Copper Particles/Epoxy Resin Thermosetting Conductive Adhesive Using Polyamide Resin as Curing Agent

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ABSTRACT: Thermosetting conductive adhesive (TCA) comprised of epoxy resin E-51 as matrix, Cu microparticles and nanoparticles modified by silane coupling KH550 as conductive fillers, polyamide resin with low molecular weight as curing agent, and some other additives. It was reported creatively a new liquid curing agent, which solved successfully some difficult problems during preparation of TCA, such as limit of quantity of conductive fillers. Therefore, application of this liquid curing agent decreased greatly the resistivity of TCA under the condition of keeping enough adhesion strength. Antioxidized and mixed Cu particles were developed as conductive fillers in place of expensive Ag. The results showed that optimum conditions of conductive adhesive composed of 16 wt % of epoxy resin E-51, 8 wt % polyamide resin, 65 wt % of Cu microparticles and nanoparticles, 1.3 wt % of silane coupling agent, and 9 wt % of other additives with curing time for 4 h at 60°C. The adhesion strength reached 16.7 MPa and the bulk resistivity was lower than 3.7×10^{-4} Ω cm. The variation of bulk resistivity was less than 15% at high temperature (100°C). © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: epoxy resin; copper particles; conductive adhesive; silane coupling agent; polyamide resin; resistivity

INTRODUCTION

Electronic packaging plays an increasingly important role in electronic industry, such as printed circuit board or interconnecting techniques of chips on substrate, which often restrict the miniaturization of electronic products. Because of the high temperature for curing, Pb/Sn solder was difficult to satisfy the increasing requirements of minielectronic packaging.[1–3] Also, because of the negative effect of Pb on the environment, policies and legislation have been proposed in Europe to limit or ban the use of Pb in solders.[4] Conductive adhesives developed a new prospective way to electrical connection of surface mount device components and printed circuit boards, because of their lower possible curing temperature, higher flexibility, fine pitch capability than thin-Pb solders.[5–7]

Besides environmental issue, conductive adhesives as one of the alternatives to solder also have the following potential advantages: (i) lower sensitivity to thermomechanical stresses, due to higher flexibility than solder; (ii) lower curing temperatures enabling the use of heat sensitive or nonsolderable materials; (iii) high-resolution capability for fine-pitch interconnects due to smaller particle size than solder pastes; and (iv) simple processing if compared with wave soldering.[8–11] The currently available conductive adhesives are mainly made of metal flakes (Ag, Ni and Cu, Ag/Pd) and a polymer matrix (such as epoxy, silicone, or polyeurethane). Normally, high performance conductive adhesives were often designed by combining the thermosetting resin and the efficient electrically conductive fillers.[12] The conductive fillers are not only to consider stability in the matrix but also to form continuous bridge between two electrical terminals.[13,14] Among the various conductive

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particles, the Ag filler has one advantage for improving the conductivity, but it results in a higher cost than that of Cu and carbon black.[15,16] Cu powder is a more common filler for the preparation of conductive adhesives. However, Cu has a limitation due to its tendency to form a nonconductive oxide surface layer.[17] The Cu corrosion prevention has attracted many researchers and numerous possible inhibitors have been investigated. Amongst them, there are many inorganic inhibitors, such as azoles, amines, amino acids, and many others.[18] The reserve stability, antioxidation ability, and electric property of Cu particles modified by coupling agent can be improved remarkably.[19] In comparison with the Ag filler, Cu has also one disadvantage of not low enough electrical resistivity. To improve the antioxidation ability of copper powder, silane coupling KH550 was used as a protective agent, which can cover the surface of the Cu particles to form a hydrophobic film [Fig. 1(a)].[20,21] Nanosized and microsized Cu particles can form the network structure in resin to improve the electrical conductivity [Fig. 1(b)].[22] With the aim of making available of the advantages of both antioxidation ability and electrical resistivity, nanosized and microsized Cu particles modified by silane coupling KH550 was used as conductive fillers in the epoxy-based adhesives.

