cm}$ for the composites with equal amounts of DGEBF and DGEPG. The polymer composites showed a lower electrical resistivity ($3.5 \times 10^{-5} \Omega \text{ cm}$) with an increased DGEPG con-

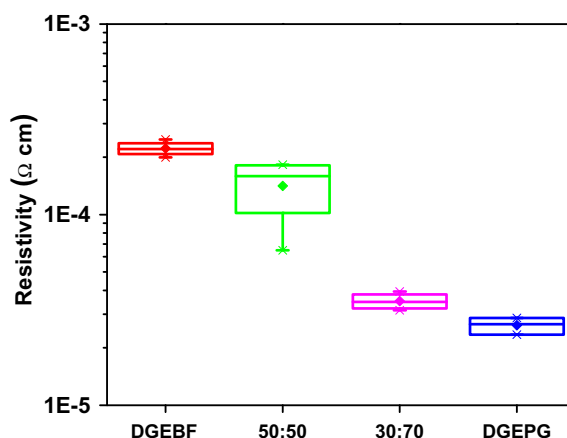


Fig. 9. Electrical resistivity of polymer composites filled with 80 wt.% silver flakes by using different polymer matrices including DGEBF (100%), a 50:50 mixture of DGEBF and DGEPG, a 30:70 mixture of DGEBF and DGEPG, and DGEPG (100%).

tent (70 wt.% of the mixture of DGEBF and DGEPG). This could be due to the enhanced reduction of silver carboxylate and increased necking area between silver flakes. The resistivity of the DGEPG filled with 80 wt.% silver flakes is $2.5 \times 10^{-5} \Omega \text{ cm}$, about one order of magnitude lower than that of the composites composed of DGEBF and 80 wt.% silver flakes. Fig. 10 shows the cross-sections of the conductive polymer composites. Without DGEPG, the surface of silver flakes within the polymer matrix was relatively smooth (Fig. 10a). There are lubricants (or possibly oxide) at the interface between silver flakes. The presence of the lubricants increases the tunneling resistance between silver flakes. With the incorporation of DGEPG, silver nano/submicron-sized particles formed both on the surface and at the edges of the silver flakes (Fig. 10b). As the content of DGEPG increased, larger particles and neckings between silver flakes formed (Fig. 10c and d). Therefore, two factors contribute to the significantly improved electrical conductivity of the polymer composites with the incorporation of DGEPG. First, the growth of highly surface reactive silver nano/submicron-sized particles facilitates the sintering between silver flakes. The sintering leads to the formation of metallurgical joints and reduces or even eliminates the contact resistance effectively. Second, the removal of surface lubricant, as verified from Fig. 8, enables direct metal–metal contacts between silver flakes, decreasing the contact resistance.

Highly conductive polymer composites have been prepared by low temperature sintering ($<200^\circ\text{C}$) of the incorporated silver nanoparticles [25,26,33]. The limitations of these approaches include (i) low dispersion efficiency of untreated nanoparticles in the epoxy matrix. Surface functionalization with short-chain diacids can enhance the dispersion and prevent the oxidation as well as facilitate the sintering, but decrease the catalytic capability and tend to result in poor mechanical properties of the conductive composite [26]; (ii) the relatively high cost of silver nanoparticles. A large amount of silver nanoparticles used to improve the electrical conductivity increases the cost; (iii) complicated and expensive processes such as surface functionalization [24], synthesis of multi-walled carbon nanotubes decorated with silver nanoparticles [33] and relatively long-period sonication [23,24]. These complicated, time-consuming steps limit their industrial applications; (iv) difficulties in printing pastes filled with nanomaterials. A high loading of nanomaterials increases the viscosity of the paste dramatically. The increased viscosity makes the paste difficult to flow and to be printed, especially for low-cost jet dispensing technologies. Compared with these studies, the present study offers a much simpler, lower cost approach to achieve highly conductive polymer composites.

