The Conductivity Behavior of Multi-Component Epoxy, Metal Particle, Carbon Black, Carbon Fibril Composites

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ABSTRACT: Following the previous studies of epoxy/silver conductive composites, a detailed investigation of the influence of ethylene glycol on the resulting resistivity of various composites was carried out. Ethylene glycol was found to have a catalytic effect on the curing process of the epoxy resin, verified by differential scanning calorimetry studies. The accelerated curing process diminishes settling of the metal particles and therefore results in better and more uniform conductivities. High temperature curing of the composites was found to have a similar effect on the conductivity. The conductivity behavior of some other composites, such as epoxy/nickel, epoxy/nickel/carbon fibrils, and epoxy/carbon black/carbon fibrils, were also studied. The structure–property relations were better understood through scanning electron microscopy observations. Silver and nickel particles were found to perform differently in the cured epoxy, showing different percolation concentrations and conductivity levels. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1706–1713, 2002

Key words: epoxy resin; metal-polymer composites; electrical conductivity

INTRODUCTION

Conductive adhesives were used extensively in the electronic industry in applications such as die attachment, liquid crystal display (LCD) assembly, and surface-mounted assembly of packaged components on printed wiring boards (PWBs). They are also being increasingly exploited to replace tin and lead solders because of environmental concerns.[1,2]

Silver-filled epoxy composites are widely used conductive adhesives, in which epoxy resins wet and bond to almost all surfaces, showing high performances, whereas silver offers advantages of a high level of conductivity and conductivity stability.[1,3] Many other kinds of conductive fillers in filled epoxy resin conductive adhesives were studied and are being explored as lower cost alternatives. The studies of the conductivity behavior of conductive adhesives are similar to those of conductive thermoplastic polymer composites filled with carbon blacks (CB), carbon fibers, or metallic particles, in applications for electromagnetic interference or radio frequency interference (EMI/RFI) shielding,[4,5] electrostatic dissipation (ESD),[6] positive temperature coefficient (PTC) materials,[7,8] and others. In our previous article,[9] a third component [i.e., carbon black, carbon fibrils (CF), SiO_2, and organic dispersants] was added to the epoxy/Ag system to obtain composites of better conductivity, or similar conductivity but at lower silver contents.

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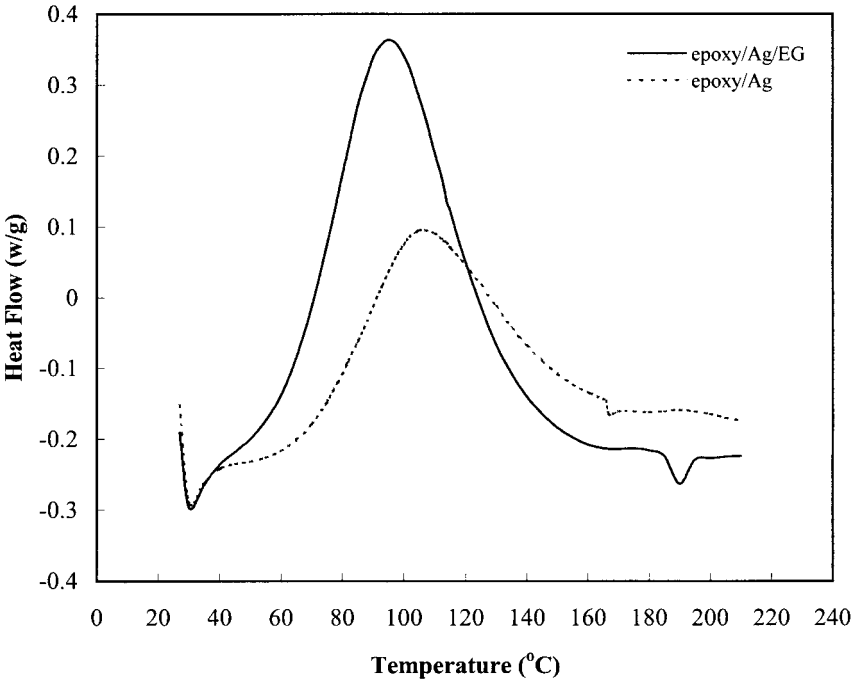

Figure 1 DSC scans of the epoxy/Ag (35/65) composite with and without ethylene glycol (EG).

