



Electrical properties of electrically conductive adhesives from epoxy and silver-coated copper powders after sintering and thermal aging

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ABSTRACT

In order to enhance the oxidation resistance of a copper substrate, silver films were deposited by three-times electroless plating onto pure copper powders. Silver-coated copper (Ag/Cu) powders were introduced into electrically conductive adhesives (ECAs) as conductive fillers. The electrical conductivity of the ECAs can be increased by the inclusion of conductive fillers into the insulating resin matrix. The structures of the Ag/Cu powders and ECAs were characterized by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS), respectively. The morphology investigation showed that the silver coatings were compact and continuous. It was found that the ECAs can be solidified through chemical sintering in air at 150 °C for 30min. The minimum volume resistivity was shown to reach $2 \times 10^{-4} \Omega \cdot \text{cm}$, suggesting excellent electrical conductivity, which makes us believe that the silver films have excellent oxidation resistance and could be broadly applied in the preparation of ECAs.

1. Introduction

The major components of ECAs are polymeric matrix and conductive fillers. The polymeric matrix can grant the physical and mechanical properties while the conductive fillers can provide electrical pathways throughout the matrix [1]. Many approaches have been made to explore ECAs with high electrical conductivity to replace the traditionally used toxic lead-based solders in electronic packaging industries [2–6]. Recently, research has focused extensively on conductive filler utilization within ECA formulations in an attempt to enhance conductivity and decrease tunneling resistance.

Metallic fillers, which have attracted a great deal of research attention, have excellent thermal, mechanical and electrical properties [7]. Particularly, metallic materials such as silver [8], copper [9] and nickel [10] fulfill an important role in the development of conductive fillers. Copper materials have been widely applied in circuit boards as conductors. They possess good mechanical properties, cheapness, and compatibility with many types of polymers. However, in many applications, copper powder suffers from oxidation at relatively high temperatures because of its low oxidation resistance [11]. Therefore, a surface coating is required to improve the oxidation resistance of pure copper powders [12–14]. In recent years, numerous methods have been

used to coat silver films onto the surfaces of copper powders to improve oxidation resistance [15,16]. Silver-coated copper powders may be prepared taking advantage of silver nitrate and reductant as raw materials. Electroless silver coating can be successfully achieved on copper powder and has a much higher deposition rate than electroplating. Silver-coated copper powders are widely used in conductor pastes, because of their environmental protection, economic and good oxidation resistance. Most Cu–Ag composites powders comprise relatively low contents of Ag. Thus, the electrical resistivity and stability of ECAs is poor [17]. Nishikawa [18] prepared ECAs using spherical silver-coated copper particles as fillers containing 10% silver and found that the electrical resistivity of the ECAs comprising such fillers was low ($10^{-4} \Omega \text{ cm}$) with little stability. The electrical resistivity of ECAs is strongly affected by the content of conductive fillers. Zhang [19] prepared ECAs using flake silver-coated copper particles, acquired from Ferro Electronic Materials Systems. The study found that the silver coating provides oxidation resistance at temperatures lower than 150 °C. The volume resistivity of ECAs was 10^{-4} – $10^{-3} \Omega \text{ cm}$ when the mass fraction of flake silver-coated copper particles was 80%. Cui [20] reported that Ag-coated Cu powders used as ECA fillers with lower electrical resistivity when the mass content of conductive fillers as much as 90%. For this paper, we present examples of silver-coated copper fillers that have

