FUNCTIONAL COMPOSITES OF EPOXY / SILVER-FILLER USING SELF-ASSEMBLY PHASE STRUCTURES

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1 Introduction
Considerable effort has been made to develop new conductive adhesives as user-friendly alternatives to lead-containing solders for electronics applications [1-7]. The electric conductive adhesives have advantages, such as low temperature processing, low residual stress, and low environmental stress. The conductive adhesives consist of metallic fillers and polymeric matrices, such as epoxy resins. Namely, the conductive adhesives are kinds of polymeric matrix composites. The most typical metallic fillers are silver (Ag) particles or flakes. In general, considerable amount of Ag fillers more than 80 wt%, are blended in the matrix resins to make the effective conducting channels. The addition of much amount of fillers tends to cause the high cost and the high viscosity, which results in the low workability and the low adhesive strength. Therefore, the shape and the size of the Ag fillers have been studied in order to achieve the high conductivity of the composites with including the small amount of the metallic fillers.

As an alternative approach under this background, we focused on developing the new matrix resin for the small Ag-amount composites with high electric conductivity. If the new composites themselves make the conducting channels using the self-assembly phase structure in the matrices, the threshold of the amount of the Ag to achieve high electric conductivity would be expected to be smaller amount. The promising self-assembly mechanism we propose here is reaction-induced phase separation of epoxy polymer blends [8, 9]. The phase separation occurs from the homogeneous solution of two components due to the elevated free energy of the mixture by the increase in the molecular weight of the epoxy resins in the curing process [8, 9]. In this paper, polymer blends of epoxy / poly ether sulfone were examined to testify the new concept. The phase structure in micrometer scale worked as a template to make the conducting channels of the Ag fillers in the composites, which gave high electric conductivity despite the small amount of the Ag fillers. The thermal conductivity of the composites will be also discussed in our presentation of the conference.

2 Experimental procedures
2.1 Materials
The epoxy resin used in this study was diglycidyl ethers of bisphenol-A (DGEBA), JER828 and JER834 (epoxy equivalent weight: 189 g/eq. and 250 g/eq., respectively, provided by Japan Epoxy Resin). Both JER828 and JER834 were liquid type epoxy resins, but JER834 had relatively higher viscosity than JER828. Diamino diphenyl methane (DDM, active amino-hydrogen equivalent weight: 49.5 g/eq.) was used as the curing agent. Poly ether sulfone (PES) with the number-average molecular weight: Mn = 23800, produced by Sumitomo Chemical, was the thermoplastic resin applied as the modifiers to make phase separation in the epoxy blends. Spherical particles of Ag with the diameters of 800 nm, produced by DOWA electronics, were blended as the conductive fillers in the epoxy composites.

The chemical structures of raw materials for the matrix resins (epoxy / PES blends) were shown in Figure 1.
2.2 Preparation of epoxy / PES polymer matrices and the Ag-filler composites

The epoxy (DGEBA) / PES matrices and the Ag-filler composites were made by the next procedure. Firstly, the PES powders were mixed with the epoxy resin (DGEBA, JER828) at room temperature. The resin mixture was heated while being stirred in an oil bath at 120°C for 4h to dissolve the PES in the DGEBA. After the mixture was cooled to lower than 80°C, the Ag fillers were added to the resin mixture with being stirred. Then, the stoichiometric amount of the curing agent (DDM) to epoxy functionality of DGEBA was mixed, and the mixture was degassed. The resin was cured at 150°C for 2h, followed by 2h-postcure at 180°C to make the epoxy / Ag composites with 80μm-thickness. After the curing, the surface-releasing tapes were removed. The thickness and width of the cured composites was measured. Then, the four-point probe method was applied using Loresta-GP MCP-T610, produced by Mitsubishi Chemical Analytech, to evaluate the bulk resistance of the cured composites. The electric conductivity is defined as the reciprocal of the bulk resistance.

2.3 Evaluation of bulk resistance (electric conductivity) of epoxy / Ag composites

Bulk resistivity of the epoxy / Ag composites was evaluated using the next specimens. Two strips of a surface-releasing tape (Nitfron tape, produced by Nitto Denko) were applied onto a pre-cleaned glass slide in parallel direction. The thickness of the tape was 80μm, and the gap of the two tapes was 5 mm. The uncured resin pastes blended with the Ag fillers were spread into the gap between the two tapes, and cured at 150°C for 2h, followed by 2h-postcure at 180°C to make the epoxy / Ag composites with 80μm-thickness. After the curing, the surface-releasing tapes were removed. The thickness and width of the cured composites was measured. Then, the four-point probe method was applied using Loresta-GP MCP-T610, produced by Mitsubishi Chemical Analytech, to evaluate the bulk resistance of the cured composites. The electric conductivity is defined as the reciprocal of the bulk resistance.

