

Copper-Filled Electrically Conductive Adhesives with Enhanced Shear Strength

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In this study, the effects of diethyl carbitol (diluent) and tertiary amines on the electrical, mechanical, and rheological properties of the Cu-filled polyurethane-based electrically conductive adhesives (ECAs) were investigated. Significant difference could be observed in the electrical resistivity and shear strength of ECA prepared with different amount of diethyl carbitol. Reduced electrical resistivity was found in ECAs prepared with addition of tertiary amines, but no obvious change was observed in the shear strength of the ECA joint. Rheological property of the ECA paste was investigated in order to understand the correlation of the viscosity of ECA paste and electrical resistivity and shear strength of ECA joint. Results revealed that decrease in viscosity of the ECA paste reduced electrical resistivity and enhanced shear strength of ECA joint. A Cu-filled polyurethane-based ECA with considerably low electrical resistivity at the magnitude order range of $10^{-3} \Omega \text{ cm}$, and significantly high shear strength (above 17 MPa) could be achieved.

Keywords conductive adhesive, copper, electrical resistivity, shear strength, viscosity

1. Introduction

The electronics packaging technologies in all levels are undergoing quick evolution due to dramatic change in electronics industries to low cost, portability, diverse functions, environmental benign, and user friendly (Ref 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. ECAs are composites of polymeric matrices and electrically conductive fillers which provide mechanical adhesion and electrical conduction, respectively. Silver (Ag)-filled epoxy-based ECA is the most commonly found ECA in the market due to the excellent electrical conductivity and chemical stability of Ag. However, the main disadvantage of Ag is being relatively expensive. Hence, alternative conductive fillers such as copper, nickel, and graphite powder have been studied as conductive fillers to manufacture low cost ECAs (Ref 2-5). Copper (Cu) can be a promising candidate for conductive metallic filler because of its low resistivity, low cost, and improved electro-migration performance compared to the commonly used Ag.

In our previous study (Ref 6-8), Cu fillers prepared by different methods were applied as conductive fillers in ECA

with phenolic resin as the adhesive binder. However, the shear strength of the resole type phenolic resin was relatively low. Hence, development of a Cu-filled ECA with enhanced mechanical strength is of great interest. Polyurethane (PU) represents an important class of thermoplastic and thermoset polymers which is widely used in the field of coatings, adhesives, and composites due to its high reactivity, high flexibility in formulation and application technologies, chemical and corrosion resistance, adhesion properties, and a wide range of mechanical strength (Ref 9-11). PU shows a very flexible chemistry with 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 (Ref 12). Polyurethanes are easily synthesized from diisocyanate and polyalcohol precursors via a condensation reaction that can be controlled by various urethane formation catalysts (Ref 13). Mainly, polyurethane catalysts can be classified into two distinct categories: organometallic (Ref 14) and amine (Ref 15).

There are some studies on Ag-filled PU conductive adhesives. For instant, Yang et al. (Ref 16) had studied the Ag-filled PU-based isotropically conductive adhesives (ICA). ICA with Ag microflakes ranging from 30 to 75 wt.% yielded electrical resistivity from 2×10^{-5} to $2 \times 10^{-3} \Omega \text{ cm}$. Besides, Novák et al. (Ref 17) had also investigated the electrical and mechanical properties of polyurethane-based adhesives filled with carbon black, Ag-coated basalt particles and fibers and graphites, respectively (Ref 5). However, PU-based Cu-filled ECA are rarely reported. In our previous study, we have investigated the effects of different silane coupling agents and post-curing on the PU-based Cu-filled ECA (Ref 18). The results showed that epoxy functionalized silane coupling agents and post-curing had improved the shear strength and electrical conductivity of the ECAs. However, post-curing at 170 °C for 1 h is considered as an additional process and post-curing temperature at 170 °C is relatively high too. Hence, we have developed a more practical and convenient way to improve the properties of PU-based Cu-filled ECA at relatively low temperature (140 °C) without additional process.

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Tertiary amines are used as catalysts during production of PU (Ref 19). Some researcher stated (Ref 20, 21) the reaction to proceed via a $R_3N...RNCO$ complex formation, while the theory of the reaction via a $R_3N...ROH$ complex is more widely accepted as amine could be a donor-acceptor reaction with the alcohol which results in a hydroxyl group activation in the latter (Ref 22-24). To the best of our knowledge, the study on modification of properties of copper-filled electrically conductive adhesive by diethyl carbitol (diluent) and tertiary amines has not yet been reported elsewhere. Diethyl carbitol was added as diluent or glycol solvent to alter the rheological property of the ECA paste, while tertiary amines were added as catalyst in the formation of polyurethane.