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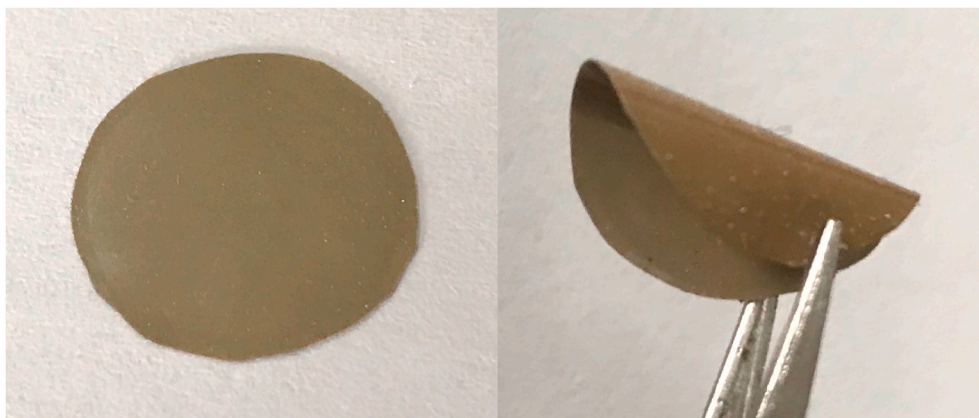


Fig. 1. Demonstrations of the printability, flexibility, and conductivity of the ECAs film. ((a) and (b) screen printed images of school badge under different deformations).

been utilized within ECA formulations to improve their electrical conductivity whilst reducing the amount of conductive fillers employed. In addition, the mechanisms of electrical conductivity enhancement are discussed.

2. Experimental

2.1. Materials and methods

All chemical reagents employed were of analytical grade and used without further purification. Two types of copper powder were studied in this program. The first, designated Cu-1, had a purity of 99.99%, a surface area of $1.3 \text{ m}^2/\text{g}$, with submicron particle sizes. The second, designated Cu-2, had a purity of 99.93%, a surface area of $0.2 \text{ m}^2/\text{g}$, particle sizes of approximately one micron. Both powders were used as the core materials. The submicron copper powders (Cu-1) coated by silver film [21] used in this study were prepared by using a DC arc plasma evaporation method [22]. The micron copper powders (Cu-2) coated by silver film used in this study were prepared by using a water atomization method (Beijing Xingrongyuan Co. Ltd., Beijing, China).

The copper nanopowders were ultrasonically washed with 5% H_2SO_4 for 30 min to remove surface oxide film. The pH value of AgNO_3 solution was adjusted to 11 by ammonia solution. Ethylene diamine tetra acetic acid (EDTA) was added to the AgNO_3 solution to allow adjustment of the deposition speed of Ag. Then, the cleaned copper nanopowders were added to the AgNO_3 solution with magnetic agitation (DF-1, Jiangsu). A solution of sodium hypophosphite (NaH_2PO_2) as reducer was added to the AgNO_3 solution by dropwise addition. Polyvinylpyrrolidone (PVP) was used as a surfactant to prevent metal particles from conglomerating. The mixed solution was heated at $50 \text{ }^\circ\text{C}$ and reduced for 20 min. Silver-coated copper nanopowders were prepared and separated from solution by centrifugation, which were added to another silver complex compound solution. The complex compound solution was fundamentally the same as above and reduced as the same as above. The double-times silver-coated copper powders were obtained and coated by silver again. The selected electroless plating conditions of silver-coated copper powders were obtained as follows, temperature $50 \text{ }^\circ\text{C}$, dosage of EDTA 3 g/L, NaH_2PO_2 20.6 g/L, molar ratio of Ag to Cu 2:1, weight fraction of surfactant PVP 5%. Ag/Cu-1 and Ag/Cu-2 composite powders were prepared by three-times plating the silver film on the Cu-1, Cu-2 powders, respectively. Ag/Cu-1 (surface area: $1.1 \text{ m}^2/\text{g}$, range of particle size) and Ag/Cu-2 (surface area: $0.15 \text{ m}^2/\text{g}$) were used as the core materials.

