Evolution of Electrical Conductivity in Silver-Loaded Electrically Conductive Adhesives Composed of an Amine-Cured Epoxy-Based Binder

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To investigate interfacial phenomena related to the evolution of electrical conductivity in electrically conductive adhesives containing silver fillers, the curing processes of model adhesives composed of an amine-cured epoxy-based binder were examined using several analytical methods. Shrinkage of the adhesives during curing was not a predominant factor in determining the electrical resistivity. Rearrangement of the fillers occurred at the onset of gelation. Afterwards, the electrical conductivity evolved in the adhesives through the following two steps: development of conduction paths during gelation of the epoxy-based binder, and microstructural evolution between the silver fillers. The use of adipic acid as a surfactant enhanced the first of these steps during gelation. The latter process occurred concurrently with cross-linking of binder molecules to increase the elastic modulus. In this step, the amine molecules probably reacted with silver fillers to induce necking between the fillers. Because interfacial chemical phenomena probably influence the electrical conductivity evolution, the conventional hypothesis, which is based on the mechanical contact concept for inter-filler contacts in electrically conductive adhesives, needs to be expanded.

Keywords: electrical conductivity, shrinkage, binder chemistry, surfactant, interfacial reaction

1. Introduction

Electrically conductive adhesives (ECAs), which are composites of an organic polymer matrix containing conductive fillers, are a type of connecting material that is widely used in electronics packaging1,2. Recently, scientists have pursued improvements in the performance of ECAs for more effectively applications to advanced electronic devices such as power devices and flexible devices. Because the electrical conductivity of an adhesive is determined by its curing process, factors that influence the evolution of electrical conductivity during curing should be clarified to establish materials design protocols for advanced ECAs.

The electrical resistivity of an ECA is influenced by the following two factors: dispersion states of the fillers (e.g., microstructure of the filler network), and inter-filler electrical resistance. To improve the electrical conductivity, several concepts for controlling the microstructure of the filler network have been proposed2,3. For example, fillers with bimodal particle-size-distributions3 are often used in ECAs for practical applications.

However, the electrical conductivity of an ECA is not only determined by the filler network microstructure. The inter-filler electrical resistance is also an important factor in determining the electrical conductivity through the filler network5. According to the conventional model5 for inter-filler conductive contacts, the inter-filler resistance can be divided into two components: the constriction resistance, and the resistance for charge transfer across the insulative gap. In the case of ECAs containing metallic fillers, such as silver (Ag), tunneling effects are thought to contribute to the latter resistance component6. However, the details of the conduction mechanism remain unclear.

As a strategy to decrease the inter-filler electrical resistance, direct bonding between fillers by sintering Ag nanoparticles7 and dendrites8 could be effective. Direct bonding between fillers could also be achieved by a transient liquid phase reaction to form intermetallic compounds using metal particles that have lower melting points9.

However, it is generally known that the electrical resistivities in ECAs vary with chemical factors, including chemical composition of the binder (binder chemistry) and surfactants adsorbed on the fillers10,11. This implies that the inter-filler electrical resistance could also be controlled by interfacial chemical phenomena. Hence, we previously proposed a strategy to decrease the inter-filler resistance in ECAs based on changing chemical factors12. This strategy could be applied to adhesives containing common fillers as well as those containing advanced fillers, such as nanoparticles and dendrites.

In the present work, the evolution of electrical conductivity during curing in model epoxy-based adhesives containing Ag micro-particles was investigated in detail. Among candidate chemicals that were evaluated for control of the inter-filler electrical contacts, an amine-based curing agent was selected for the epoxy-based binder because amine molecules may participate in an interfacial chemical reaction with the Ag particles. In addition, a dicarboxylic acid surfactant was selected for the Ag particles. These chemicals can influence electrical conductivity evolution in the adhesive through conductive path development in the gelation stage of curing and subsequent necking between the particles. The results obtained in this work will be useful for establishing materials design protocols based on the control of interfacial chemistry for ECAs containing Ag fillers.