In this study, we focused on improving the electrical conductivity and shear strength joint of the ECA through modification of rheological property of the ECA paste. The effects of diluent (diethyl carbitol) content and different types of tertiary amines (*n*-tripropylamine and *N,N*-dimethylbenzylamine) on the electrical resistivity and shear strength joint of PU-based Cu-filled ECA were investigated.

2. Experimental

2.1 Materials

Cu fillers (I400Y) 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). Tertiary amines which were *n*-tripropylamine and *N,N*-dimethylbenzylamine were purchased from Kishida Chemical 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 Fig. 1.

2.2 Fabrication and Characterization of ECA Paste

To fabricate ECA paste, Cu fillers of 80 mass% were mixed with resin, diethyl carbitol and ethylene glycol in an agate mortar

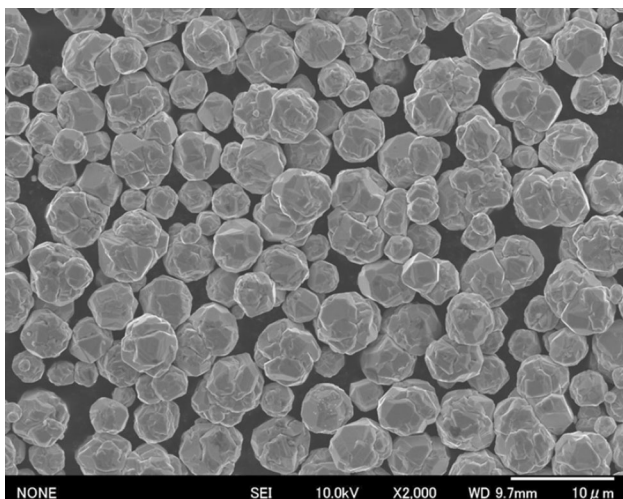


Fig. 1 SEM image of Cu filler used in this study

at room temperature. For ECA with addition of tertiary amine, the amine was added simultaneously during mixing of each ECA paste. It was then mixed and defoamed in a hybrid planetary centrifugal mixer (Model: ARE 250, Thinky Corp.) which enables simultaneous mixing, dispersion, and deaeration of high-viscosity adhesives with added fillers. As a control sample, ECA paste without diethyl carbitol was prepared and assigned as ECA 0. ECAs prepared with different diethyl carbitol content and tertiary amines in this study were shown in Tables 1 and 2. To confirm distribution of the fillers inside the polymer matrix, the cross section morphology of the as-cured ECA 1 was observed by SEM as shown in Fig. 2. Others ECAs in this study were found to possess the similar morphology of filler distribution.

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.

Table 1 ECAs prepared with different diethyl carbitol content in this study

ECAs	Mass ratio of resin:diethyl carbitol
ECA 0	1:0
ECA 1	10:1
ECA 2	10:2
ECA 3	10:3

Table 2 ECAs prepared with diethyl carbitol and different tertiary amines in this study

ECAs	Tertiary amine	Mass ratio of resin:diethyl carbitol:tertiary amine
ECA P	<i>n</i> -Tripropylamine	10:3:0.05
ECA D	<i>N,N</i> -Dimethylbenzylamine	10:3:0.05

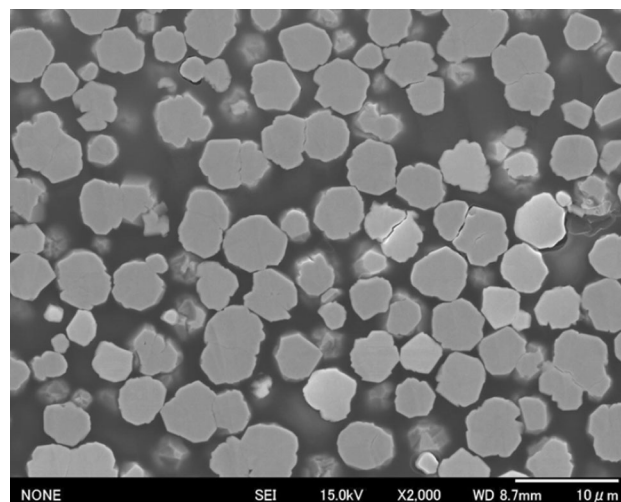


Fig. 2 SEM image of the cross section of as-cured ECA 1 in this study

2.3 Evaluation of As-Cured ECAs

A standard size of 50 × 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 five specimens were prepared on a single FR-4 board for each ECA sample (Fig. 3). Then, it was placed into a convection oven and preheated at 80 °C for 20 min, then cured 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 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:

$$\rho = \frac{t \times w}{l} \times R, \quad (\text{Eq 1})$$

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 Fig. 4. 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).