2.2. ECA preparation

The synthesized silver-coated copper powders were added to the polymer matrix and mixed in an agate mortar. The polymer matrix consisted of epoxy resin, tris(2-hydroxyethyl) amine, defoamer and toluene with weight ratios of 1:0.4:0.05:0.15. Epoxy resin (E51), used as an epoxy binder, was purchased from Nantong Xingchen Trade Co. Ltd. The tris(2-hydroxyethyl) amine, defoamer and toluene were supplied by Qingtian (Jinan) Chemical Technology Co. Ltd. All of the chemicals were used directly without further purification. The ECA could tightly adhere to both hydrophilic and hydrophobic substrate surfaces, such as polyethylene terephthalate (PET), copper, ceramic and glass. The ECAs were screen printed onto the PET substrates with dimensions of 25 mm (diameter) \times 0.2 mm (thicknesses), and cured in air at $150 \text{ }^\circ\text{C}$ for 30 min. The resistivities (ρ) of ECAs were determined using a 4-point probe station system. As can be seen from Fig. 1(a) and (b), the pattern is legible and distinguishable on the PET substrate, demonstrating the printability and versatility of the ECAs (with 60% Ag). The pattern shows a flat state (Fig. 1(a)) and intense curling state (Fig. 1(b)). The results indicate that the ECAs can perform as excellent and robust stretchable electrodes produced by a facile and efficient printing method. The ECAs exhibit good flexibility and electrical conductivity, which can be used as strain sensors. Use of an accelerator (tris(2-hydroxyethyl) amine) in the curing reaction helped in “locking in” the dispersed morphology by reducing the curing reaction time. The chemical reactions derive from five reactive materials and the chemical formula are shown in Fig. 2 as follows: epoxy resin (a), structure forms of epoxy resin (b), tris(2-hydroxyethyl) amine (c), structure forms of tris(2-hydroxyethyl) amine (d) and methyl tetrahydrophthalic anhydride (e). Via the reactions between epoxy resin, tris(2-hydroxyethyl) amine, and methyl tetrahydrophthalic anhydride, a three-dimensional network was formed and the typical epoxy curing reaction schemes are also shown in Fig. 2 as follows: (1-1), (1-2) and (1-3).

2.3. Characterization

Scanning electron microscopy (SEM) and energy disperse spectroscopy (EDS) were used to investigate the surface microstructures of silver-coated copper powders and ECAs. Seven resistivity and tensile strength measurements were made for each sample, and the values were averaged to obtain the resistivity and tensile strength of the fabricated ECAs. Here, the fabrication of ECA thin films and their performance were also made for comparison purpose. Resistivity measurement was performed by using a RTS-8 4-point probe station system (Guangzhou Four-Probe Electronic Technology Limited Liability Co.).