In the present investigation, a detailed study of the influence of dispersants on various multicomponent composites was carried out. Also, some other conductive adhesive systems, such as epoxy/nickel (Ni), epoxy/Ni/CF, and epoxy/CB/CF composites were studied.

EXPERIMENTAL

Materials

Epoxy polymer based on bisphenol-A resin (GY-257, Ciba Ltd., Basel, Switzerland) and an aliphatic polyamine hardener, diethyltriamine (DETA) were used. The ratio of epoxy to hardener was kept constant at 90/10. Silver powder having an average aggregate size of 0.2–0.5 μm was supplied by NanoPowders Industries (Israel).

The carbon black used (iodine adsorption of 1000–1150 mg/g) was Ketjenblack EC-600 of Akzo, Netherlands. Carbon fibril is a vapor-grown carbon fiber (VGCF), a product of Applied Sciences, Inc., USA. The fibrils have an average length of 10 μm and a diameter of 0.3 μm. The nickel powder used was Inco Type 255, having an average particle size of 1 μm, provided by Inco Special Products (Toronto, Canada). Compositions of the prepared blends are expressed in weight percentage, except for CB, which is expressed in phr (parts per hundred parts of the epoxy/hardener system).

Composite Preparation

Epoxy/Ag and Epoxy/Ni Composites

To prepare an epoxy/Ag concentrate, 75 wt % silver powder was dispersed in the epoxy resin first by hand mixing and then on a three-roll paint mill. The concentrate of this composition was blended with some additional amounts of epoxy resin to attain the desired different silver concentrations, followed by the addition of the hardener, mixing, and casting into Teflon molds. Two types of molds were used: a disc mold (2 cm diameter, 2.5 mm thick) and a rectangular rod mold (5 cm long, 2 mm wide, and 0.5 mm thick). Samples were cured at room temperature for 18–24 h, followed by 3 h postcuring at 60°C. A high temperature curing procedure was performed at 100°C for 2 h without postcuring. Epoxy/Ni composites were prepared the same way.

Three-Component Composites

For epoxy/Ag/CB composites, the epoxy resin was separately mixed with the desired amounts of

Table I Effect of Ethylene Glycol and High-Temperature Curing on the Resistivity of Various Composites

Composites	Resistivity With Dispersant (ohm-cm) (room temp. curing)	Resistivity Without Dispersant (ohm-cm) (room temp. curing)	Resistivity Without Dispersant (ohm-cm) (100°C curing)
Epoxy/Ag (rod) (35/65)	$(5.0 \times 10^{0})^{a}$	2.4×10^{3}	1.2×10^{-1}
Epoxy/Ag/CF (rod) (35/65, 0.9% CF)	$(6.0 \times 10^{-2})^{a}$	1.2×10^{2}	1.1×10^{1}
Epoxy/Ag/CB (rod) (35/65, 0.5 phr CB)	$(1.0 \times 10^{2})^{a}$	2.4×10^{3}	3.0×10^{0}
Epoxy/Ni (rod) (35/65)	$(9.2 \times 10^{-2})^{a}$	3.2×10^{-1}	7.2×10^{-2}
Epoxy/CB (disc) (0.5 phr CB)	$(1.7 \times 10^{5})^{b}$	5.6×10^{4}	4.8×10^{4}
Epoxy/CF (disc) (0.9% CF)	$(1.1 \times 10^{4})^{b}$	1.9×10^{4}	5.6×10^{3}

[a]Adding 1.5 phr dispersant (ethylene glycol).
[b]Adding 2.5 phr dispersant (ethylene glycol).