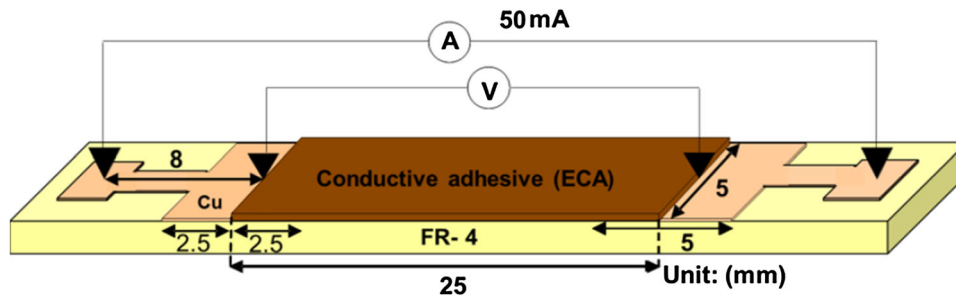


Fig. 3 Schematic diagram of FR-4 for electrical resistance measurement of ECA

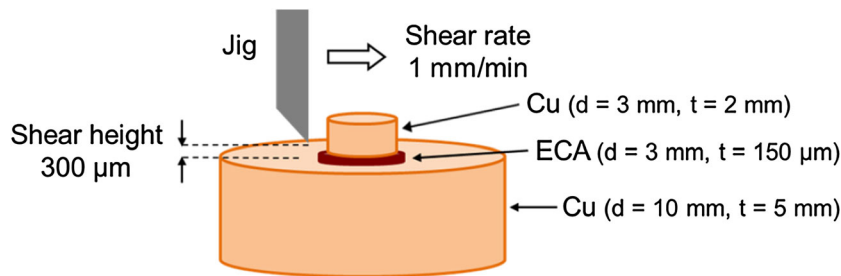


Fig. 4 Schematic diagram of Cu/Cu joint specimens for shear test (d = diameter, t = thickness)

3. Results and Discussion

3.1 Rheological Properties of ECA Paste

Rheology is the study of the flow behavior of a material under conditions in which they flow rather than showing elastic or plastic deformation in response to an applied force (Ref 25, 26). The rheological properties of polymer composites depend on factors such as the material microstructure, filler loading, aspect ratio and dispersion and, the interaction between the polymer and filler (Ref 27-29). Figure 5(a) presents the viscosity-shear rate curve of ECA paste affected by diethyl carbitol in this study. It could be observed that all ECA paste showed shear thinning behavior, but it was especially pronounced in ECA 0 which was prepared without diethyl carbitol. The effect is more apparent at low frequency and the relative effect diminished with increase in frequency due to shear thinning (Ref 30). As the shear rate is increased, the array of particles becomes directional and the interaction between particles is decreased. This phenomenon was also observed in our previous study of Ag flake-filled ECA (Ref 31). The shear thinning behavior of ECA 0 could be due to the relatively high viscosity in which the motion of the polymer chains becomes restricted or the long polymer chain relaxation in the ECA paste is effectively restrained. As diethyl carbitol was used as diluent to reduce the viscosity of the ECA paste, increasing the amount of diethyl carbitol increased the viscosity of the ECA paste accordingly from ECA 0 to ECA 3. This indicated that diethyl carbitol has apparent effect on the rheological property of ECA paste in this study.

Figure 5(b) depicted the viscosity-shear rate curve of ECA paste affected by tertiary amines in this study. Similar shear thinning behavior was found in all ECA paste and no significant difference could be observed in ECA D and ECA P. Thus, it could be considered that there was no significant effect on the rheological property of ECA paste modified by

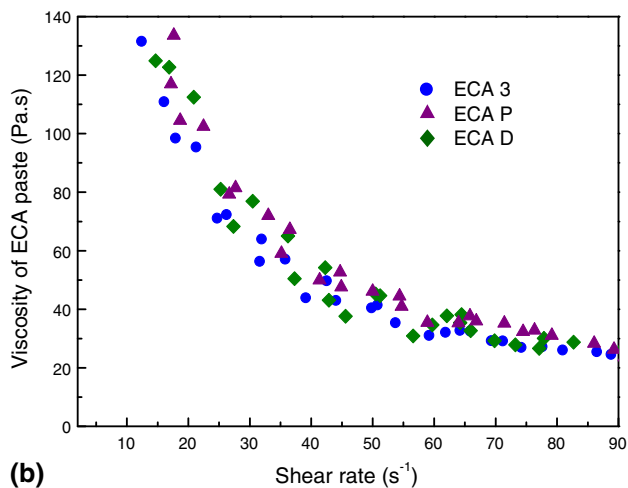
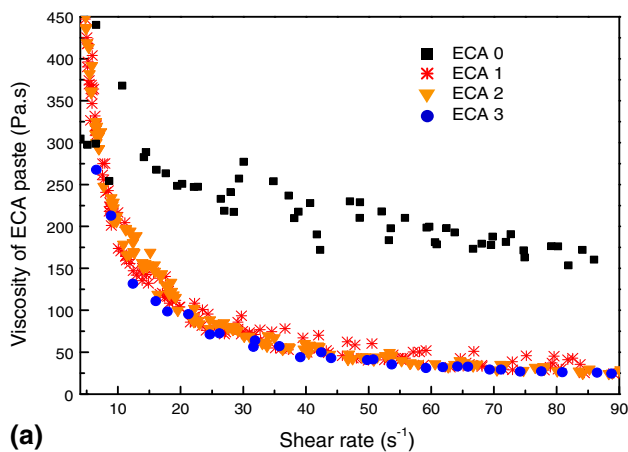