2. Experimental

2.1 Materials

An epoxy resin, 4,4-methylenedis(N,N-diglycidylaniline) (Sigma-Aldrich, St. Louis, MO, USA) was selected as the main component of the binder for the ECAs. Tetraethylpentamine (mixture of ethyleneamine) (Wako Pure Chemical...
Industries, Osaka, Japan) was used as the curing agent for the binder. An excess of the curing agent (amount-of-substance fraction = 165% of the stoichiometric composition) was mixed into the epoxy resin to prepare the epoxy-based binder. Silver micro-particles (average particle size = 2.5 μm) prepared by the water-atomization process (Fukuda Metals & Foils Co. Ltd., Kyoto, Japan) were used as fillers. Because no surfactants were used during preparation of the water-atomized particles, surface treatment was conducted using adipic acid (Wako Pure Chemical Industries) in some cases.

The surface treatment was performed as follows. First, Ag particles (6 × 10^{-3} kg) were added into an ethanol solution (1 × 10^{-4} m^{3} containing 14.0 kg m^{-3} of adipic acid. The ethanol solution was then sonicated for 6 h using an ultrasonic cleaner (Sono Cleaner 100D, Kajo Co. Ltd., Japan). After sonication, the Ag particles were separated from the ethanol solution using a sedimentation technique, and then washed by sonicatin in 5 × 10^{-5} m^{3} of ethanol for 6 h. The washed particles were separated from the ethanol and then dried at 343 K for 10 h.

After surface treatment, approximately 6 × 10^{-4}% (mass fraction) of the adipic acid was adsorbed on the Ag particles. To obtain the ECA pastes, the particles were mixed into the binder at a mass fraction of 85%. All the chemicals were used as received.

### 2.2 Measurement of electrical resistivity

Lines of the ECA pastes (3.0 mm × 76 mm × 30 μm) were formed on a glass substrate by screen printing. The adhesives were cured at 353–473 K for 1 h in air. The electrical resistivity values of the cured adhesives were measured by the four-point probe method using a low resistivity meter (MCP-T610, Mitsubishi Chemical Analytech Co. Ltd., Kanagawa, Japan). If the electrical resistivity of an adhesive exceeded the measuring range of the equipment, a digital electrometer (8340A, ADC Co. Ltd., Tokyo, Japan) was used to measure the electrical resistivity under an applied voltage of 50 V.

### 2.3 Analytical method of filler dispersion in the adhesives

The cross-sectional microstructure of each cured adhesive was observed by scanning electron microscopy (SEM). To characterize the dispersion states of fillers in the ECAs, two types of statistical analyses were conducted on the SEM images, including a quadrat method using Morisita’s overlap index \( I_{0} \) and inter-centroid distance measurement for adjacent particles. Each image analysis was performed using a random area of 1200 μm^{2} that contained about 300 particles.

In the quadrat method, the index \( I_{0} \), which is an important parameter to characterize the dispersion state of fillers, is given by the following equations:

\[
I_{0} = q \delta \tag{1}
\]

\[
\delta = \sum n_{i}(n_{i} - 1)/\left( N(N - 1) \right) \tag{2}
\]

where \( N \) is the total number of particles, \( q \) is the dividing number, and \( n_{i} \) is the number of particles in the \( i \)-th section.

In the distance method, the inter-centroid distance of adjacent Ag particles in the cross-sections was calculated using an original algorithm. In this analysis, the coordinates of the centroid, \( G(x_{0}, y_{0}) \), were calculated by dividing static moment of area by cross-sectional area for each particle. Then, the inter-centroid distance was defined as the distance between nearest neighbor particles. Image analysis of the cross-sections was performed using the following procedure. First, the particles in the cross-sections were divided into elemental areas with cross-sectional areas of \( A_{i} \). The cross-sectional area of a particle, \( A \), is represented by eq. (3).

\[
A = \sum A_{i} \tag{3}
\]

The static moment of area for each particle was calculated using the coordinates of the centroid for these elemental areas, \( G(x_{i}, y_{i}) \):

\[
S_{x} = \sum A_{i} y_{i} = A y_{0} \tag{4}
\]

\[
S_{y} = \sum A_{i} x_{i} = A x_{0} \tag{5}
\]

where \( S_{x} \) and \( S_{y} \) are the static moments of a particle based on the \( x \)- and \( y \)-coordinates, respectively. The coordinates of the centroid, \( G(x_{0}, y_{0}) \), were obtained using eqs. (4) and (5). After calculating the coordinates of the centroid for all particles in the cross-sections, the inter-centroid distance between nearest neighbor particles was calculated.

