Effects of hybrid fillers based on micro- and nano-sized silver particles on the electrical performance of epoxy composites

M. Zulkarnain · M. Mariatti · I. A. Azid

Abstract In the present study, electrically conductive adhesives produced from hybrid fillers based on micro- and nano-sized silver (Ag) was developed. The influence of the hybrid filler composition on the electrical properties of the hybrid system was studied. The electrical conductivity of the epoxy composites filled with micro- and nano-silver was correlated with their morphologies. A positive effect was observed in the electrical conductivity result when the composition of micro- and nano-sized Ag particles reached a 50:50 weight ratio. The nano-sized Ag particles became interconnecting particles in the interstitial spaces between micro-sized particles. Micrograph scanning shows that the particles were well distributed and dispersed, the separation between lumps of Ag filler by the insulating matrix was significantly reduced, leading to the formation of continuous linkages. The increased electrical conductivity resulted in a charge around the particle distribution, which led to the high capacity. Hence, these particles increased the conductivity of the system.

1 Introduction

Electrically conductive adhesives (ECAs) are mainly composed of a polymer binder and a metal filler that offer electrical conduction for electronic applications. The early usage of ECAs is to provide an alternative to solders containing Pb because of its toxicity [1, 2]. ECAs offer numerous advantages than tin–lead solders, such as a fine pitch ability owing to the availability of small-sized conductive fillers, minimum processing temperature, and environmentally friendly. The performance of the electrical properties of ECAs strongly depends on the concentration (volume fraction) of the filler, morphology of the filler, filler distribution within the polymer matrix, interaction between filler surfaces, contact resistance between adjacent particles, as well as particle size [2, 3]. High-performance ECAs using metal non-oxide fillers are being extensively used because of their high electrical conductivity [2].

Previous studies have considered various particle parameters to improve the percolation threshold of ECAs [4, 5]. Studies on the size effect of silver (Ag) particles on the conductivity of ECAs have been conducted [6–9]. Ag nano-filler sizes have been proposed as conductive fillers in ECAs for fine pitch interconnects. Nano-Ag particles can improve the percolation threshold because of their tendency to form a number of contacts between small particles [2]. Common conductive fillers used in ECAs are micro-sized Ag particles due to their lower resistivity and good processability [10–14]. ECAs filled with various sizes of Ag particles have been previously reported [6, 13]. Wu et al. [6] studied the electrical properties of ECAs using Ag spherical particles with sizes ranging from 10 to 200 nm. Particles with an average diameter of 50 nm show a higher conductivity percolation threshold with 63 wt% filler loading. Suriati et al. [13] reported that the conductivity of micro-sized particles is slightly higher than nano-sized particles. However, percolation thresholds of the electrical conductivity of these two composite systems are slightly

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similar and occurs at 6 vol.% filler loading. Generally, micro-sized ECAs achieve greater interconnection at a low loading than nano-sized fillers [13, 14]. Ag micro-particles present good distribution because they require a lower energy for particle agglomeration.

Hybrid micro- and nano-scale Ag particles are gaining acceptance because of their cost and performance [8, 15]. Hybrids can decrease the cost of materials for the performance of a specified electrical property. Fu et al. [15] used a bimodal distribution of metal filler to identify the conductivity of hybrid micro- and nano-sized metal fillers in ECAs. The critical volume percentage at which the percolation threshold occurs decreases with increased nano-scale density in the conductive adhesive. Lee et al. [8] substituted nano-sized Ag particles with micro-sized particles in polyvinyl acetate (PVAc). They reported that the advantage of using nano-sized particles is the avoidance of the settling problem encountered in some micro-sized Ag particle systems. When the composite based on micro-sized Ag flakes in the PVAc is near the percolation threshold, the additions of a small amount of nano-sized Ag colloids help establish the conductive path and thereby lower the resistivity. However, research on the electrical conductivity of hybrid micro- and nano-Ag-filled epoxy composites is limited.

This study aims to investigate the effect of hybrid Ag (micro- and nano-sized) particles on the electrical conductivity of a conductive adhesive. The nano-sized filler is used to form an aggregated network of conducting particles among micro-sized fillers in the conductive adhesive. In these systems, the effects of hybrid micro- and nano-sized fillers on the electrical and morphological properties of conductive composites are investigated.

