Properties of Cu Filled Electrically Conductive Adhesive (ECA) Affected by Viscosity of the ECA Paste†

HO Li-Ngee*, NISHIKAWA Hiroshi**

Abstract

In this study, electrical and mechanical properties of the Cu filled polyurethane based electrically conductive adhesives (ECAs) affected by viscosity of the ECA paste were investigated. The viscosity of the ECA paste was controlled by adding different amount of diethyl carbitol as diluent. Significant difference could be observed in the electrical resistivity and shear strength joint of ECA by varying the viscosity of the ECA paste. The correlation between viscosity of the ECA paste and electrical resistivity and shear strength of ECA joint were studied, respectively. Result showed that reduced electrical resistivity and enhanced shear strength of ECA joint was observed following the decrease of viscosity of the ECA paste. Finally, polyurethane based Cu filled ECA with electrical resistivity at a magnitude order of 10-3 Ω.cm and enhanced shear strength (above 17 MPa) was achieved.

KEY WORDS: (Copper filler), (Conductive adhesive), (Shear strength), (Electrical resistivity), (Viscosity)

1. Introduction

The electronics packaging technologies in all levels are undergoing quick evolution due to dramatic changes in the electronics industries towords low cost, portability, diverse functions, environmental benign and user friendliness [1]. Hence, interconnect materials such as lead-free solders and electrically conductive adhesives (ECAs) which provide electrical and mechanical joint of the components to form functional circuits in electronic packaging are considered as the promising alternatives to the conventional lead-based solder interconnection technology. ECA is a type of composite material which consists of conductive metallic fillers that provide electrical conduction and polymeric resin for mechanical adhesion.

In our previous studies [2-5], Cu fillers with different morphology prepared by different methods were applied as conductive fillers in ECA with phenolic resin as the adhesive binder. However, the shear strength of this type of phenolic resin was relatively low. Hence, development of a Cu filled ECA with enhanced mechanical strength is of great interest. Polyurethane (PU) is a unique material having a very flexible chemistry containing soft and hard blocks in its polymeric structure. In adhesives, the hard -NCO segments provide the necessary physico-mechanical strength while the soft -OH segments provide the wetting property [6]. PU represents an important class of thermoplastic and thermoset polymers which are widely used in the field of coatings, adhesives and composites due to high reactivity, high flexibility in formulation and application technologies, chemical and corrosion resistance, adhesion properties and a wide range of mechanical strength [7, 8].

In this study, we investigated the electrical resistivity and shear strength joint of PU based Cu filled ECA affected by the viscosity of the ECA paste that was controlled by the amount of diluent (diethyl carbitol). The objective of this study is to obtain a Cu filled ECA with low electrical resistivity and enhanced shear strength.

2. Experimental

2.1 Materials

Cu fillers (1400Y) used in this study were purchased from Mitsui Mining & Smelting Co. Ltd. (Tokyo, Japan). Resin (Desmodur BL3175SN) was provided by Sumika Bayer Urethane Co. Ltd. (Osaka, Japan). Diethyl carbitol from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) was used as diluent during mixing of the ECA paste. Morphology of Cu fillers was observed using FE-SEM (Model: JSM-6500F) from JEOL Ltd., (Tokyo, Japan) which revealed the morphology of the Cu fillers with uniform spherical-like particles and median particle size about 5.5 μm as shown in **Figure 1**.

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* JSPS Postdoctoral Fellowship for Foreign Researcher
** Associate Professor

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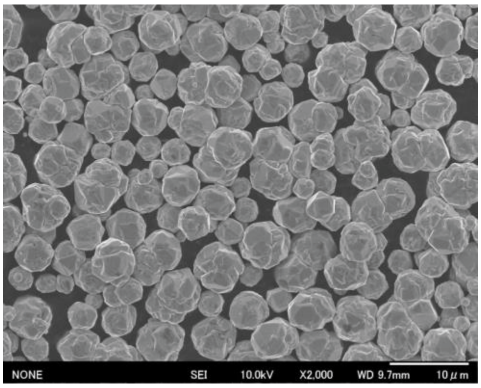

Fig. 1 SEM image of Cu filler used in this study.