### 2.4 Analysis of the adhesive curing process

Shrinking of the adhesives during curing was monitored by noncontact measurement using a laser displacement meter (CUSTROM, Sentech Co. Ltd., Osaka, Japan). In this measurement, changes in the height of the substrate and the adhesive sample were monitored concurrently using laser displacement meters to estimate the shrinkage ratio, \( \Delta h/h_{0} \), where \( \Delta h \) is the change in height from the initial height \( (h_{0}) \). In addition, reactions that occurred in the adhesives (sample weight = 10 mg) during curing were analyzed using thermogravimetric-differential thermal analysis (TG-DTA). The composition of the gas produced from the adhesives (sample weight = 5 mg) during curing was analyzed using pyrolysis-gas chromatography-mass spectrometry and evolved gas analysis-mass spectrometry (EGA/MS).

In these analyses, the adhesive specimens were heated at a rate 1.67 × 10^{-1} K s^{-1} from ambient temperature to the curing temperature, and then held at the curing temperature for 1 h.

### 2.5 Simultaneous measurement of changes in viscoelasticity and electrical resistance

To investigate the relationship between the electrical conductivity evolution and curing behavior of the adhesives, a free-damped oscillation method (FDOM) using a ridge-body pendulum (RPT-300W, A&D Co. Ltd., Tokyo, Japan) was applied for viscoelastic characterization of the ECAs during curing. In this method, variations in the viscoelastic properties of the adhesives were analyzed based on the period and logarithmic damping ratio of a free-damped oscillation of a rigid-body pendulum. The storage modulus and loss modulus were calculated as follows:

\[
t_{p} \propto (1/E')^{1/2} \tag{6}
\]

\[
\Lambda \propto E'' \tag{7}
\]
where \( t_p \) is the period, \( \Lambda \) is the logarithmic damping ratio, \( E' \) is the storage modulus, and \( E'' \) is the loss modulus.

Variation in the electrical resistance of the adhesives during curing was monitored simultaneously using a digital electrometer during curing. The initial applied voltage was 5 V, and this was halved if the current exceeded 20 mA. Repeating the operation enabled continuous measurement of electrical resistance of the specimens during curing.

The adhesives were heated at a rate of \( 1.67 \times 10^{-1} \) K s\(^{-1}\) from ambient temperature to the curing temperature, and then the temperature was held at the curing temperature for 1 h. The adhesives were subsequently cooled at a rate of \( 8.33 \times 10^{-2} \) K s\(^{-1}\) to 323 K.

3. Results and Discussion

3.1 Electrical resistivities of the ECAs

Figure 1 shows the relationship between electrical resistivity and curing temperature for the adhesives containing Ag particles, with and without adipic acid as a surfactant. The electrical resistivities of these adhesives greatly decreased when the curing temperature was increased from 403 to 423 K.

In addition, the adhesives with surfactant exhibited lower electrical resistivity than those with no surfactant at curing temperatures from 353 to 473 K. When the adhesives were cured at 473 K, the electrical resistivity reached \( 3 \times 10^{-5} \) \( \Omega \) m for the adhesive with no surfactant and \( 1 \times 10^{-5} \) \( \Omega \) m for that with surfactant.

The electrical resistivity of each adhesive was found to vary depending on the curing temperature and surface treatment of the fillers. It has been proposed that the electrical resistivity of an ECA is mostly determined by shrinkage of the binder during curing\(^{16,17}\). By contrast, Kohinata et al.\(^{18}\) recently pointed out that shrinkage during curing does not always influence the electrical resistivity of an ECA. Therefore, we investigated the effect of shrinkage during curing on the electrical resistivities of these adhesives.

Figure 2 shows the relationship between curing temperature and shrinkage after cooling from the curing temperature to ambient temperature. The shrinkage ratio for each adhesive varied depending on the curing temperature, regardless of the surface treatment of fillers. A large increase was observed in the shrinkage ratio as the curing temperature was increased from 373 to 403 K. After this, the shrinkage ratio remained constant between 403 and 423 K. Then, the ratio increased again with increasing curing temperature.

A comparison between the dependencies of the electrical resistivities and shrinkage ratios on the curing temperature showed that shrinkage during curing was not a predominant factor in determining the electrical resistivities of the adhesives. Although the shrinkage ratio remained relatively constant, the electrical resistivity greatly decreased when the curing temperature was increased from 403 to 423 K. In addition, the electrical resistivity decreased with surface treatment of the fillers, while surface treatment did not affect the shrinkage ratio. Therefore, during curing, the electrical resistivities and shrinkage of the adhesives were influenced by different phenomena.