Fig. 5 (a) Shear stress-shear rate curves of ECA paste affected by diethyl carbitol in this study. (b) Shear stress-shear rate curves of ECA paste affected by tertiary amines in this study

addition of *n*-tripropylamine and *N,N*-dimethylbenzylamine in this study. This may be due to the low miscibility of these tertiary amines into the ECA paste.

3.2 Electrical Resistivity and Shear Strength of ECAs

Effects of different diethyl carbitol content and tertiary amines on the electrical properties of ECAs were investigated as presented in Fig. 6(a) and (b), respectively. Electrical resistivity of ECA 0 prepared without addition of diethyl carbitol showed significant high resistivity at $5.9 \times 10^{-2} \Omega \text{ cm}$ as shown in Fig. 6(a). However, with addition of diethyl carbitol at mass ratio of resin:diethyl carbitol: 10:1, ECA 1 showed almost two times of reduced electrical resistivity ($3.0 \times 10^{-2} \Omega \text{ cm}$) compared to that of the ECA 0. When the amount of diethyl carbitol increased up to mass ratio of resin:diethyl carbitol: 10:3, ECA 3 showed electrical resistivity at the magnitude order of $10^{-3} \Omega \text{ cm}$ ($5.7 \times 10^{-3} \Omega \text{ cm}$) which is almost ten times lower than that of the ECA 0. This revealed that addition of diethyl carbitol had significantly enhanced the electrical conductivity of the ECAs.

Furthermore, it was found that electrical resistivity was especially low in the ECAs prepared with addition of tertiary amines as depicted in Fig. 6(b), where ECA P and ECA D

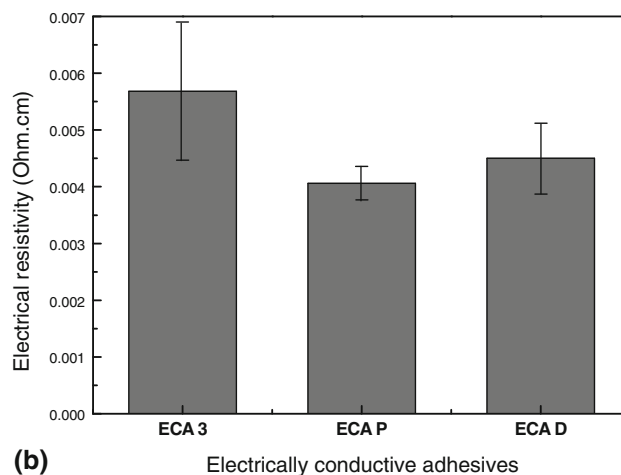
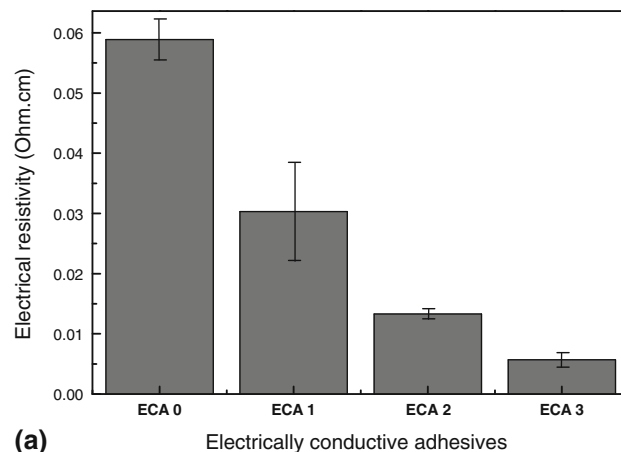


Fig. 6 (a) Effect of diethyl carbitol on the electrical resistivity of ECAs in this study. (b) Effect of tertiary amines on the electrical resistivity of ECAs in this study

possessed electrical resistivity of 4.0×10^{-3} and $4.5 \times 10^{-3} \Omega \text{ cm}$, respectively. This may be due to the addition of tertiary amine as catalyst which had improved the polymerization reaction (or gelation reaction) during formation of polyurethane (Ref 13).