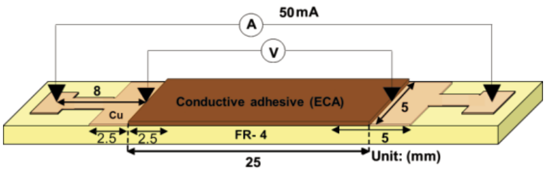

Fig. 2 Schematic diagram of FR-4 for electrical resistance measurement of ECA.

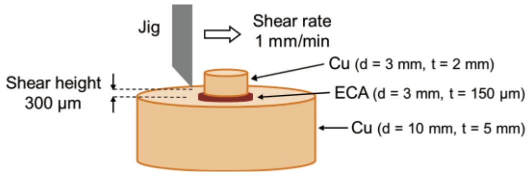

Fig. 3 Schematic diagram of Cu/Cu joint specimens for shear test.

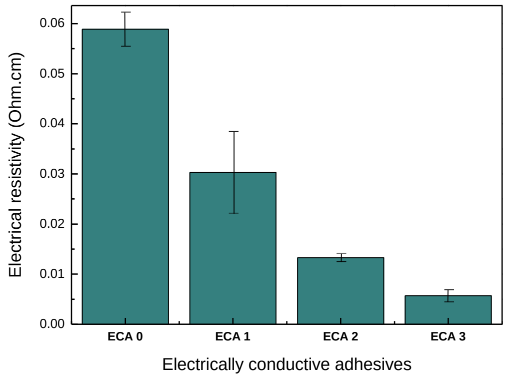

Fig. 4 Effect of diluent on the electrical resistivity of ECAs in this study.

2.2 Fabrication and characterization of ECA paste

To fabricate ECA paste, Cu fillers of 80 mass % were mixed with resin, diluent (diethyl carbitol) and ethylene glycol in an agate mortar. It was then mixed and defoamed in a hybrid planetary centrifugal mixer (Model: ARE 250) from Thinky Corp. (Osaka, Japan). As a control sample, ECA paste without diluent was prepared which was assigned as ECA 0. ECAs prepared with different amount of diluent in this study were shown in Table 1. Rheological property of each ECA paste was evaluated by using a cone-plate rotary rheometer (Haake, Model: RheoStress 6000) from Thermo Fisher Scientific Inc. (Yokohama, Japan). The diameter of the cone-plate was 20 mm and the measurement temperature was 20°C. The gap between the plate and cone was set at 0.052 mm.

2.3 Evaluation of as cured ECAs

A standard size of 50 x 95 mm flame retardant (FR-4) board with copper pads at both ends was used to measure the electrical resistivity of ECA. Two parallel strips of cellophane tape were placed apart along the length of 95 mm of the FR-4 board. Then, another two strips of the tape were placed perpendicular to the parallel strips in order to create a test specimen opening with 25 mm length and 5 mm width. The ECA paste was then spread on the specimen opening to create a uniform thin film of ECA. A total of 5 specimens were prepared on a single FR-4 board for each ECA sample as shown in **figure 2**. It was then placed into a convection oven and preheated at 80ºC for 20 min followed by curing at 140°C for 30 min. After curing, it was allowed to cool to room temperature. The electrical resistance of the ECAs was measured from the ends of the pattern using Nanovoltmeter (Model: 2182A) and Precision Current Source (Model: 6220) from Keithley Instruments Inc. (Tokyo, Japan), with a four-point probe method. The thickness of the cured ECA samples on the FR-4 board was measured by using a charge-coupled device (CCD) laser displacement sensor (Model: LK-G Series) from Keyence Corp. (Osaka, Japan) together with software MAP-3D from COMS Corp. (Hyogo, Japan). The electrical resistivity (ρ) of the ECA was calculated using the following equation:

$$\rho = (t \times w) / l \times R \qquad (1)$$

where R is the electrical resistance and t, w, and l are the thickness, width and length of the ECA sample, respectively.