3.2 Microstructural features of the adhesives

Figure 3 (a) and (b) shows cross-sectional SEM images of adhesives with no surfactant cured at 373 and 453 K, respectively. The adhesive cured at 453 K had a higher packing density of the fillers than that cured at 373 K. Microstructural analyses were performed using the SEM images.

Figure 4 shows the relationship between the Morisita's overlap index (\( I_o \)) and dividing number (\( q \)) of the cross-sectional images calculated using eqs. (1) and (2). The \( I_o \) values were calculated for the adhesives with and without the surfactant cured at 373 and 453 K. These specimens exhibited similar behavior for the \( I_o \) values versus \( q \). The \( I_o \) values decreased with increasing dividing number. The shapes of the \( I_o-q \) curves indicated the fillers in these specimens had similar uniform distributions\(^{2,13}\).

By contrast, a large difference was observed in the distribution of the inter-centroid distance between adjacent Ag fillers in the cross-sectional images. Figure 5 shows histograms of the inter-centroid distance between adjacent fillers for the adhesive with no surfactant after curing at 373 and 453 K. The mode of the inter-centroid distance slightly decreased with increasing curing temperature, although no differences were
observed in the shapes of the histograms.

In addition to variation in the inter-centroid distance between adjacent fillers, the interfacial structure between the fillers evolved during curing at 453 K. Figure 6 shows a high magnification cross-sectional SEM image of the adhesive with no surfactant after curing at 453 K. Necking was apparent between some fillers. This means that the filler network in this specimen includes domains that are formed by necking among several fillers. The detailed microstructural characterization of ECAs cured at several temperatures showed that necking between the particles occurred at approximately 423 K. Furthermore, no large differences in the microstructural features were observed in the adhesives with and without the surfactant.

The microstructural evolution in the adhesives suggests an interfacial reaction occurs between the binder and fillers during curing. The necking between the fillers could contribute to a decrease in the electrical resistivity of the adhesives because the interfacial electrical resistance should decrease. Additionally, the adhesive with the surfactant exhibited lower electrical resistivity than that with no surfactant suggesting that an interfacial reaction occurred, decreasing the electrical resistivity. To clarify the effect of these interfacial phenomena on evolution of the electrical conductivity, the curing process of the adhesives should be analyzed in detail.

### 3.3 Effect of Ag fillers on the curing reaction of the binder

To investigate electrical conductivity development in the ECAs, the curing process was analyzed, because electrical conductivity always evolves during curing. First, changes in curing reaction of the epoxy-based binder caused by addition of Ag particles were investigated by measuring TG-DTA...
curves during isothermal heating at 453 K for 1 h (heating rate $= 1.67 \times 10^{-1} \text{ K s}^{-1}$, cooling rate $= 8.33 \times 10^{-2} \text{ K s}^{-1}$).

Figure 7 (a) and (b) shows the TG-DTA curves of the epoxy-based binder without Ag fillers and the adhesive containing Ag fillers with no surfactant, respectively. In the case of the epoxy-based binder without Ag fillers (Fig. 7 (a)), an exothermic peak that was caused by the curing reaction of the epoxy resin was detected at 343–393 K. An endothermic peak was observed after this. The exothermic curing reaction of the epoxy resin with the Ag filler (Fig. 7 (b)) occurred at a similar temperature range to that without the fillers. However, rather than showing an endothermic peak after the exothermic peak, the adhesive with the fillers exhibited another exothermic peak.

Although these adhesives exhibited different reaction behavior after the curing reaction, they both decreased in weight because of the release of gases during curing. EGA/MS spectroscopy was used to determine the composition of the gases released by curing. Figure 8 shows the EGA/MS ion chromatograms of the Ag-loaded adhesive during heating at a rate of $1.67 \times 10^{-1} \text{ K s}^{-1}$ and a subsequent isothermal hold at 453 K.

Figure 9 also shows the variation in electrical resistance of the adhesive during curing. Although the electrical resistance tended to decrease in Stage (1), the resistance greatly increased at the onset of the gelation. This increase in electrical resistance was caused by rearrangement of the Ag fillers between ethyleneamine and water impurities.

Although an endothermic peak caused by the volatilization of curing agent was detected in the epoxy-based binder without Ag fillers, an exothermic peak was observed in the Ag-loaded adhesive. This suggests an interfacial chemical reaction occurred between the amine molecules and surfaces of the Ag fillers.