2.4 Evaluation of phase structure of resin blends and epoxy / Ag composites

The phase structures of the cured blends and the dispersibility of the Ag fillers in the composites were evaluated by scanning electron microscopy (SEM, JSM-7001F produced by JEOL) both in the secondary electron mode and the reflection electron mode with X-ray microanalysis (XMA). The 3-dimensional connectivity of Ag fillers and the phase structures were also examined using a SEM with focused ion beam (FIB-SEM).

2.5 Evaluation of tensile shear adhesive strength of epoxy / Ag composites

Test specimens for the lap shear adhesive strength of the epoxy / Ag composites were prepared using steel substrates (SPCC-SB). The steel substrates had been wiped with acetone and treated with UV / ozone atmosphere to prepare the surfaces for bonding. The dimensions of the steel substrate were...
length of 125 mm, width of 25 mm, and thickness of 1.6 mm. Adhesive resin was applied to the substrates and then brought into contact, and the bonded joint was cured at 150°C for 2h, followed by 2h-postcure at 180°C. The lap joint length was 12.5 mm and the width was 25 mm. The tensile shear adhesive strength of the specimens was evaluated using the test machine “SHIMADZU AGS-J” in accordance with JIS K 6850 at a crosshead speed of 5 mm/min at 23 °C.

3 Results and Discussion

Figure 2 shows the fracture surfaces of the cured epoxy / PES blends with several amounts of PES, observed by SEM in the secondary electron mode. The PES was once dissolved in the liquid epoxy resin before curing. Then, the phase structure was made in the curing process of the epoxy resin by the reaction-induced phase separation mechanism [8, 9]. The epoxy / 10wt% PES blend showed relatively smooth fracture surface in the low magnified image, Fig.2a. In the high magnified image as shown in Fig.2b, micrometer-sized spherical domains were dispersed in the smooth matrix. The domains were supposed to be the PES-rich phases dispersed in the epoxy-rich continuous phase. Figs. 2c and 2d show the fracture surfaces of the epoxy / 15wt% PES blend (Fig. 2c: low-magnified, Fig.2d: high-magnified). Co-continuous phase structures in micrometer scale were observed in the images. One continuous phase showed the relatively smooth fracture surface, and the other continuous phase made the rough fracture surface. The rough fracture surface would be made because the continuous phase included many dispersed spherical domains consisting of the other component, as shown in Fig.2d. The component in each phase would be analyzed later in Figure 3. Figs. 2e and 2f show the fracture surfaces of the epoxy / 20wt% PES blend (Fig. 2e: low-magnified, Fig.2f: high-magnified). The blend also showed rough fracture surface, in which many spherical domains of the major component were dispersed in the continuous phase of the minor component. In the epoxy / 20wt% PES blend, the epoxy / curing agent should be the major component. Therefore, the dispersed domain was estimated as the epoxy-rich phase and the continuous matrix was estimated as the PES-rich phase.

By the way, the objective of this study is to find the epoxy matrix resin for achieving high electric conductivity of the Ag composites. Within these three epoxy / PES blends, we chose the epoxy / 15wt% PES blend as the suitable matrix resin for the Ag composites, because the co-continuous phase structure would be favourable structure as the template to make the connecting channels of the Ag fillers. The polished surface of the epoxy / 15wt% PES blend having the co-continuous phase structure was analyzed by SEM in the reflection electron mode with X-ray micro analysis (XMA) to characterize the phase components clearly. Figure 3 using the XMA revealed that the brighter phase (the area B) had more sulfur element than the darker phase (the area A). This means the brighter area B is the PES-rich phase having sulfur element in the chemical structure, and the darker area A as the counter part is the epoxy-rich phase. It was also found that both continuous phases included dispersed domains consisting of the other component.

Then, the epoxy / 15wt% PES blend was applied for the matrix resin of the Ag composites. Actually, several amounts of the Ag fillers were mixed to the blends. Figure 4 shows one of the composites with the 60wt% (14.6 vol. %) fillers of the Ag. Here, the Ag fillers with the diameters of 800 nm are shown as the white particles by the SEM in the reflection electron mode, because lots of reflection electron is emitted from the Ag fillers. The microscopy clarified that the Ag fillers were selectively localized in the epoxy-rich (darker) phases. This means the epoxy-rich phase has more affinity to the surfaces of the Ag fillers than the PES-rich phase. The system made the Ag-localized structure by self-assembly mechanisms to minimize the interfacial free energy between the fillers and the polymeric components.
Figure 5 and Figure 6 show the low-magnified images of the polished surfaces of the composites (14.6 vol.% Ag) blended with or without the PES, which were observed by SEM in the reflection electron mode. The connectivity of the Ag fillers in the PES-modified epoxy composites (Fig. 5) was better than that of the epoxy composites without the PES (Fig. 6).