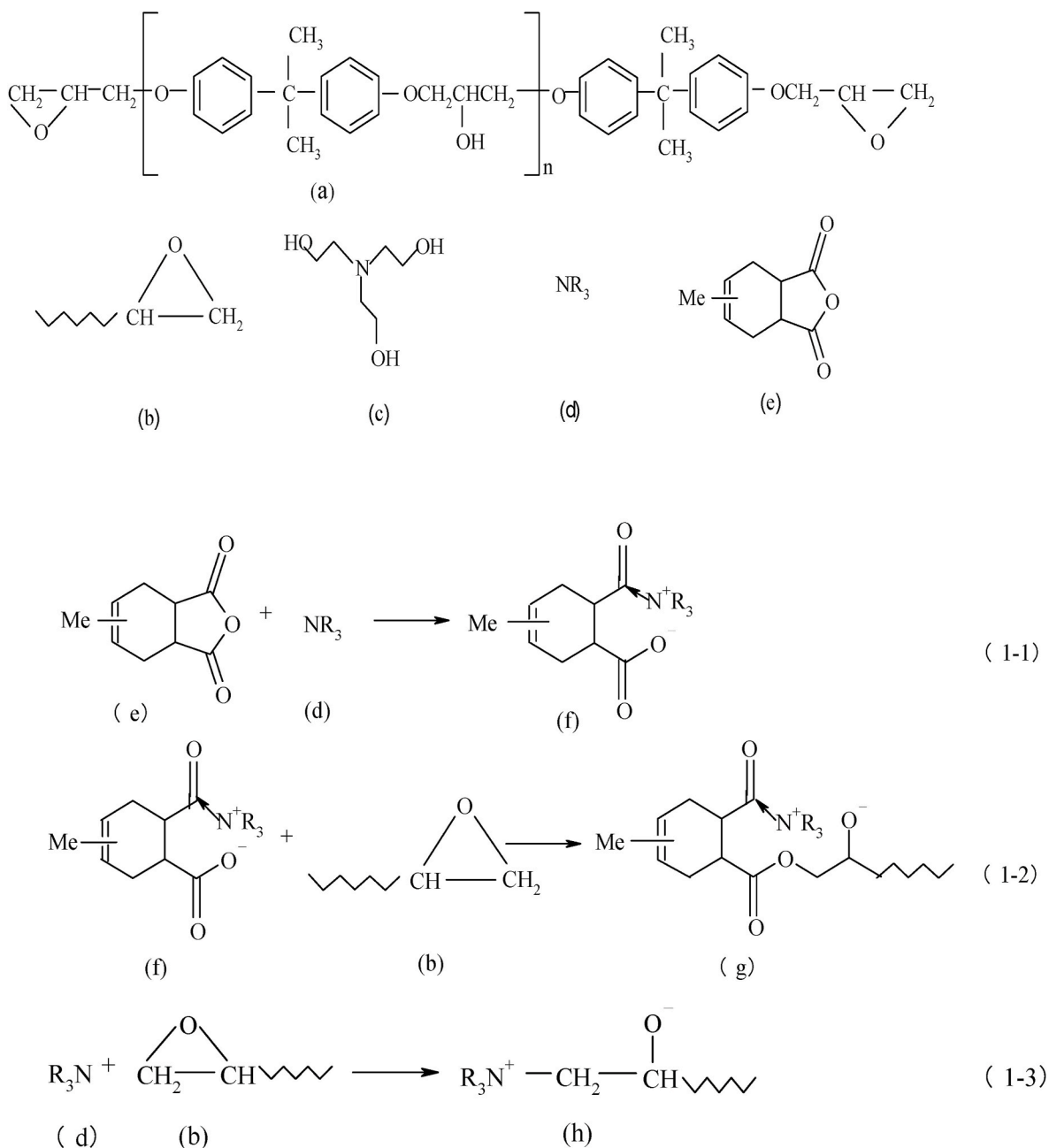


Fig. 2. Typical epoxy-amine curing reaction scheme.

3. Results and discussion

3.1. Microstructure of silver-coated copper powders

Fig. 3 represents the SEM images of central copper powders for Cu-1 (Fig. 3(a)) and Cu-2 (Fig. 3(b)), respectively. The main differences which can be observed are in terms of particle size, Cu-1 possess relatively small particle size values compared with Cu-2. Fig. 3(a) reveals copper powders with a round and smooth microstructure, the overall particle size are $\leq 1 \mu\text{m}$. Fig. 3(b) shows that micron copper powders consisting of particles with an irregular shape with a size range of $50 \mu\text{m}$ – $100 \mu\text{m}$.

Fig. 4 shows SEM images of silver-coated copper powders (a. Ag/Cu-1 synthesized with Cu-1, b. Ag/Cu-2 synthesized with Cu-2). As shown in Fig. 4(a), silver is homogeneously distributed around the spherical copper powders. Silver deposits at the active sites of submicron copper powders and forms a thin silver coating. Fig. 4(b) shows silver deposited

on the surface of the copper with relatively large spherical silver particles. Fig. 4(c) and (d) show results from EDS analysis relating to the images from Fig. 4(a) and (b) respectively conducted to characterise and confirm the oxidation resistant protective effect of the Ag/Cu fillers. Peaks for silver are due to the presence of Cu powders coated with a layer of dense nano-sized Ag particles. Differences can be observed in degrees of surface roughness between the two kinds of silver-coated copper powders in terms of silver films. The surface of Ag/Cu-1 is relatively round compared with that of the Ag/Cu-2 which is rough and uneven. The results show that the submicron copper powders have higher activity than micron copper powders.