Shear strength of the ECAs was evaluated by using Cu/Cu joint specimens as shown in **figure 3**. The shear rate and shear height of the jig was set at 1.0 mm/min and 300 µm, respectively. The shear tester instrument (Model: STR-1000) used was from Rhesca Corp. (Tokyo, Japan).

3. Results and Discussions

3.1 Electrical Resistivity and Shear Strength of ECAs

Figure 4 shows the effects of different amount of diluent on the electrical properties of ECAs. For ECA prepared without diluent, electrical resistivity of ECA 0 showed significant high resistivity at the magnitude order range of 10^{-2} Ω.cm. However, with addition of diluent at mass ratio of resin : diluent : 10 : 1, almost two times of reduced electrical resistivity could be observed in ECA 1 (3.0×10^{-2} Ω.cm) compared to that of the ECA 0 (5.9×10^{-2} Ω.cm). When the amount of diluent increased up to mass ratio of resin : diluent : 10 : 3, ECA 3 showed

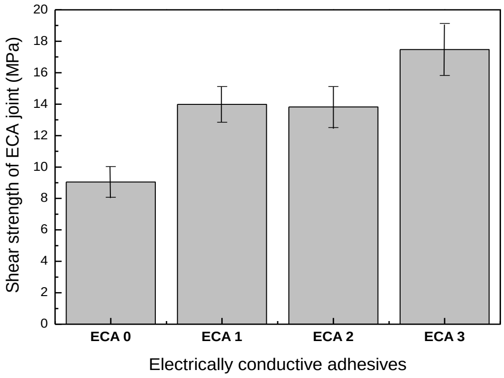

Fig. 5 Effect of diluent on the shear strength of ECA joint in this study.

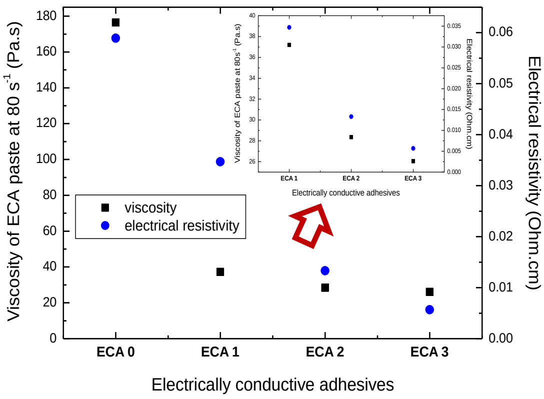

Fig. 6 Correlation between electrical resistivity of ECA and viscosity of ECA paste affected by amount of diluent in this study.

electrical resistivity at the magnitude order of 10^{-3} Ω.cm (5.7 x 10^{-3} Ω.cm) which is almost 10 times lower than that of the ECA 0. This revealed that addition of diluent had significantly enhanced the electrical conductivity of the ECAs.

Besides electrical resistivity, ECAs were evaluated through shear strength of ECA joint as shown in **figure 5**. Apparently, lowest shear strength could be found in the ECA prepared without diluent (ECA 0) which was about 9.0 MPa. With addition of diluent, ECA 1 and ECA 2 showed increased shear strength at 13.9 and 13.8 MPa, respectively, which was about 1.5 times compared to that of the ECA 0. By further increasing the amount of diluent, enhanced shear strength was shown in ECA 3 which was above 17 MPa. This indicated that amount of diluent played an important role in the shear strength of ECA joint in this study.