silver powder and carbon black and then the two mixtures were combined by hand mixing. For the epoxy/Ag/CF composite, CF was added to the epoxy/Ag composite and mixed by hand. Epoxy/Ni/CF and epoxy/CB/CF composites were prepared by the same procedure. The contents of all the fillers are related to the epoxy resin plus hardener. The curing procedure for the ternary component composites was the same as for the two-component components. The dispersant used, ethylene glycol, was added to the mixture in an amount of 1.5 wt %, based on metal fillers, or 2.5 wt % based on the epoxy resin when the fillers are CB or CF.

Electrical Measurements

Prior to measurement, the two ends of the rod sample and the two surfaces of the disc sample were coated with silver paint to eliminate contact resistance. Bulk resistance of rod samples was measured by connecting the two ends of the rod with two copper strips which were connected to a Keithley 175A autoranging multimeter. Bulk resistance of the disc samples was measured with the same multimeter when the resistance was less than 2×10^{8} Ω. For resistance levels exceeding 2×10^{8} Ω, disc samples were measured according to DIN 53596, using a Keithley 240A high voltage supply and a Keithley 614 electrometer. A DC voltage of 1.0 V was applied across the sample thickness. At least two samples of each type were measured shortly after postcuring. Volume resistivity was calculated from the bulk resistance of samples with the dimensions of the corresponding mold.

Morphology Studies

The filler distribution in the epoxy matrix was studied by scanning electron microscopy (SEM; JEOL-JSM 5400, Japan). Disc samples were first sawcut into strips. A cordless-refillable butane gas-powered soldering tool (model P-1K) with a hot blow nozzle was used to heat up the center of the strip for a while until it became soft, and then the strip was fractured. A similar procedure was used for the rod samples. This method of fracturing leads to a rather smooth surface, similar to the neat epoxy resin surface. Thus, the development of structure owing to the filler presence throughout the matrix volume is easily observed. The fractured cross section of the samples was gold sputtered prior to observation.

Gel Time Measurement

Gel times of 2 g epoxy/Ag composite samples with and without ethylene glycol were measured by using a standard test method described in ASTM D2471 (1979). Wooden sticks were used to stir the reacting resins by hand every 5 min during the test. The end point is recorded when the reacting resin does not adhere to the end of a clean stick.

Thermal Analysis

Differential scanning calorimetry (DSC) thermograms were measured by using a Mettler DSC30 under nitrogen purge. A 12-mg freshly mixed sample was placed in a DSC cell and heated from 25 to 200°C at a rate of 10°C/min.