Compared to the other prior work done on the research of Cu-filled ECAs, for example, bulk resistivity of the silane coupling agent modified Cu-filled ECA reported by Yim et al. (Ref 32) was $1.28 \times 10^{-3} \Omega \text{ cm}$ for the ECA filled with $1.5 \mu\text{m}$ Cu filler. Besides, Zhao et al. (Ref 33) also reported a Cu-filled ECA modified by SiO_2 nanoparticles with a lowest bulk resistivity of $1.34 \times 10^{-3} \Omega \text{ cm}$. Lin et al. (Ref 34) showed bulk resistivity of $2.0 \times 10^{-3} \Omega \text{ cm}$ for a silver-coated spherical-shaped copper powder-filled ECAs. As the resistivity of ECAs in this study could be achieved at the magnitude order of $10^{-3} \Omega \text{ cm}$, it could be considered that the ECAs in this study are compatible to that of the prior work.

Compared with commercial ECAs (Table 3), electrical resistivity of ECA 3, ECA P, and ECA D is relatively higher than most of the Ag-filled ECAs (except 8331s), but they are significantly lower than that of the ECAs filled with Ag-coated Ni, Ni, and graphite fillers. Hence, it could be considered that electrical resistivity of ECAs produced in this study is compatible to that of the commercial ECAs in the market.

Table 3 Electrical resistivity and shear strength of commercial epoxy-based ECAs

ECAs	Company	Filler	Electrical resistivity, Ω cm	Shear strength, MPa
E0-23 M	Epoxy Set Inc.	Ag	4×10^{-4}	11.9
APTEK 6500-PMF	APTEK Laboratories, Inc.	Ag	2×10^{-4}	15.2
8331s	MG Chemicals Ltd.	Ag	6×10^{-3}	1.0
EP 79	Master Bond Inc.	Ag-coated Ni	$\leq 5.0 \times 10^{-3}$	13.8
64C Eccobond	Ellsworth Adhesive Corp.	Ni	2.0×10^{-2}	5.5
EP 79 M	Master Bond Inc.	Ni	5–10	13.8
EP 75-1	Master Bond Inc.	Graphite	50–100	9.6

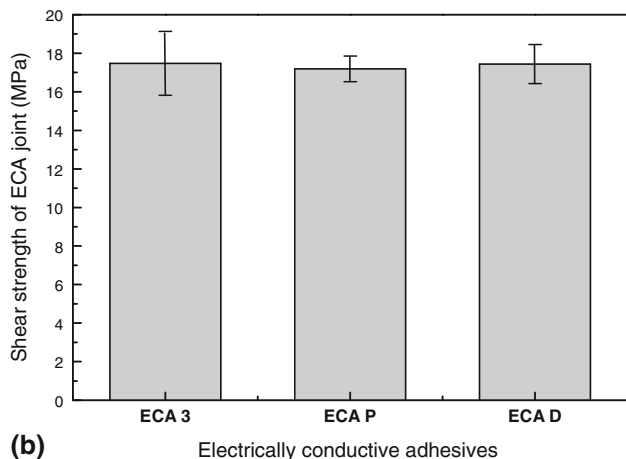
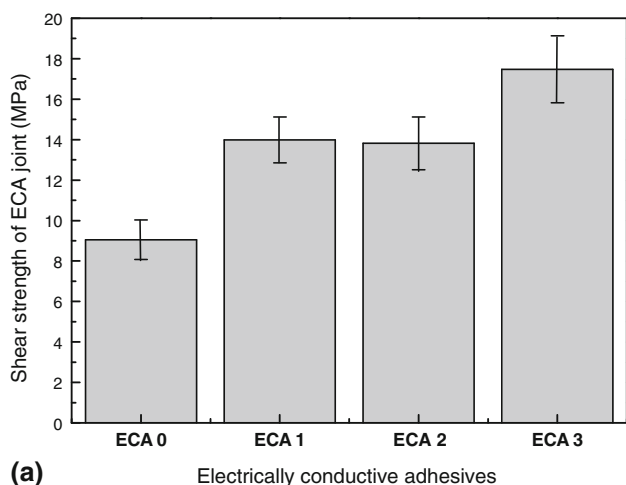


Fig. 7 (a) Effect of diethyl carbitol on the shear strength of ECA joint in this study. (b) Effect of tertiary amines on the shear strength of ECA joint in this study