Curing agents greatly influence the electrical resistivity of epoxy resin composed isotropic conductive adhesive (ICA). The different curing mechanisms were linked to the different resistivity of ICA cured by different agents. Most curing agents were solid substances, such as dicyandiamide (DICY), boron-amine complex (594), and imidazole derivate (MZ), which were used for formulating one-package epoxy-based ICA, frequently.[23] However, this is tantamount to increase the proportion of solid filler, which limited the quantity of metal powder and resulted in the difficulty to mix fully the fillers with epoxy resin. Polyamide resin with low molecular weight as liquid curing agent was used at the first time. The curing of conductive adhesives can be performed by thermal or photo process, currently, thermal process is popular because of its low cost. Thermal curing process has some disadvantages: (1) causes environmental pollution because of organic solvent volatilization during curing and (2) high energy consumption.[24] In our current work, polyamide resin as environmentally friendly curing agent achieved rapidly curing at a lower temperature.

In this work, an ICA with the superior adhesion strength was produced. We report a conductive fillers comprising of the nanosized and microsized Cu particles modified by silane coupling KH550 has superior dispersibility and low electrical resistivity. Methanal as a reductant was added to the epoxy adhesives to improve antioxidation ability of Cu particles. Polyamide resin with low formula weight as curing agent was used, and cured completely at 60°C for 4 h. Then, the electrical properties and thermal stabilities of the conductive adhesives as well as mechanical properties of the adhesive joints were investigated.

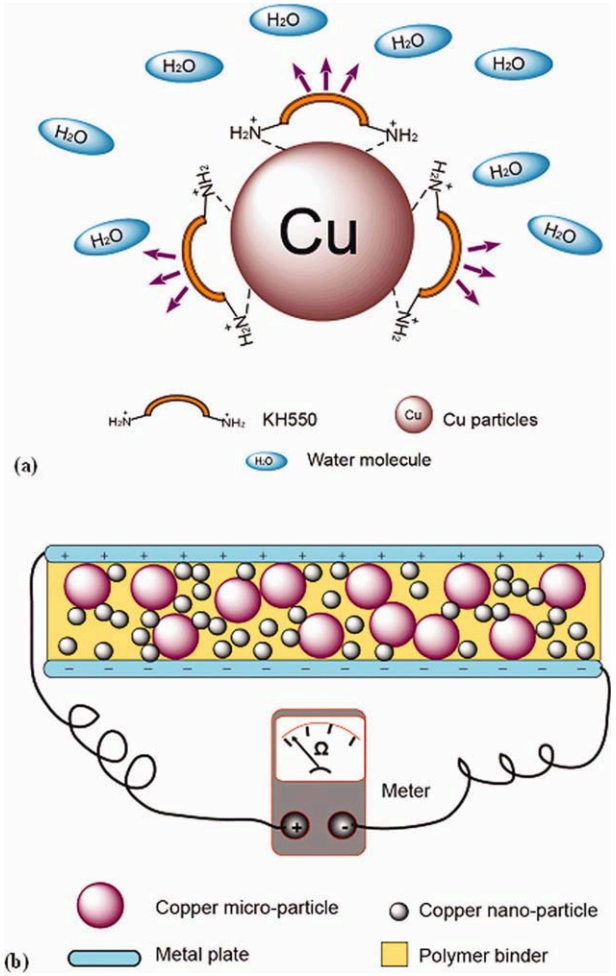

Figure 1 (a) The schematic diagram of copper particle modified by silane coupling KH550. (b) Schematic diagram of electrical conduction of copper microparticles and nanoparticles filled conductive adhesive. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

The matrix adhesive was an E-51-type epoxy resin manufactured by Shanghai Juxing Chemical Company, China. Polyamide resin with low formula weight used in this study was obtained from Tianjin Yanhai Chemical Company, China. Nanosized and microsized (diameters were 100 nm and 70 μm) spherical-Cu particles were purchased from Qinhuangdao Taijihuan Nano Company, which was used as conductive fillers. Before use, the spherical-Cu particles were

modified by silane coupling KH550 (Nanjing Yudeheng Fine Chemical Co.).