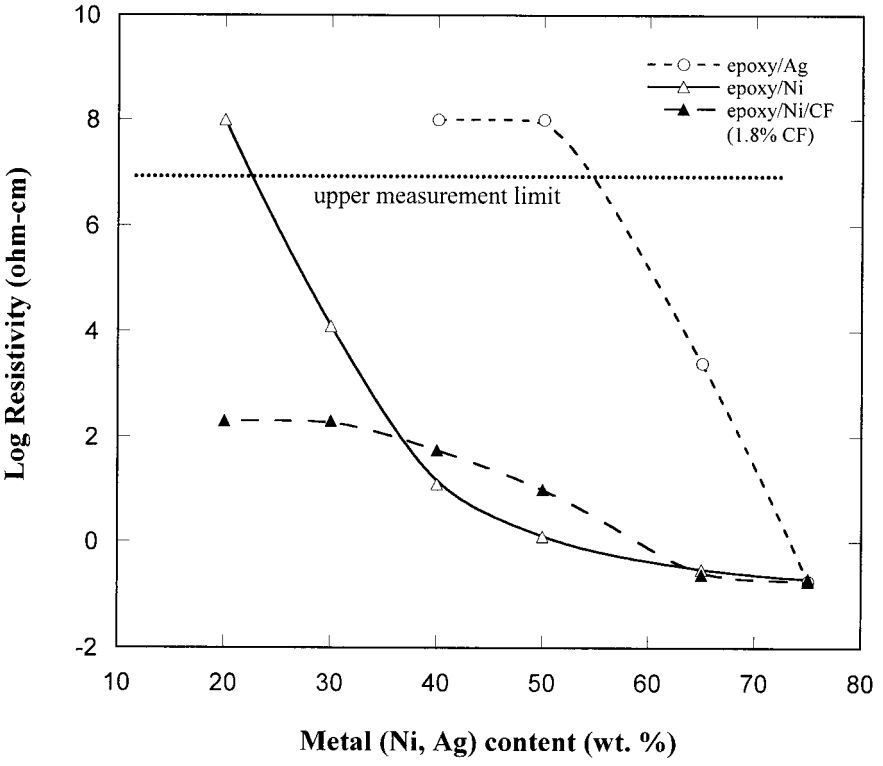

Figure 2 Variation of resistivity of epoxy/Ag, epoxy/Ni, and epoxy/Ni/1.8% CF composites (rod samples) with Ag or Ni content. Samples were cured at room temperature without EG.

RESULTS AND DISCUSSION

Hydroxy-terminated ethers, $HOCH_2(CH_2OCH_2)_n CH_2OH$, with n being within the range of 2–10, were reported[10] to be effective in promoting dispersion of conductive particles, such as silver or copper in liquid epoxy resin systems. In our previous studies,[9] ethylene glycol and glycerol as dispersants for the silver-filled epoxy resin were found to significantly reduce the resistivity of the epoxy/Ag composites. Also, the viscosity of such systems was found to dramatically increase after the addition of the curing agent. However, SEM micrographs did not show a significant improvement of silver dispersion by using a dispersant. Thus, one may assume that the prominent role of the polyols' presence is in their catalytic effect on the cure reaction, and consequently, leads to the reduction of particle sedimentation.

DSC is useful to investigate the cure kinetics of epoxy resins.[11,12] Figure 1 depicts the DSC scans of epoxy/Ag composites with and without ethylene glycol. It clearly shows that the addition of ethylene glycol accelerates the curing reaction (the reaction mechanism is not known yet), thus making the exothermic peak appear at a lower temperature. Gel time measurements also show that the gel time of epoxy/Ag composite with and without ethylene glycol are 1.5 and 2.5 h, respectively. A fast cure process is important for the epoxy/Ag system, because it reduces the extent of sedimentation of silver particles, as has been previously discussed.[9] Table I summarizes the effect of ethylene glycol on the resistivity of various composites. It can be seen that the addition of a small amount of ethylene glycol decreases the resistivity of epoxy/Ag (35/65) composite by $\sim$ 2.5 orders of magnitude, the epoxy/Ag/CF (35/65, 0.9 wt % CF) composite by more than three orders of magnitude, and the epoxy/Ag/CB (35/65, 0.5 phr CB) composite by one order of magnitude. Interestingly, ethylene glycol has a very little influence on the conductivity of nickel, carbon black, and carbon fibril filled epoxy resins. However, a DSC study shows the same catalytic effect of ethylene glycol on the epoxy/hardener system, regardless