2 Experimental method

2.1 Materials

The epoxy used in this study was bisphenol-A-(epichlorohydrin), also known as EPON™ Resin 8281 (EPON 8281), supplied by Hexion Specialty Chemical, USA. Polyetheramine D230 (PEA; density = 0.946 g/mL at 298 K), which was used as a curing agent for EPON 8281, was manufactured by BASF Corporation. The mixing ratio of EPON 8281 and PEA was set to 100:32. The Ag particles used in this study were purchased from Sigma–Aldrich, Inc. Data from the supplier indicate that the average particle sizes were 80 nm and 2–3.5 μm, and the density was 10.49 g/cm^3. Chloroform (99.0–99.4 %) purity was used in the study to lubricate the particle distributions in the epoxy resin.

2.2 Preparation of ECA composite

Single-filler (micro- and nano-sized) conductive adhesives were prepared using 2–8 vol.% fillers. For the hybrid system, the total Ag micro- and nano-sized filler loading was fixed at 6 vol.%. The volume ratios of the hybrid system using micro- and nano-sized particles were varied in three sets: 75:25, 50:50, and 25:75 (the number on the left indicates the micro-sized particle content; that on the right indicates the nano-sized particle content). The epoxy and Ag filler mixture was stirred for approximately 10 min using a homogenizer, then the mixture was sonicated for 30 min to facilitate filler dispersion. The mixture was subsequently vacuumed for approximately 0.5 h at room temperature (35 °C) to remove bubbles. The curing agent (32 parts by weight) was added into EPON 8281 (100 parts), and the mixture was stirred for another 10 min. Finally, the mixture was stored in a vacuum oven for 2 h at room temperature before it was cured in the oven at 100 °C for 1 h and post-cured at 125 °C for 3 h.

2.3 Characterization

The electrical conductivities of the ECA samples were measured using Instek LCR-817. The voltage supplied was 1 V and the testing was conducted at room temperature. Specimens with 2 cm × 2 cm dimensions were prepared for the electrical conductivity tests. The electrical conductivity (σ) was defined as the electrical resistance of a material and determined according to Ohm's Law. The value of volume resistivity is defined as the electrical resistance through a plate of ECAs material, the volume resistance (R_v) is measured using Eq. (1)

$$R_v = \frac{V_v}{I_v} \tag{1}$$

The resistance was used to calculate the volume resistivity of the specimen and expressed as

$$\rho_v = \frac{R_v A}{t} \tag{2}$$

The ρ_v denotes the volume resistivity, R_v is volume resistance, A is the area of the conductor, while t is the average thickness of the sample which is 1. The volume electrical conductivity (σ) for ECAs can be determined using Eq. (3).

$$\sigma_v = \frac{1}{\rho_v} \tag{3}$$

A field emission scanning electron microscopy (FESEM) system (model ZEISS SUPRA™ 35VP) with a Gemini field emission column was used to study the sample morphology on fracture surface of ECAs. The particle size

distribution was measured by Malvern model Master Sizer/ E Version 2.15 and Zeta Sizer Nano Series Version 6.01 for micron and nano size of fillers, respectively.

3 Results and discussion

3.1 Characteristics of the raw materials

Figure 1 a, b show the intensity versus size distribution of micro and nano size Ag particles. The average sizes of the micro and nano size Ag particle are 3.16 μm and 110.1 nm, respectively, which are comparable to the values claimed by the suppliers (Table 1).