Besides electrical resistivity, ECAs were evaluated through shear strength of ECA joint as shown in Fig. 7(a) and (b). As shown in Fig. 7(a), lowest shear strength was found in the ECA prepared without diethyl carbitol (ECA 0) which was about 9.0 MPa. With addition of diethyl carbitol, ECA 1 and ECA 2 showed increased shear strength, respectively, at 13.9 and 13.8 MPa, which was about 1.5 times to that of the ECA 0. By further increasing the amount of diethyl carbitol, enhanced shear strength of ECA joint was yielded in ECA 3 which was above 17 MPa. This indicated that amount of diethyl carbitol

played an important role in the shear strength of ECA joint in this study.

As shown in Fig. 7(b), ECA 3, ECA P, and ECA D showed comparable shear strength about 17 MPa. This revealed that no significant effect was found in the shear strength of ECAs added with *n*-triisopropylamine (ECA P) and *N,N*-dimethylbenzylamine (ECA D).

Refer to Table 3, the shear strength of the commercial ECAs is apparently low compared with most of the ECAs produced in this study especially ECA 3, ECA P, and ECA D. The highest shear strength of the commercial ECAs shown in Table 3 is 15.2 MPa (APTEK 6500-PMK) and the lowest is 1.0 MPa (8331s). However, in this study, shear strength ≥ 17 MPa was achieved in ECA 3, ECA P, and ECA D, while the lowest shear strength at 9 MPa was obtained in ECA 0. This reveals that the shear strength of ECA joint obtained in this study is comparable or even superior to that of the commercial ECAs available.

Figure 8(a) and (b) presents the shear stress as a function of shear displacement during shear test of ECAs in this study. It could be observed that ECA 0 shows failure at short shear displacement which was less than 0.8 mm. Shear displacement increased up to 1.12 mm for ECA 1 and continued to raise up to 1.21 mm for ECA 3. This indicated that addition of diethyl carbitol into the ECA paste in this study had increased both the shear strength and shear displacement of the ECA joint.

Besides, ECA P and ECA D showed relatively long shear displacement where the longest shear displacement was found in ECA D which was above 1.3 mm as depicted in Fig. 8(b). Hence, it could be considered that addition of *n*-triisopropylamine and *N,N*-dimethylbenzylamine into the ECA paste has improved the deformation capability of the ECA joint in this study.

3.3 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 depicted in Fig. 9(a) and (b), respectively. Significantly, ECA 0 paste prepared without diethyl carbitol showed highest viscosity among the ECAs paste prepared in this study as shown in Fig. 9(a). ECAs paste prepared with diethyl carbitol possessed relatively low and similar viscosity except ECA 1 paste that showed slightly higher viscosity. 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 reduced viscosity of the respective ECA paste from ECA 0 to ECA 3. ECA 0 paste which

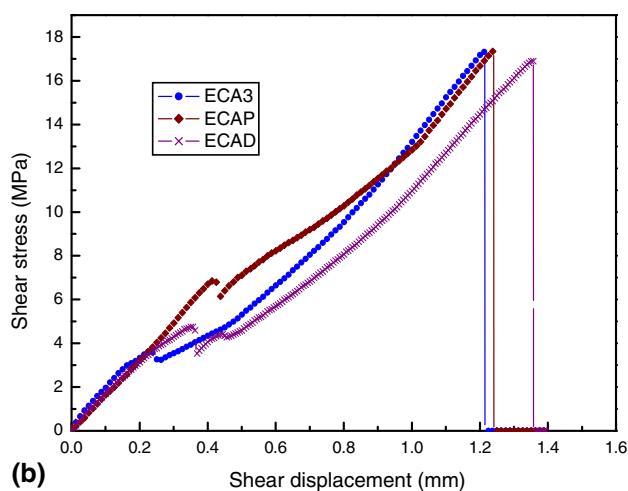
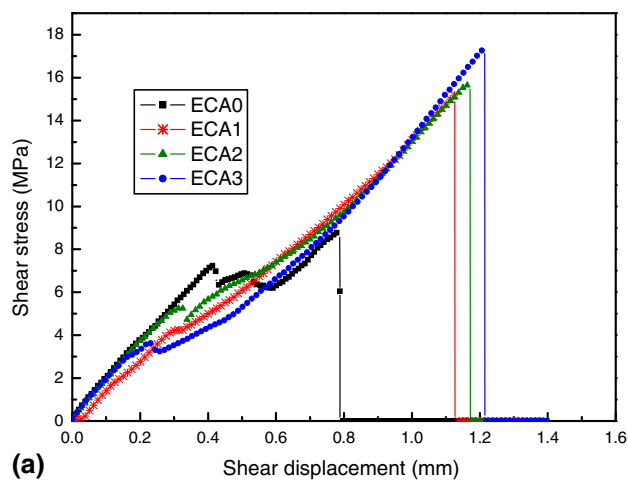
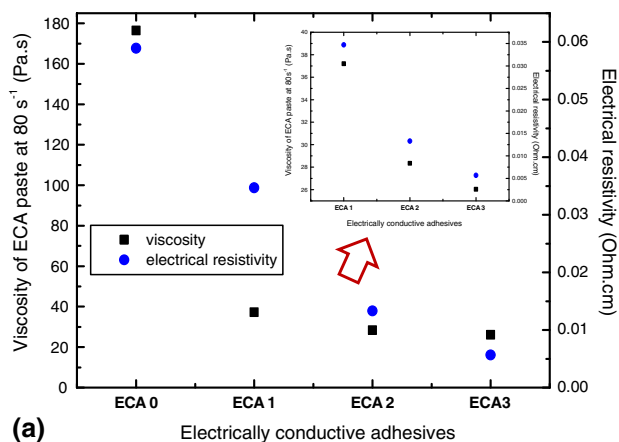