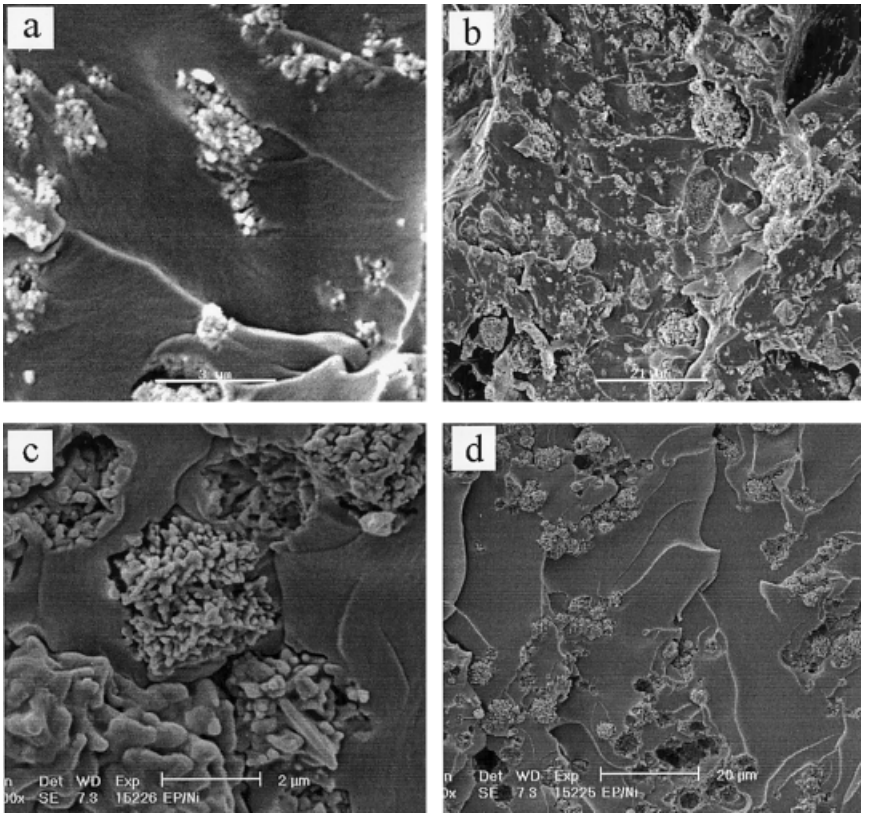

Figure 3 SEM micrographs of (a) and (b), epoxy/Ag (50/50) composite; (c) and (d), epoxy/Ni (50/50) composite at two magnifications. Samples were cured at room temperature without EG.

of the presence of the conductive components. The results in the following parts of this article imply that Ni particles have much stronger tendency than Ag particles to sediment, whereas CB and CF do not show sedimentation phenomenon during the curing process. Therefore, the resistivity of Ni-, CB-, and CF-filled epoxy resin composites is not greatly influenced by the speed of the curing process.

Comparison of the effect of ethylene glycol with that of high temperature curing (100°C) on the resistivity of the composites, which is shown in the last column of Table I, indicates that some similarities can be noted. High temperature curing greatly reduces the resistivity of the silver containing composites (i.e., epoxy/Ag, epoxy/Ag/CF, epoxy/Ag/CB composites), whereas little effect on the resistivity of Ni-, CB-, and CF-filled epoxy composites can be noted. It is known that high temperature curing also expedites the curing process[13]; therefore, it similarly affects the conductivity of the epoxy/Ag binary and ternary composite systems as ethylene glycol does.

Epoxy/Ni conductive composites were studied for comparison with the epoxy/Ag composites. The variation of the resistivity of the epoxy/Ni composites with Ni content is shown in Figure 2. The percolation threshold of epoxy/Ni composites is around 35 wt % Ni, compared with ~ 65 wt % Ag for the epoxy/Ag composites. In Figure 3, SEM micrographs showing the distribution of Ag and Ni particles in epoxy resin are presented. The tiny spherical Ag particles tend to produce compact, hard agglomerates, whereas the Ni particles tend to form grapelike, large spherical agglomerates. The much lower percolation threshold of the epoxy/Ni composites is probably partly owing to the different Ni-agglomerated structures, which enhances the formation of conductive paths.