3.2 Electrical conductivity

3.2.1 Micro- and nano-sized systems

The electrical conductivity of ECAs was generally characterized by the percolation threshold that varied with the volume fraction of the filler loading [2]. Figure 2 illustrates the relationship between the experimentally measured electrical conductivity and Ag volume fraction in the epoxy composites. Both epoxy composites filled with micro-sized and nano-sized Ag particles showed similar conductivity trends. The electrical conductivity of the epoxy composite filled with Ag particles at 4 vol.% showed an insignificant

Table 1 Characteristics of the silver micro- and nano-sized particles

	Micro-sized	Nano-sized
Shape	Spherical	Spherical
Mean size[a]	2–3.5 μm	80 nm
Mean size[b]	3.16 μm	110.1 nm
Condition	Dry powder	Dry powder

[a] Information provided by the supplier

[b] Measured experimentally

increase in the conductivity because some particle fillers were still isolated by the matrix without any contact to perform a continuous linkage. This electrical property showed the percolation threshold that was characterized by a sudden increase in the electrical properties at 6 vol.%. Both micro- and nano-sized Ag particles reached the percolation threshold at the same filler loading. The electrical conductivity at the percolation threshold of nano-sized Ag particles was obtained at 1.03×10^{-2} S/cm. At this percolation threshold, the Ag nanoparticles began to make contact and enabled electrical transport inside the composite materials. At 8 vol.% nano-Ag loading, the ECAs presented a conductivity value of 2.2×10^{-2} S/cm. The ECA conductivity was only studied at 8 vol.% filler loading because of the insignificant increase in the current conductivity at a high filler loading. The loading level of conductive fillers was sufficient for interparticle contact, and the conductivity stabilized beyond the percolation threshold. The micro-sized Ag particle adhesives showed a slightly higher electrical conductivity than the nano-sized system, i.e., 1.55×10^{-2} and 2.69×10^{-1} S/cm at 6 and 8 vol.%, respectively. This finding may be due to the different contact resistances that existed in the nano-sized system and affected the electrical conductivity of the adhesive. Two types of resistances were observed in the composite system. First was restriction resistance caused by a small contact area, and second was tunneling resistance that existed when the nano-sized particles were included in the system. Tunneling occurred when the electrons in one filler particle penetrated the potential barrier and reached the next particle within a critical separation distance. A conductive channel was formed between the resins before the direct contact between the particles. The effect of tunneling on nano-sized Ag particles in ECAs is reportedly around 100 nm [9]. A previous study has indicated that the electrical conductivity of Ag conductive adhesives is 10^3 S/cm at the percolation threshold with approximately 63 wt% filler loading [6]. Suriati et al. [13] reported that the electrical conductivity of Ag nanoparticles is about 10^{-2} S/cm, which corresponds to the critical volume at 33 wt% filler loading. Hence, the percolation threshold phenomenon varies with the size of the conductivity filler in the polymer matrix. The addition
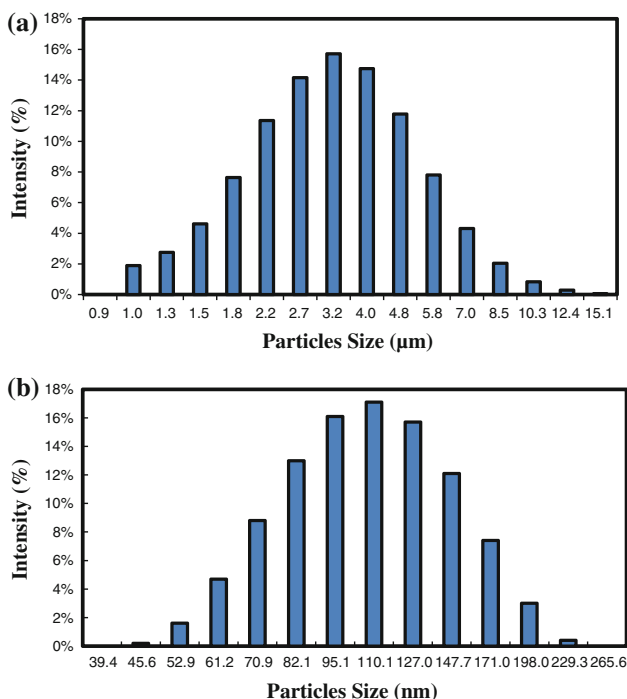