Fig. 8 (a) Shear stress as a function of shear displacement of ECAs affected by diethyl carbitol in this study. (b) Shear stress as a function of shear displacement of ECAs affected by tertiary amines in this study

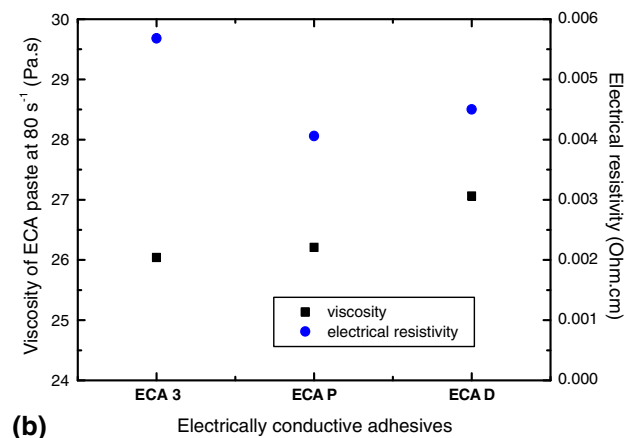
possessed highest viscosity showed highest electrical resistivity. The outcome of this study is comparable to studies by other researchers (Ref 35-37). Kasaliwal et al. (Ref 35) showed that composites processed at low viscosity level had lower resistivity values compared to those prepared at high-viscosity level. Liebscher et al. (Ref 37) reported that multi-walled carbon nanotube-filled blend composite prepared with low viscosity of polycarbonate yielded the lowest electrical volume resistivity. They also observed that an increase in the viscosity ratio corresponded with an increase in electrical resistivity. It is assumed that the low viscosity polycarbonate is able to better infiltrate into the CNT agglomerates, resulting in a better wetting behavior of the polymer to the agglomerates.

In this study, the low viscosity of the ECA paste possessed low surface tension which leads to better surface wetting of Cu fillers inside the polymer matrices (Ref 38). Thus, relatively low electrical resistivity could be found in ECA with its paste at low viscosity. This indicated that the presence of diethyl carbitol has apparent effect on the electrical resistivity of ECA in this study.

On the other hand, relationship of viscosity of ECA paste and electrical resistivity of ECAs affected by tertiary amines in this study is shown in Fig. 9(b). It was worth notice that



(a) Electrically conductive adhesives



(b) Electrically conductive adhesives

Fig. 9 (a) Correlation between electrical resistivity of ECA and viscosity of ECA paste affected by diethyl carbitol in this study. (b) Correlation between electrical resistivity of ECA and viscosity of ECA paste affected by tertiary amines in this study

electrical resistivity was relatively high in ECA 3 compared to that of the ECA P and ECA D, although viscosity of ECA 3 paste was the lowest. However, a similar phenomenon as observed in Fig. 9(a) could be found in ECA P and ECA D, where increased resistivity was observed in ECA D following the increase of viscosity of the ECA paste. In this case, it suggested that the function of tertiary amine was not only affecting the viscosity of the ECA paste, but it revealed its role as a catalyst in which it had improved the polymerization reaction during formation of polyurethane as mentioned in section 3.2.