### 3.4 Evolution of electrical conductivity in the adhesive with no surfactant

To investigate the curing process of the adhesive in more detail, viscoelastic characterization using the FDOM was performed simultaneously with electrical resistance monitoring. Figure 9 shows the results of the simultaneous measurement of the viscoelastic properties (period and logarithmic damping ratio of the oscillation of pendulum) and electrical resistance for the adhesive with no surfactant during curing at 453 K for 1 h. The curing behavior of the adhesive occurred in three stages. The logarithmic damping ratio of oscillation of the pendulum gradually increased between 320 and 420 K, although the period of the oscillation exhibited no significant changes. This indicates that gelation of the epoxy-based binder occurred in this temperature range (Stage (2) in Fig. 9). Then, the period of the oscillation began to decrease rapidly at 420 K. This decrease in the period indicates cross-linking of the polymer structure was induced in the adhesive to increase the elastic modulus (Stage (3) in Fig. 9). In addition, a decrease in viscosity was induced before gelation, although this was not detected under the present conditions of the viscoelastic characterization (Stage (1) in Fig. 9). The decrease in viscosity before gelation was confirmed using a different viscometer (Brookfield viscometer with thermosel system).

A comparison of the results from TG-DTA (Fig. 7 (b)) and the viscoelastic characterization (Fig. 9) showed that the onset of the exothermic peak, caused by the curing reaction of the epoxy resin, agreed well with the onset of gelation. Therefore, the cross-linking reaction was apparently induced in the latter part of the exothermic curing reaction.

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Figure 9 also shows the variation in electrical resistance of the adhesive during curing. Although the electrical resistance tended to decrease in Stage (1), the resistance greatly increased at the onset of the gelation. This increase in electrical resistance was caused by rearrangement of the Ag fillers between ethyleneamine and water impurities.
cause of rapid shrinkage of the binder\textsuperscript{(11)}. However, the electrical resistance decreased over two stages after the rearrangement of fillers. First, the electrical resistance decreased in Stage (2) as the electrical conduction paths evolved rapidly during gelation of the binder. Then, the electrical resistance began to decrease again at approximately 440 K. The onset of the decrease in resistance agrees with the second exothermic peak observed in the DTA curve shown in Fig. 7 (b). This implies that an interfacial reaction occurred between the amine molecules and surface of Ag particles in this step, and this reaction induced the decrease in inter-filler electrical resistance in this step. Necking between Ag particles is inferred to occur in this step.

3.5 Relationship between evolution of electrical conductivity and shrinkage in the adhesive during curing

The effect of shrinkage on the electrical conductivity evolution in the adhesive during curing was evaluated. Figure 10 (a) and (b) shows the shrinkage behavior of the adhesive during curing at 373 and 453 K, respectively. In these cases, the adhesive was heated to the curing temperatures at a rate of $1.67 \times 10^{-1}$ K s\textsuperscript{-1}, and this was followed by isothermal heating for 1 h. The adhesive thermally expanded during the heating step, and then shrunk.

To examine the cause of this shrinkage, viscoelastic characterization was performed using the FDOM simultaneously with electrical resistance monitoring. The results obtained during curing at 453 K are shown in Fig. 9. The results obtained during curing at 373 K are presented in Fig. 11. The viscoelastic characterization indicated gelation was initiated at approximately 320 K during the heating step because the logarithmic damping ratio gradually increased. Figure 10 (a) and (b) suggests that shrinkage caused by the curing reaction appeared to compete with the thermal expansion after gelation was initiated. The volume of the adhesive decreased to less than the initial volume in the final stage of gelation.

Figures 9 and 11 also show changes in the electrical resistance during curing. These results show the electrical conductivity was initiated during gelation. Figure 10 (a) and (b) suggests that the adhesive expanded to more than the initial volume when the electrical conductivity was initiated. This implies shrinkage caused by the curing reaction was a dominant factor in the initiation of electrical conductivity.

When the adhesive was cured at 453 K, the electrical resistance started to decrease again at approximately 440 K. Figure 10 (b) suggests that the adhesive shrunk to less than the initial volume in this step. The electrical resistance continued to decrease until 400–600 s after the initiation of isothermal heating. However, because necking between Ag particles oc-
curred in this adhesive, the electrical conductivity evolution in this step could not be explained by the conventional theory, which is based only on enhancement of inter-/filler contacts caused by shrinking. To interpret this electrical conductivity evolution, the theory for analyzing inter-/filler conductive contacts should be expanded to include necking between the particles.