Fig. 1 The curve plot of size distribution by intensity of Ag particles, **a** micro-sized, and **b** nano-sized
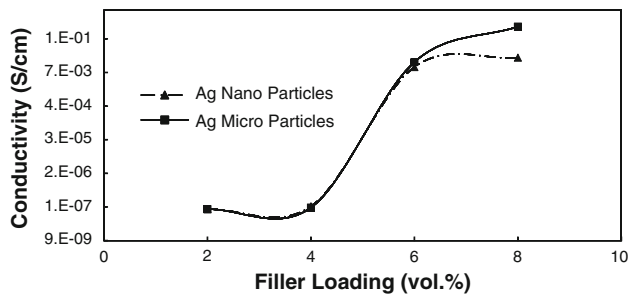
Fig. 2 Electrical conductivity of Ag-filled epoxy composites versus the volume fraction of Ag fillers

of nano-sized Ag particles reportedly exerts a negative effect on the electrical conductivity [9, 13] because of the tendency of particle agglomeration in the ECAs.

FESEM observations on the fracture surface of the Ag/epoxy composite containing 4 and 6 vol.% filler were performed to determine the morphology of the ECAs near the percolation threshold. Figure 3 shows the FESEM images of the cross-section of Ag-filled conductive adhesive materials. In the micrograph, the epoxy matrix and Ag particles can be easily distinguished; the Ag particles are the small particles dispersed in the continuous epoxy matrix. An insufficient filler amount was the main reason for the low electrical conductivity at 4 vol.%. Figure 3a shows that the particle-to-particle contact on the networks of nano-sized Ag particles was not obvious in the system, which led to a low electrical conductivity. The figure shows a clear separation of the micro-sized Ag particles in the epoxy matrix. The network began to form in Fig. 3b, which subsequently increased the electrical conductivity.

The electrical conduction was established via a particle path or tunneling connection between particles in ECAs. Figure 3c shows a clear separation of the micro-sized Ag particles in the epoxy matrix that resulted in a low electrical conductivity. Figure 3d shows that a sufficient filler amount led to physical contact between fillers that further led to the formation of continuous linkages, thereby increasing the current flow and electrical conductivity.

3.3 Hybrid of micro- and nano-sized systems

A study on the hybrid of micro- and nano-sized Ag fillers was conducted at 6 vol.%. Three ratios of micro-:nano-Ag particles were used: 75:25, 50:50, and 25:75. The electrical conductivities of these hybrid micro- and nano-Ag particles are shown in Fig. 4. Based on the volume loading ratios, the electrical conductivity levels varied depending on the particle size combination. The conductivity results were 1.12×10^{-3}, 4.03×10^{-1}, and 1.11×10^{-5} S/cm for the volume loading ratios of 75:25, 50:50, and 25:75, respectively. A volume loading ratio of 75:25 resulted in moderate electrical conductivity. The conductivity value dropped compared with the micro-sized and nano-sized particles at 6 vol.% filler loading. This phenomenon may be due to the inability of the nano-Ag particles to occupy forcibly the spaces between micro-sized particles. However, when each particle size reached 50 % filler loading in a 50:50 volume ratio, the electrical conductivity increased to a value that was slightly higher than that obtained at a 75:25 ratio. This phenomenon proved that the increase in particle contacts caused by nano-sized Ag particles helped
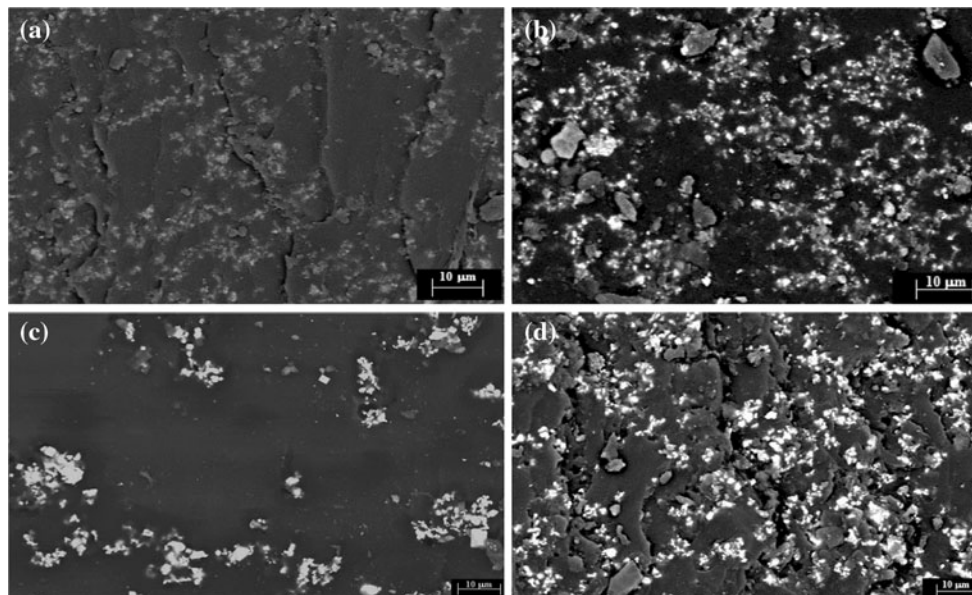