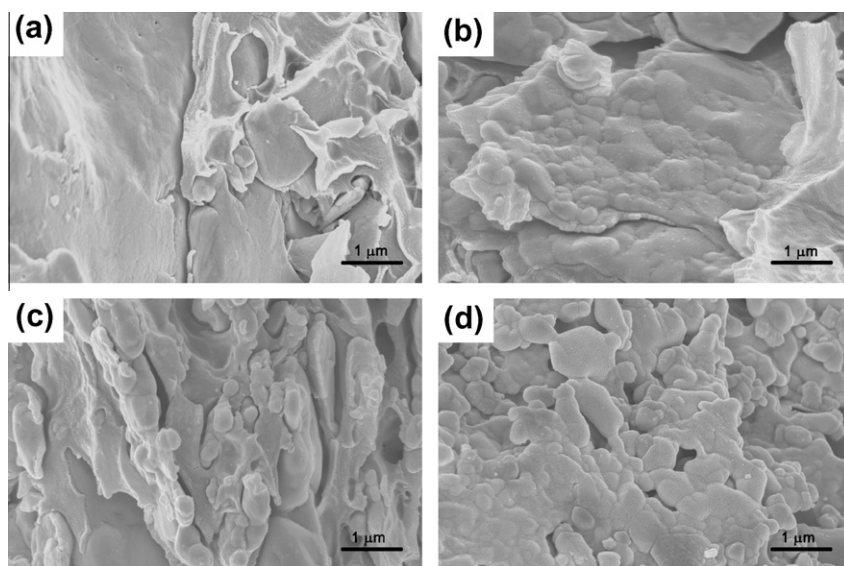


Fig. 10. SEM images of cross-sections of polymer composites filled with 80 wt.% Ag flakes by using different polymer matrices (a) DGEBF (100%); (b) 50:50 mixture of DGEBF and DGEPG, (c) 30:70 mixture of DGEBF and DGEPG, (d) DGEPG (100%).

Flexible highly conductive polymer composites with ratios of 70:30 and 50:50 of DGEPG to DGEBF exhibited die shear strengths of 9.8 and 14.7 MPa on a gold surface, respectively. The adhesion strength on the gold surface can be improved significantly by surface modification with a coupling agent and increased to 14.2 and 32.9 MPa correspondingly [8]. The resistivity of flexible highly conductive polymer composites with ratios of 70:30 and 50:50 of DGEPG to DGEBF increased by $43.9 \pm 8\%$ and $66.3 \pm 24\%$, when the radius of curvature of the samples was changed from 30 mm to 14 mm, respectively. Simple device level tests indicated that interconnects based on the flexible highly conductive polymer composites are robust during the substrate rolling/bending, enabling the application of the flexible highly conductive polymer composites in flexible electronics [8].

4. Conclusions

Flexible highly conductive polymer composites with electrical resistivity as low as $2.5 \times 10^{-5} \Omega \text{ cm}$ were prepared at 150°C by simply incorporating flexible epoxy (DGEPG) into the composite formulation. DGEPG functioned as a mild reducing agent for the *in situ* reduction of silver carboxylate on the surface of silver flakes. The reduction of silver flakes by DGEPG removed the surface lubricant and allowed the metallurgical joints and direct metal–metal contacts between the conductive fillers. This reduced or even eliminated the contact resistance effectively, enabling the preparation of flexible highly conductive polymer composites at a low temperature. The approach developed offers many significant advantages such as (i) reduced materials cost; (ii) low processing temperature compatible with low cost, flexible substrates such as paper and PET; (iii) simple processing; (iv) low viscosity of the formulated pastes with DGEPG. This allows them to be used for low-cost jet dispensing technologies; (v) tunable mechanical properties; (vi) flexibility and high electrical conductivity. Future printed electronics require the epoxy-based polymer composites to be mechanically compliant to fit the non-planar forms, to have a high conductivity, to have strong adhesion on many substrates and to have low processing temperatures to be compatible with low cost, flexible substrates. The multi-functional polymer composites developed in this study are attractive for current and emerging applications in flexible electronics.

Acknowledgement

The authors thank NSF (#0621115) for the financial supports and Ferro Corp. for their donation of silver flakes.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.compscitech.2011.01.001.

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