The pure copper powders and silver-coated copper nanopowders were calcined at different temperature from 100 to 800 °C for 20 min in a muffle, then their weights were measured again. The oxidation resistance of the silver-coated copper nanopowders were characterized by their increased weight percentage. The weight gain of silver-coated

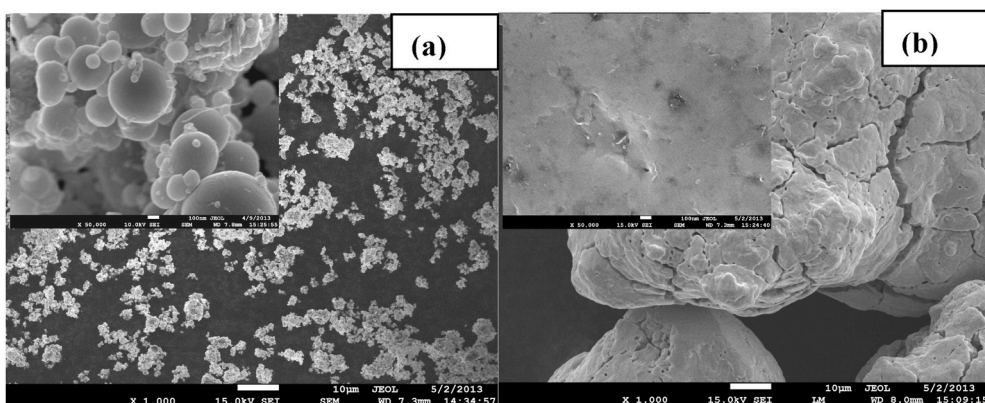


Fig. 3. SEM images of copper powders with different size (a.Cu-1. b.Cu-2).

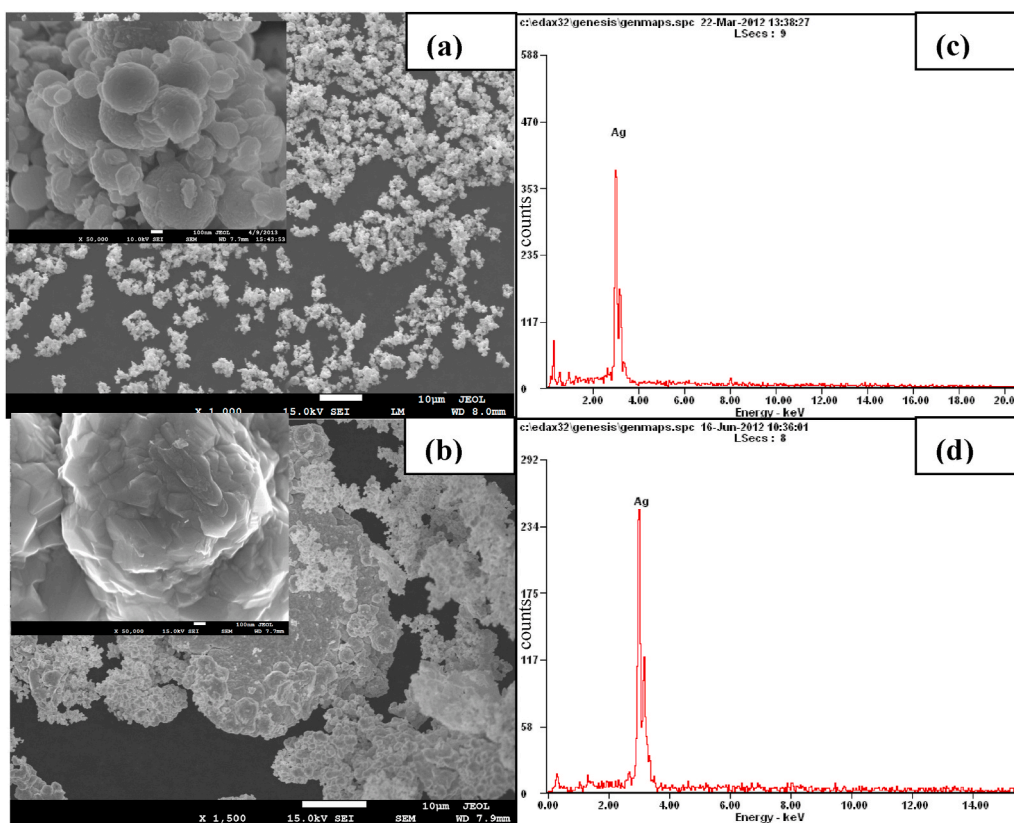


Fig. 4. SEM images and EDS of silver-coated copper powders synthesized with different central copper powders (a,c. Ag/Cu-1; b,d. Ag/Cu-2).

copper nanopowder and pure copper nanopowder calcined at different temperature is shown in Fig. 5. Compared with the copper nanopowders calcined at different temperatures, the significant increase of oxidation resistance of the silver-coated copper nanopowders is apparent.