Fig. 3 SEM images of the cross-sectional view of Ag-filled epoxy composites at various filler loadings: **a** 4 vol.% nano-Ag filler loading, **b** 6 vol.% nano-Ag filler loading, **c** 4 vol.% micro-sized Ag, and **d** 6 vol.% micro-sized Ag. Magnification, ×500
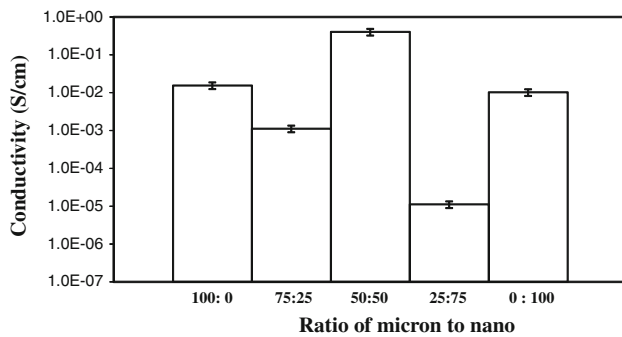
Fig. 4 Conductivity of ECA with 6 vol.% Ag filler loading vs. the ratio of micro- and nano-Ag particles

build and improve the particle network among them. Hence, the ECA conductivity increased. A positive hybrid effect resulted from the increased particle dispersion. This result was consistent with theoretical models of size effects [2], in which the smaller nano-sized particles surround the larger micro-sized particles in a 50:50 ratio. When the ratio was 25:75, the mixing of a large number of nanoparticles seemed to reduce the conductivity. The low performance of nano-sized Ag particles incorporated in the ECA was possibly due to the increased agglomeration and contact resistance of nanoparticles in the ECA. A negative hybrid effect in the particle dispersion was observed when nano-sized Ag particles were dominant. Previous studies have reported a similar phenomenon, i.e., the addition of nanoparticles negatively affect the electrical conductivity of composites [12].