3.2 Effect of viscosity of ECA paste on electrical resistivity and shear strength

In order to investigate the correlation between viscosity of ECA paste on electrical resistivity of ECAs in this study, relationship of electrical resistivity of ECA and viscosity of ECA paste at shear rate of 80 s-1 is

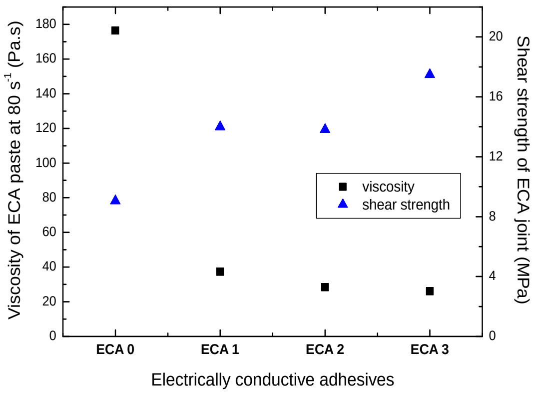

Fig. 7 Correlation between shear strength of ECA joint and viscosity of ECA paste at shear rate of 80 s-1 affected by amount of diluent in this study.

depicted in **figure 6**. Significantly, the paste of ECA 0 prepared without diluent showed highest viscosity among the ECAs paste prepared in this study. With addition of diluent, reduced viscosity could be observed. It is interesting to find that the trend of electrical resistivity of the ECA was very similar to that of the viscosity of the ECA paste. Electrical resistivity of the ECA decreased following the reduction of viscosity of the respective ECA paste from ECA 0 to ECA 3. The paste of ECA 0 that showed highest viscosity possessed highest electrical resistivity. This may be due to the low viscosity of the ECA paste yielding low surface tension which leads to better surface wetting of Cu fillers inside the polymer matrices [9]. Thus, relatively low electrical resistivity could be found in ECA with ECA paste at low viscosity. This indicated that the amount of diluent has pronounced effect on the electrical resistivity of ECA in this study.

Besides electrical resistivity, correlation between viscosity of ECA paste and shear strength of ECA joint was also investigated. **Figure 7** shows the correlation between shear strength of ECA joint and viscosity of ECA paste at shear rate of 80 s-1. Contrary to electrical resistivity, shear strength of the ECA joint showed the exact opposite trend to the viscosity of ECA paste. Shear strength of ECA joint enhanced with reduced viscosity of ECA paste. Shear strength of ECA joint improved with reduced viscosity of ECA paste as having good adherence behavior is a solid-like behavior with a low elasticity to obtain a good adhesion [10]. Apparently, highest viscosity in the paste of ECA 0 yielded lowest shear strength of ECA joint. Shear strength of the ECA joint increased significantly (about 1.5 times) when viscosity of the ECA paste decreased drastically from ECA 0 to ECA 1. Besides, it is obvious that highest shear strength above 17 MPa was found in ECA 3 with the lowest viscosity in the ECA paste. This could be due to the low viscosity of ECA 3 paste improving wetting of the surface of Cu substrates used in the shear test. Hence, this enhanced resin wetting contact angles and wetting tension, results in better physical adhesion of resin to the

Cu surface, leading to enhanced shear strength properties [11]. In contrary, the paste of ECA 0 with high viscosity showed low shear strength due to low wettability of the ECA paste to the surface of the Cu specimens. Hence, deteriorated shear strength was found in ECA 0. This result revealed that diluent in the ECA paste in this study played an important role in the shear strength of ECA joint, as it could alter the viscosity of the ECA paste.

4. Conclusion

In summary, it could be concluded that electrical resistivity and shear strength of the polyurethane based Cu filled ECA in this study is affected by the viscosity of the ECA paste modified by diluent (diethyl carbitol). Low viscosity led to lower electrical resistivity and higher shear strength which due to better surface wetting of Cu filler in the polymer matrices enhances surface wetting of the ECA paste to the Cu specimens of shear test. Results showed that increased amount of the diethyl carbitol improved the electrical conductivity and shear strength of ECA in this study.

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