3.2. Electrical resistivity of the as cured ECAs

Fig. 6 presents the electrical resistivity of ECAs filled and cured with different fillers. Five types of filler (Cu-1, Cu-2, Ag/Cu-1, Ag/Cu-2, Ag/Cu-3) were used in the ECAs as shown in Fig. 6. The Ag/Cu-3 filler was composed of 50% Ag/Cu-1 and 50% Ag/Cu-2. Like most polymers, epoxy resins are electrically nonconductive. The content of the conductive fillers has a significant impact on the conductive performance. The silver-coated copper nanopowders were employed as conductive fillers in the epoxy resin polymer matrix due to its low

price and high electrical conductivity. The ECAs filled with Ag/Cu-3 show relatively low resistivity compared with Ag/Cu-1, Ag/Cu-2, Cu-1 and Cu-2. Fig. 6 shows a well-defined percolation curve where a percolation threshold of 60% can be identified in the form of a sharp decrease in the measured resistivity by several orders of magnitude with an increase in the Ag/Cu concentration. The excellent electrically conductive channels are formed from Ag/Cu-3 by the use of different particle sizes. The figure shows that the percolation threshold of copper powders is 65% and the resistivity is much higher than with the Ag/Cu fillers. The resistivity of the ECAs beyond the percolation region slightly decreases due to the formation of new conductive paths and eventually levels off to values on the order of $10^{-4} \Omega \text{ cm}$. The ECAs using lower contents of spherical silver-coated copper particles as fillers have lower electrical resistivity and higher stability when compared to the commercial products.

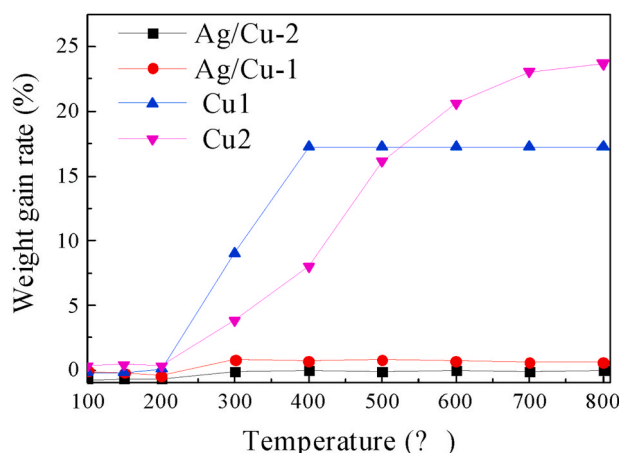


Fig. 5. wt gain of copper nanopowders calcined at different temperatures.

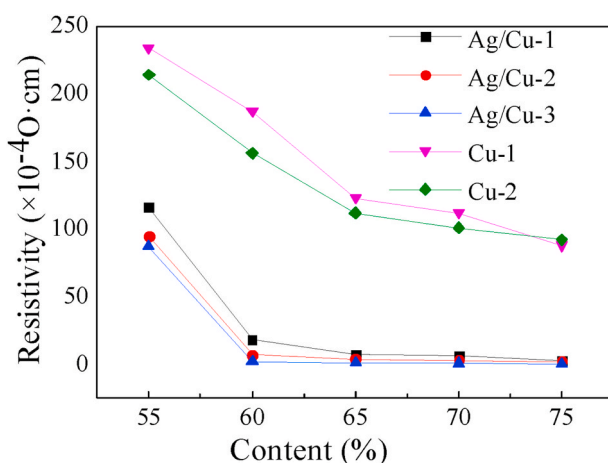


Fig. 6. Electrical resistivity of the as cured ECAs prepared with five different fillers.