Figure 5 confirms that the hybrid system had different dispersion behaviors for each set of volume ratio. Figure 5a shows that the Ag particles were not well distributed and resulted in agglomeration, as observed on the micrograph. However, the pathway of particle networks of nano-sized Ag was obvious in the system, which led to a moderate electrical conductivity value. The addition of a small amount of nano-sized Ag built the conductive network. For a fixed amount of filler addition, the nano-sized particles contained a larger number of particle contacts but also inevitably increased the contact resistance. Figure 5b shows that the particles were well distributed and dispersed. The distribution and dispersion were slightly better than those in Fig. 5a. The increased electrical conductivity resulted in a charge around the particle distribution, which led to the high capacity. This finding was verified by comparing the FESEM images of the 6 vol.% particles before and after combining the micro- and nano-Ag, as shown in Figs. 3b, d, and 5b. The conduction path performance can be evenly spread in the entire ECA, which subsequently increased the electrical conductivity. Figure 6 shows a simpler method wherein a hybrid particle agglomerate was used to create the segregated network by forcing the conductive particles into the interstitial space between micro-sized particles during mixing. Once the micro- and nano-sized particles were mixed in the epoxy paste, the particles were dispersed in the solution. During the mixing process, the particles coalesced with one another, and the bonding energy motivated the nanoparticles to surround the micro-sized particles. At the same time, the nano-sized particles exerted a bridging force between micro-sized
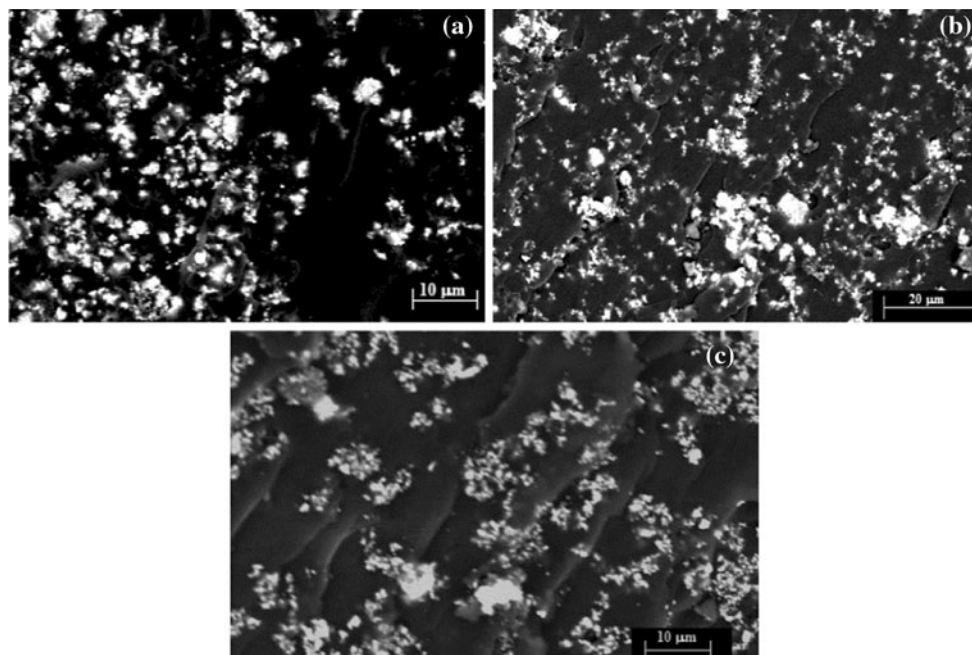

Fig. 5 SEM images of the cross-section of micro- and nano-Ag (6 vol.%) at different ratios: (**a**) 75:25, (**b**) 50: 50, and (**c**) 25: 75. Magnification, ×500
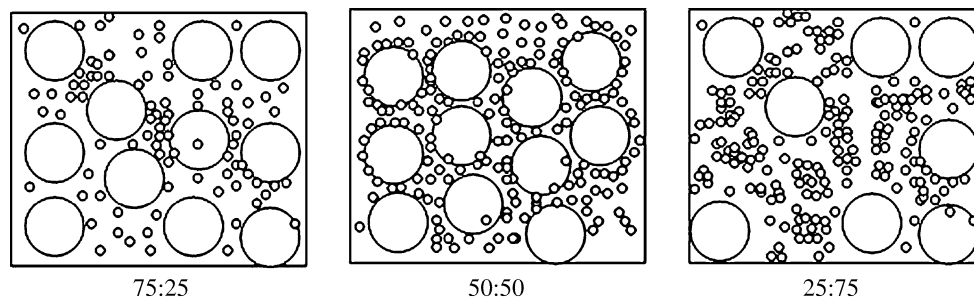
Fig. 6 Schematic illustration of different ratio of micro to nano particles distribution in hybrid polymer matrix

particles. Finally, the electrical conductive pathway was effectively built at the contact points among the micro-sized particles. The negative effect of the hybrid system is shown in Fig. 5c. The typical distribution was dominated by the nano-sized Ag particle distribution where a large number of agglomerates and too much space among particles existed. Consequently, a segregated network of particles formed at a much lower filler loading, and the resistivity increased upon the addition of nano-sized particles. The filler particles were more separated by the epoxy matrix and at this condition, and the electrical conductivity values were lower than other systems. By contrast, Fig. 5a, b revealed a connectivity that was consistent with the conductivity results.