Moreover, many cross sections of the cured composites with the 60wt% Ag fillers were cut using focused ion beam, then observed by SEM to examine the detail of the connectivity of the Ag fillers. The 3-dimensional images integrated from the observed cross sections clarified that the Ag fillers were selectively localized in the epoxy-rich phases and made the connecting structure. Namely, the connecting Ag structures continued 3-dimensionally in the epoxy-rich phases of the PES-modified epoxy blends. The connectivity of the Ag fillers in the PES-modified resin was clearly better than that in the conventional epoxy matrix without the phase separation. The phase structure worked as a template, which made the 3D-continuous structure of the Ag fillers effectively.

Figure 7 shows the electric conductivity of the composites including several amounts of the Ag fillers. The epoxy / PES / 15vol % Ag composites showed 10^4-fold in the electric conductivity, compared to the corresponding epoxy / 15vol % Ag composites without the PES. Also, the threshold to achieve the high conductivity of the Ag composites shifted to the region of the small Ag amount by the incorporation of the PES, compared to the epoxy / Ag composites without the PES. This is because the localized Ag fillers in the epoxy-rich phase had more chance to contact each other, which made the effective conductive channels in the PES-blended epoxy having the phase structure.

The lap shear adhesive strengths of the conductive adhesives were also evaluated. Figure 8 shows the relationship between the shear adhesive strength and the electric conductivity of the Ag composites with or without the PES. The epoxy / PES / Ag composites showed significantly higher adhesive strength to steel substrates than the epoxy / Ag composites without the PES. The epoxy / PES / Ag composites achieved both high electric conductivity and high adhesive strength, as shown in Figure 8. In case of the epoxy / Ag composite without the PES, the fracture occurred mainly in interfacial failure mode between the composites layer and the steel substrates. On the other hand, cohesive failure occurred in the resin layer of the epoxy / PES / Ag composites. The fracture surfaces of the specimens with 80wt% Ag after the shear adhesive tests were observed by SEM (Fig. 9a: secondary electron mode of epoxy / PES / Ag, Fig. 9b: reflection electron mode of epoxy / PES / Ag, Fig. 9c: secondary electron mode of epoxy / PES / Ag, Fig. 9d: the reflection electron mode of epoxy / PES / Ag). The epoxy / PES / Ag composites showed complex fracture surface with the large plastic deformation of the PES-rich phases. The plastic deformation would absorb large energy to fracture. The PES is known as a toughening modifier for epoxy resins [10-13]. The increased fracture toughness of the composites would be the reason of the increased adhesion strength in the cohesive failure mode.

4 Conclusions

Epox / thermoplastic polymer blend made phase structures for the matrix resins of the conductive composites including metal fillers. In the phase separated matrix resin, the metal fillers were localized in the phases which have high affinity to the surface of the fillers. In our experiments, Ag fillers were localized in the epoxy-rich continuous phases of the epoxy / PES blends. The phase structure worked as a template for the Ag fillers to make 3-dimensionally continuous structure. The self-assembly phase structure in micrometer scale gave the high electric conductivity even using a small amount of the Ag fillers in the composites. Moreover, the epoxy / PES / Ag composites showed the high shear adhesive strength to steel substrates. Control of the phase structure of the epoxy blends would be a key technology to give high performance & low cost electric conductive composites.
Figure 2: Fracture surfaces of epoxy / PES blends: 10wt%PES (a, b), 15wt%PES (c, d), 20wt%PES (e, f)
Figure 3: Phase structures of DDM cured epoxy / 15wt%PES blend observed by SEM in reflection electron mode with the X-ray micro analyses: The area B includes more sulphur (S) element than the area A, which indicates the bright area B is the PES-rich phase and the dark area A is the epoxy-rich phase.

Figure 4: Phase structures of epoxy / PES / Ag (14.6 vol%) composites

Figure 5: Reflection electron image of epoxy composites with PES (15wt% in the epoxy / PES blend) and Ag fillers (14.6 vol% in the composites).

Figure 6: Reflection electron image of epoxy composites with Ag fillers (14.6 vol% in the composites).
Figure 7: Electric conductivity of epoxy / Ag composites.
○: epoxy / PES /Ag composites
X: epoxy / Ag composites

Figure 8: Relationship between tensile shear adhesive strength and electric conductivity of epoxy / Ag composites with or without the PES.
○: epoxy / PES /Ag composites
×: epoxy /Ag composites
Figure 9: Fracture surfaces of epoxy / PES / Ag (80 wt%) composites (a, b) and epoxy / Ag (80 wt%) composites (c, d), observed by SEM [secondary electron mode (a, c) and reflection electron mode (b, d)]. The large plastic deformation of the PES-rich phase are shown in the epoxy / PES / Ag (80 wt%) composites (a, b).

References