3.3. Microstructure of ECAs

In order to research the correlative performance of ECA-1, ECA-2 and ECA-3 filled with Ag/Cu-1, Ag/Cu-2 and Ag/Cu-3, respectively, microstructures were studied by means of SEM and EDS as shown in Fig. 7. With the same proportions (60%) of the three different fillers added into each ECA, larger amounts of the Ag/Cu fillers were found inside the ECA-1, ECA-2 and ECA-3 adhesives.

The research shows that electrically conductive channels are formed with 60% Ag/Cu fillers which are combined together by the bonding effects of the epoxy resin. As shown in Fig. 7(a), some of the Ag/Cu-1 fillers are arranged loose to each other. A similar phenomenon can be observed in Fig. 7(b) where the Ag/Cu-2 fillers are loosely packed inside the polymer matrix. However, as shown in Fig. 7(c), ECA-3 shows a densely packed structure which is clearly different from that observed with ECA-1 and ECA-2. The pore porosity, particle size and particle shape of the fillers could influence the electrical resistivity of the ECAs [15]. ECA-3 exhibits a wide particle size distribution range and a low pore porosity gain at low electrical resistivity. The results indicate that the pore porosity can be affected and adjusted by the particle size distribution.

Fig. 7(d), (e) and (f) show the EDS analysis come from Fig. 7(a), (b) and (c). The composition of the ECA can be analyzed by EDS method. Peaks for silver and copper are due to the Ag/Cu fillers and those related to Pt are due to the coating of the samples with Pt thin film for imaging by SEM. Peaks corresponding to 'Ca', 'Al', 'O', 'C', 'Mg', 'Na' and 'Si' are due to signals from the ceramic substrate.

3.4. Ageing-resistant performance

Fig. 8 presents electrical resistivity data for each ECA during high temperature exposure at 100 °C for 480 h, where it can be observed that the resistivity of ECAs filled with Ag/Cu powders are lower than ECA filled with Cu powders. The resistivity of ECAs filled with Ag/Cu powders increased slowly and stable over 100 h. This indicates that the ECAs prepared by silver-coated copper powders have excellent thermal stability which could withstand high temperature exposure at 100 °C for 480 h.

4. Conclusions

The ECAs were prepared using copper and silver-coated copper powders (Cu-1, Cu-2, Ag/Cu-1, Ag/Cu-2, Ag/Cu-3) as conductive fillers. The electrical conductivity properties of the films were greatly affected by the fillers parameters. ECA-3 filled with Ag/Cu-3 shows a lower electrical resistivity compared to ECA-1 and ECA-2 where an order of magnitude reduction of $10^{-4} \Omega \cdot \text{cm}$ could be achieved. The ECAs using a lower content of spherical silver-coated copper particles as fillers have lower electrical resistivity values when compared to the commercial products. The pore porosity and the range of the particle size of the fillers were considered as the important factors in enhancing electrical conductivity and contact area between the conductive fillers and the polymer matrix.