The resistivity dependence of epoxy/Ni/CF ternary composites containing 1.8 wt % CF on Ni content is also plotted in Figure 2. At lower Ni contents (20–30 wt % Ni), the resistivity is one order of magnitude lower than that of the epoxy/CF composite at the same CF content (see Fig. 5), but it is significantly lower than that of

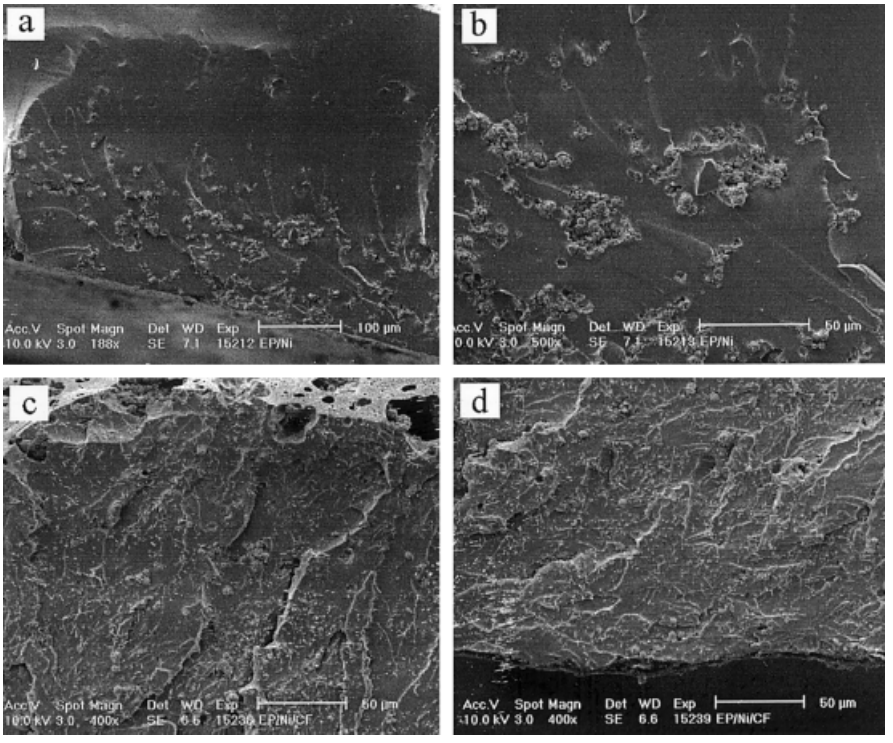

Figure 4 SEM micrographs of (a) and (b), Ni particle distribution in epoxy/Ni (80/20) composite at two magnifications; (c) and (d), Ni and CF distribution in epoxy/Ni/CF (80/20, 1.8% CF) composite at the upper and bottom surfaces of the rod sample. Samples were cured at room temperature without EG.

the epoxy/Ni composite, thus the composite resistivity is mainly contributed by CF. In the range of around 40–60 wt % Ni content, the resistivity of the epoxy/Ni/CF composites is somewhat higher than that of the epoxy/Ni composite. SEM micrographs in Figure 4(a,b) show that Ni particles have a strong tendency to sediment in the epoxy/Ni system. Such sedimentation makes the sample more conductive in the horizontal direction and less conductive in the perpendicular direction. Upon the addition of CF, the denser bottom part of Ni particles is diluted, and the distribution of Ni particles becomes more uniform throughout the sample volume, as shown in Figure 4(c,d). Although the resistivity of epoxy/Ag/CF composites is a little higher than that of the epoxy/Ni composites in the medium Ni loading, the method of adding CF is recommended on the basis of the consideration of making the composites isotropically conductive. Above 65 wt % Ni content, the higher Ni loading makes the viscosity of the sample higher, thus Ni particle sedimentation is less obvious. The more conductive Ni network dominates the conductivity of the composites; hence, the addition of CF does not really have any effect.