After this electrical conductivity development with necking between the particles, the adhesive continued shrinking until the isothermal heating was complete, and in this time it shrunk an additional 10–15%. However, this additional shrinkage during isothermal heating did not increase the electrical conductivity any further.

3.6 Evolution of electrical conductivity in the adhesive with surfactant

Surface treatment using adipic acid was effective to improve the electrical conductivity of the adhesive as shown in Fig. 1. To investigate how the adipic acid surfactant affected evolution of the electrical conductivity in the adhesive, viscoelastic characterization using a rigid-body pendulum was conducted simultaneously with electrical resistance monitoring.

Figure 12 shows the results of the simultaneous measurement of the viscoelastic properties and electrical resistance for the adhesive with adipic acid surfactant during curing at 453 K for 1 h. The curing process of this adhesive occurred in three stages that were similar to those observed for the adhesive with no surfactant. In addition, the electrical resistance of this adhesive also exhibited similar behavior to that without the surfactant during curing. The surfactant effectively enhanced the decrease in electrical resistance during gelation but did not change the electrical conductivity evolution behavior. No large differences were observed between the adhesives with and without the surfactant for their microstructural features, such as necking between the fillers. Therefore, the adipic acid surfactant does not affect the interfacial reaction that results in necking and occurs at temperatures above approximately 440 K.

3.7 The mechanism of electrical conductivity evolution

The investigation of the curing process clarified that electrical conductivity evolved in the adhesives through the following two steps: conduction path development during gela-
tion of the epoxy-based binder, and microstructural evolution between Ag particles. Adipic acid surfactant effectively enhanced conduction path development to improve electrical conductivity of the adhesive. Some scientists believe that adipic acid can reduce oxides present on the surface of Ag fillers during curing to decrease the electrical resistivity of ECAs. In the present study, we confirmed that this type of reaction could occur at temperatures above approximately 500 K for the Ag particles. Therefore, the reaction induced by adipic acid at 350–400 K is probably not reduction of oxides on the surfaces of the Ag fillers.

According to our previous report, the process of conduction path development commonly occurs in ECAs during curing. The conduction paths can be formed even in the gelation stage. Although the exact details of the reaction mechanism remain unclear, some interfacial phenomena probably influence formation of inter-filler conductive contacts.

In the present adhesives, microstructural evolution between Ag fillers occurred concurrently with the cross-linking of binder molecules, and this was probably induced by the interfacial reaction between the amine molecules and surface of Ag fillers. A chemical reaction, such as the formation and decomposition of organometallic compounds (i.e. silver-amine complexes), may occur to induce necking between the fillers.

The electrical conductivity of ECAs is usually interpreted based on the mechanical inter-filler contact model. However, this work suggests that some interfacial reactions can influence the inter-filler conductive contacts to improve the electrical conductivity of the adhesives. Therefore, the conventional hypothesis for inter-filler conducting contacts in ECAs needs to be expanded to take into consideration inter-filler conductive contact formation and microstructural evolution with interfacial chemical phenomena. Studies of inter-filler contacts based on this expanded viewpoint will lead to large improvements in the electrical conductivity of ECAs.

4. Conclusion

This work investigated the evolution of electrical conduction paths in adhesives composed of an amine-cured epoxy-based binder containing Ag fillers. The results were used to determine what factors influence electrical conductivity in the adhesives. The main results obtained in this work are summarized below:

1. Shrinkage of the binder during curing was not a predominant factor in determining electrical resistivity of the adhesives.
2. Investigation of the curing process clarified that the electrical conductivity evolved in the adhesives through conduction path development during gelation of the epoxy-based binder and microstructural evolution between the Ag fillers.
3. Addition of adipic acid as a surfactant effectively enhanced the electrical conductivity evolution during gelation.
4. Necking between Ag particles was induced by some interfacial reactions with amine molecules, which decreased the electrical resistivities of the adhesives.
5. The conventional hypothesis based on the mechanical contact concept for inter-filler conducting contacts in ECAs needs to be expanded to take into consideration interfacial chemistry to enhance the contacts.
6. Materials design protocols based on the control of interfacial chemistry for ECAs containing Ag fillers will be useful for developing advanced ECAs.

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