Besides electrical resistivity, correlation between viscosity of ECA paste and shear strength of ECA joint was also investigated. Figure 10(a) and (b) showed the relationship of 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 an exact opposite trend to the viscosity of ECA paste (Fig. 10a). Shear strength of ECA joint enhanced with reduced viscosity of ECA paste. Adherence properties are always related to the rheological behavior of the adhesive (Ref 39). 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 (Ref 39). Apparently, ECA 0 paste with highest viscosity showed lowest shear strength of ECA joint. Shear strength of the ECA joint increased significantly (about 1.5

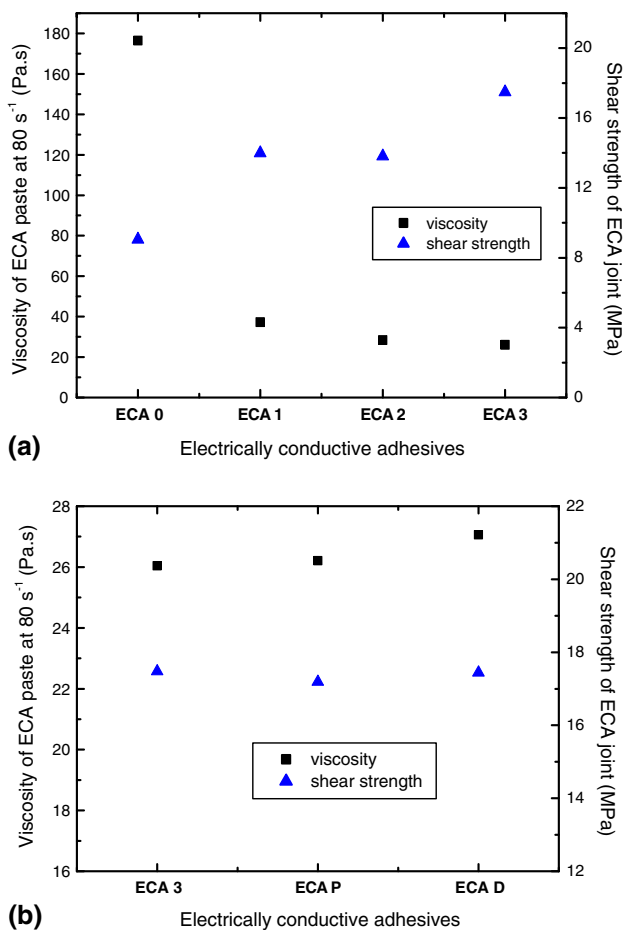


Fig. 10 (a) Correlation between shear strength of ECA joint and viscosity of ECA paste at shear rate of 80 s⁻¹ affected by diethyl carbitol in this study. (b) Correlation between shear strength of ECA joint and viscosity of ECA paste at shear rate of 80 s⁻¹ affected by tertiary amines in this study

times) when viscosity of the ECA paste decreased drastically from ECA 0 to ECA 1. Besides, it is clear that ECA 3 paste that possessed relatively low viscosity yielded relatively high shear strength at about 17 MPa. This could be due to the low viscosity of ECA 3 paste improved wetting of the surface of Cu substrates used in the shear test. Hence, this enhanced resin wetting contact angles and wetting tension, resulting in better physical adhesion of resin to the Cu surface, leading to enhanced shear strength properties (Ref 40). Similar phenomenon was observed in our previous study in shear strength joint of Ag-filled ECA (Ref 31). In contrary, ECA 0 with high viscosity possessed 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 diethyl carbitol which used as the diluent in the ECA paste in this study played a significant role in the shear strength of ECA joint, as it could be used to control the viscosity of the ECA paste.

In addition, effect of tertiary amine on the correlation between shear strength of ECA joint and viscosity of ECA paste in this study was studied as presented in Fig. 10(b). Similar viscosity of the ECA paste yielded comparable shear strength of ECA joint (about 17 MPa) in all cases. This implied that effect of tertiary amines on the shear strength of ECA joint

in this study was minute. Consequently, it could be considered that viscosity of the ECA paste played an important role in both electrical resistivity and shear strength of the ECA in this study.

4. Conclusion

In summary, we could conclude that electrical resistivity and shear strength of the polyurethane-based Cu-filled ECA in this study could be affected by the viscosity of ECA paste through altering the amount of diethyl carbitol. Results showed that increased diethyl carbitol content improved electrical conductivity and shear strength of the ECAs in this study. Low viscosity of ECA paste reduced electrical resistivity and enhanced shear strength of ECA joint due to better surface wetting of Cu filler in the polymer matrices and enhanced surface wetting of the ECA paste to the Cu specimens of shear test. Although the effect of tertiary amines used in this study was not obvious on the shear strength of ECA joint, significant difference could be found in shear displacement especially in ECA D. Reduce in electrical resistivity could be observed in ECAs prepared with addition of tertiary amines (ECA P and ECA D). Hence, it could be considered that addition of diethyl carbitol and tertiary amines into the ECA paste had improved the properties of ECAs in this study.

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