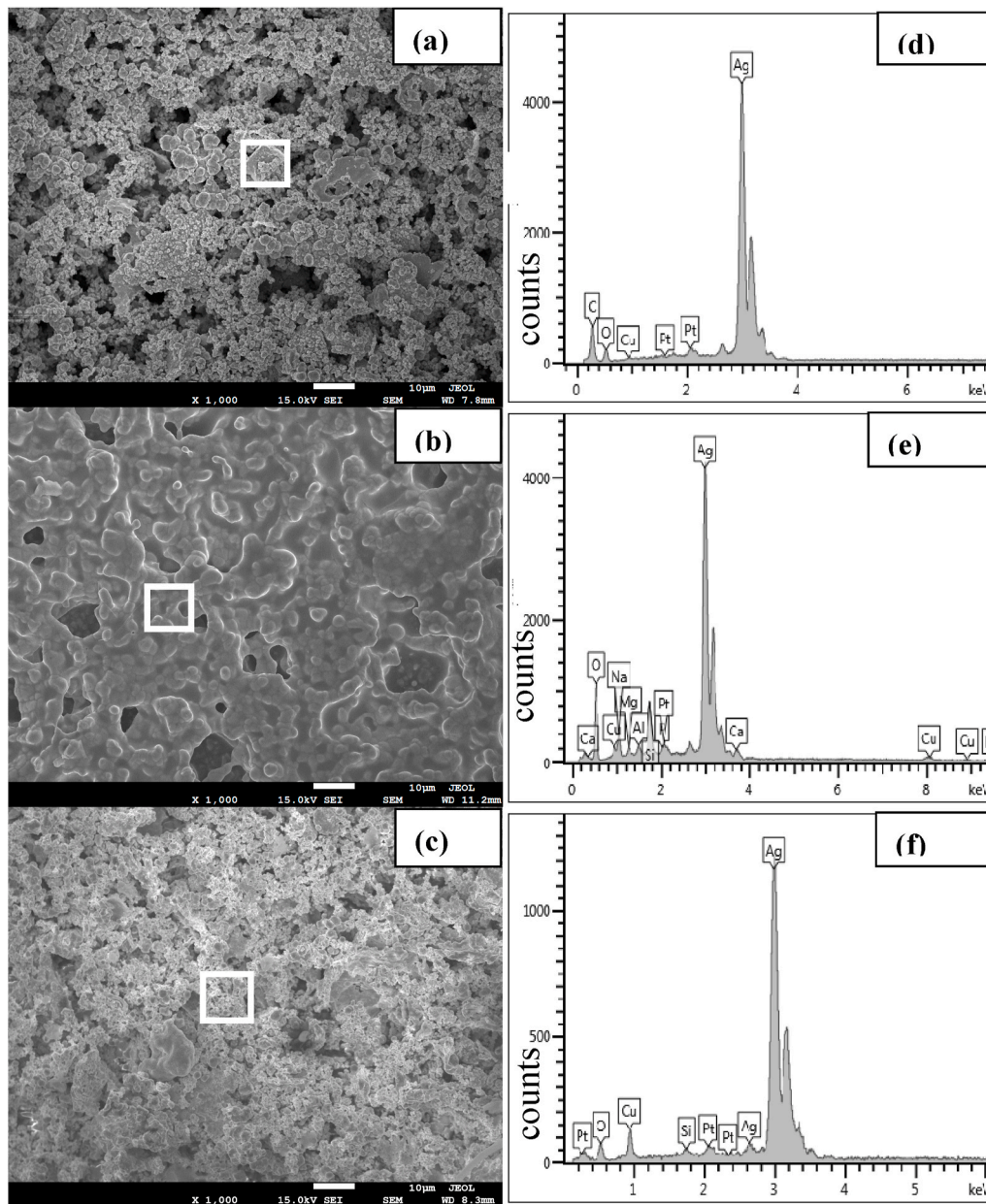


Fig. 7. SEM images and EDS of the ECAs synthesized with different fillers ((a),(d). Fillers-1; (b),(e). Fillers-2; (c),(f). Fillers-3) solidified in air at 150 °C for 30 min.

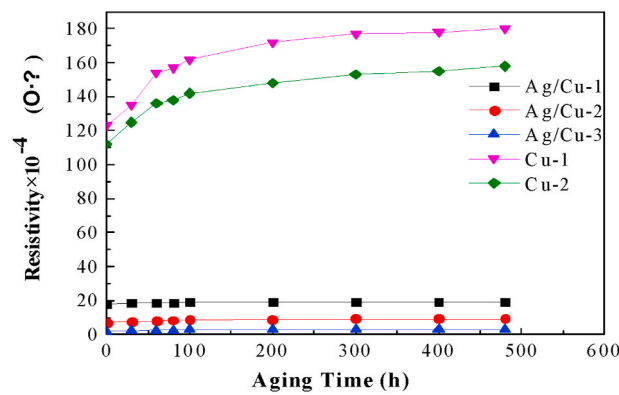


Fig. 8. Electrical resistivity of the ECAs during high temperature exposure at 100 °C for 480 h.

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