Epoxy/CB/CF ternary conductive composites show an interesting resistivity behavior with the variation of CB or CF content, which is different from the behavior of the epoxy/CB and epoxy/CF binary conductive composites. The variation of the resistivity of epoxy/CB/CF composite at a constant CB content (0.5 phr) versus CF content is plotted together with the epoxy/CF composites in Figure 5. The variation of the resistivities of epoxy/CB/CF composites containing two constant CF contents (0.2 and 1.8 wt % CF) versus CB content is plotted together with the epoxy/CB composite in Figure 6. Figure 5 clearly shows that in the presence of carbon black (0.5 phr), which is beyond the CB percolation threshold, the resistivity of the epoxy/CB/CF composites is lower than that of the epoxy/CF binary composite. Below the CF percolation threshold (0.3 wt % CF), the already formed CB conductive network (0.5 phr) determines the conductivity of the composite. The resistivity difference between the binary and ternary composites is about two orders of magnitude.

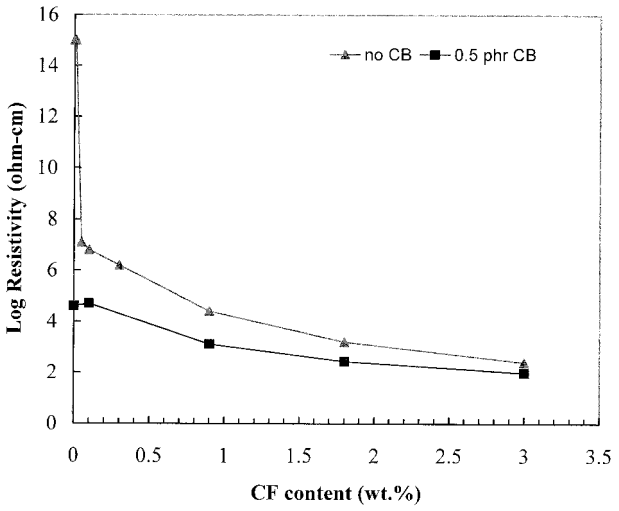

Figure 5 Variation of resistivity of epoxy/CF and epoxy/CF.0.5 phr CB composites (rod samples) versus CF content. Samples were cured at room temperature without EG.

Upon increasing the CF content, a CF conductive network begins to play an important role, and the resistivity difference gradually decreases. From Figure 6, one can see that, with a CF content at the CF percolation threshold (0.2 wt % CF), the resistivity of epoxy/CB/CF ternary composite is lower than that of the epoxy/CB binary composite below CB percolation, whereas at or above CB percolation, the resistivity of ternary composite is approximately equal to or higher than that of the binary composite. It demonstrates that below CB percolation, the CF conductive network dominates the conductivity of the composites, whereas at or above CB percolation, the CB conductive network largely dominates the conductivity of the composite. The higher resistivity of the epoxy/CB/CF composite at 1 phr CB content (well above CB percolation) than that of the epoxy/CB composite at the same CB content is probably because the presence of the small amount of CF disturbs the well-formed CB network.

At a fixed CF content, well above CF percolation (1.8 wt % CF), the resistivity of the epoxy/CB/CF composites is determined by the highly conductive CF network and changes only slightly with the increase of CB content. Figure 7(a,b) shows SEM micrographs of the epoxy/CB/CF composites containing 1 phr CB, 0.2 wt % CF, and 1 phr CB, 1.8 wt % CF, respectively. It is seen that when both CF and CB contents are high, the conductive paths of CF and CB are well formed. It is also noted that carbon fibrils seem to locate along carbon black chains, but do not interconnect them. Therefore, the carbon black conductive chains may be somewhat disturbed by CF when CF content is very low, which negatively affects the conductivity of the composites.

CONCLUSION

The addition of a small amount of ethylene glycol greatly reduces the resistivity of the silver containing epoxy composites, such as epoxy/Ag, epoxy/Ag/CF, and epoxy/Ag/CB composites. DSC studies demonstrate that ethylene glycol has a catalytic effect that accelerates the epoxy resin curing process. A fast cure process reduces the extent of sedimentation of silver particles and thus improves the conductivity uniformity of the composites. High temperature curing of the composites was found to have a similar effect.