Filler agglomeration normally occurs in the fabrication of the conductive adhesive. In the paste condition, aggregation can also occur in the dispersion if the repulsive

interactions among particles are not sufficiently strong to overcome van der Waals attraction. Both micro- and nano-sized particles are susceptible to aggregation in a suspension. By forming connections between conductive Ag particles, aggregation creates a conductive path for electrons to jump from aggregate to aggregate. Figure 6 illustrates the schematic illustration of systems micron to nano Ag particles distribution in epoxy. In the 75:25 hybrid size system, the nanoparticles were present in insufficient number that produced a particle segregation network throughout the entire system dispersion. A small amount of nanoparticle dispersion built several bridges to the micro-Ag particles. A sufficient number of nanoparticles that filled the segregation network in the particle dispersion were observed in the 50:50 hybrid system. During the segregation, the nanoparticle size enabled the distribution

Table 2 Comparison of the electrical conductivities of different ECAs reported in previous studies

ECA system	Electrical conductivity (S/cm)	Critical volume (V_c)	Reference
Epoxy resin (E-44 (6101))	10^3	20−25 vol.% (63 wt%)	Wu et al. [6]
Silver nanoparticles (average size = 50 nm)			
Epoxy A type resin (EPON™ 8281)	10^{-3}	5 vol.% (28.7 wt%)	Tee et al. [4].
Silver nano-sized (average size = 70 nm)			
Epoxy A type resin (EPON™ 8281)	10^{-1}	6 vol.% (33 wt%)	Suriati et al. [13]
Silver flakes (average size = 4–8 μm)			
Silver nanoparticles (average size = 80 nm)			
Epoxy F type resin (EPON™ 862)	10^1	10 vol.% (54 wt%)	Khairul et al. [14]
Silver type A (average size = 10.59 μm)			
Epoxy A type resin (DER™ D230)	10^{-2}	20 vol.% (72 wt%)	Khairul et al. [14]
Silver type A (average size = 10.59 μm)			
Present study			
Epoxy A type resin (EPON™ 8281)			
Silver micro size (average size = 3.16 μm)	10^{-2}	6 vol.%	–
Silver nano-sized (average size = 110.1 nm)	10^{-2}	6 vol.%	–
Hybrid system (micro:nano)			
25:75	10^{-3}	6 vol.%	–
50:50	10^{-1}	6 vol.%	–
75:25	10^{-5}	6 vol.%	–

to be forced to in the spaces between the microparticles. These nanoparticles likely influenced the electron path between micro-sized particles in the ECAs. On the other hand, a negative impression on the 25:75 hybrid system was found. The nanoparticles strongly influenced the dispersion of particles in ECAs.

Table 2 compares the different conductive systems and their corresponding electrical conductivities at critical volumes based on previous studies [4, 6, 13, 14]. The electrical conductivities in these studies are found to range from 10^{-5} to 10^3 by different filler loadings, which is within the conductive range measured in the present study. The variations in the electrical conductivity of ECAs are governed by many factors such as the processing method, filler loading, curing conditions, purity of the conductive fillers, and conductivity of the matrix itself. In the present study, the critical volume loading was approximately 33 wt%, which was obviously lower than in previously reported composite systems [6, 14], which exhibited at least 54–72 wt% to reach the percolation threshold. The present study obtained a similar critical volume percolation to that reported in literature [13], and a slightly higher electrical conductivity than the one obtained by Tee et al. [4]. In our hybrid-system conductive adhesives, a positive effect was observed in a 50:50 ratio, where the electrical conductivity reached 10^{-1} S/cm.

4 Conclusions

1. The trend of electrical conductivity near the percolation threshold occurs between 4 and 6 vol.%, and this finding is supported by morphological analysis results, which indicates that, the particles begin to form an electrical network at 6 vol.% for both micro- and nano-sized Ag particle systems.
2. The epoxy composite filled with Ag nanoparticles shows a lower conductivity than the epoxy composite filled with micro-sized particles, which can be attributed to the higher resistance between nano-sized particles and the poor dispersion throughout the matrix. The distribution of fillers in the epoxy matrix, which affect the properties of the composite, is revealed by SEM images.
3. In the hybrid system (6 vol.% of Ag filler) observation, a 50:50 volume ratios gives the highest electrical conductivity.

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