Epoxy/Ni-conductive composites have a much lower percolation threshold than that of the epoxy/Ag composites, which may be related to the different agglomerate structures of Ni and Ag particles. Epoxy/Ni/CF and epoxy/CB/CF ternary composites show a different conductivity behavior from that of the corresponding binary conductive

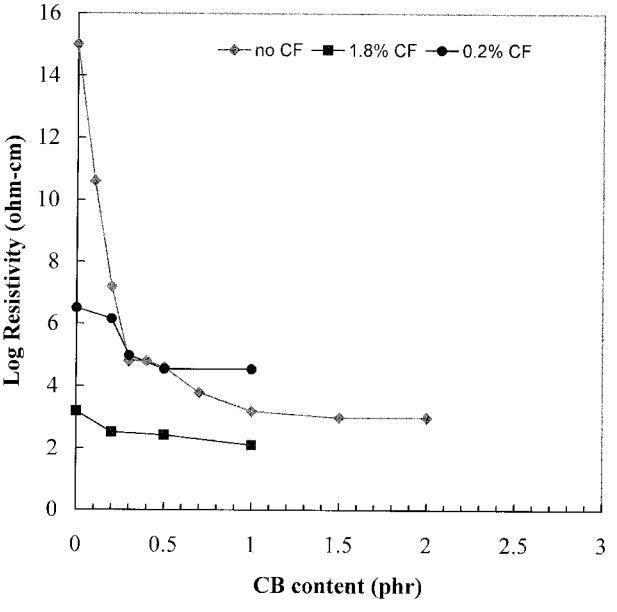

Figure 6 Variation of resistivity of epoxy/CB, epoxy/CB/0.2% CF, and epoxy/CB/1.8% CF composites (rod samples) versus CB content. Samples were cured at room temperature without EG.

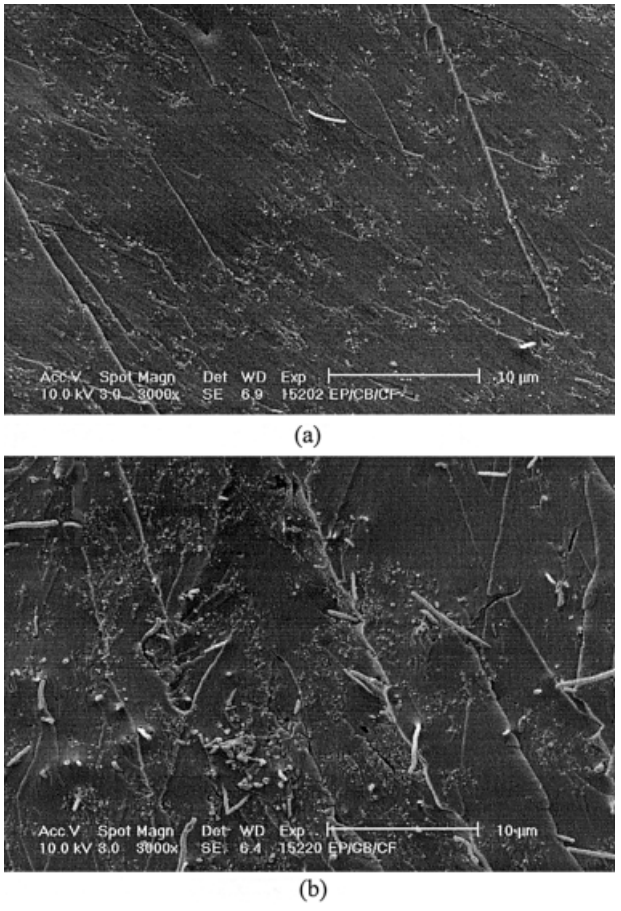

Figure 7 SEM micrographs of (a) epoxy/1 phr CB/0.2% CF composite (rod); (b) epoxy/1 phr CB/1.8% CF composite (rod). Samples were cured at room temperature without EG.

composites. The conductivity level, loading level of each conductive filler, and the interactions of two fillers are the main factors that determine the conductivity behavior of the three-component composites.

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