Preparation of conductive adhesives

The electrically conductive adhesives comprised of E-51-type epoxy resin matrix, conductive fillers, curing agent, and other additives. The electrically conductive fillers included nanosized and microsized Cu particles. Some mass of Cu particles was put into a beaker filled with 2% silane coupling KH550 and 30 mL ethanol modified in an ultrasonic cell crusher (JY92-11DN, Nanjing Newchen Biotechnology Co.). After drying in vacuum oven (DZF-01, Changzhou Guohua Electric Appliance Co.), Cu particles, oven dried epoxy resin E-51, and formaldehyde were mixed in different ratio. The solution was churned up, and then dispersed by three-roll mill (SG65, Qinhuangdao Manguo Chemical Machinery Co.) for 30 min. To remove bubbles, the mixed solution was deposited in vacuum oven for 10 min. Curing agent was put into epoxy resin in 50% mass ratio, and then fully mixed. Therefore, conductive adhesives would be curing after 4 h at 60°C.

Testing and characterization

The dispersion of Cu particles in conductive adhesives was observed using a scanning electron microscopy (SEM, S-250-III, Cambridge, UK Co.). The modified Cu particles and the curing process of polymeric matrix were traced by Fourier transform infrared spectroscopy (FTIR, 5DX, Nicolet, USA). Samples can be milled with potassium bromide to form a very fine powder. This powder is then compressed into a thin pellet, which can be analyzed for ATR/FTIR. The electrical resistivity of the conductive adhesives was measured by digital four-probe meter (SX1934(SZ-82), Suzhou Telecom Instrument Factory). The single adhesive joints were prepared by bonding Cu sheets. The dimensions of the copper sheets were 1 cm × 1 cm × 0.1 mm. Based on the length of the Cu sheets, the bonded area of each adhesive joint was 1 cm^2. The volume resistivity (ρ_v) was directly obtained by the meter.

The specimen for tensile testing was prepared by overlapping two Al plates, with dimensions of 60 mm × 20 mm × 3 mm, bonded with the electrically conductive adhesives. The strength of the specimen was measured using electronic tensile machine (CMT4104, Shenzhen SANS Measurement Technology). With the change of temperature and frequency, alternating current electrical resistivity was observed by impedance analyzer (Agilent 4294A). The thermal properties of the conductive adhesive were investigated using thermogravimetric analysis (TGA, PCT-1A, Beijing Optical Instrument Factory) with a heating rate of 10 K/min in the range from 30°C to 400°C.

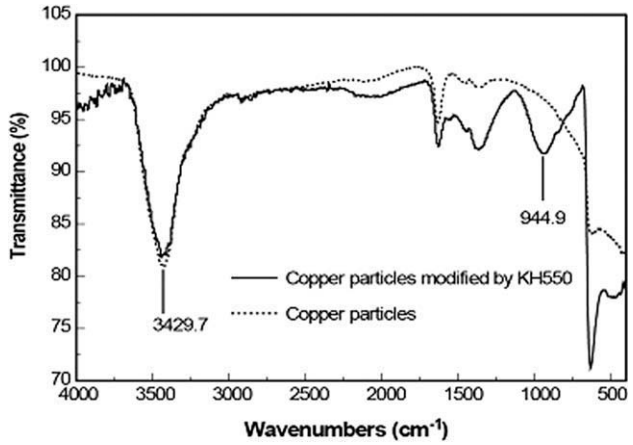

Figure 2 FTIR spectra of copper powder before and after modified by silane coupling KH550.

RESULTS AND DISCUSSION

Surface modification and dispersion of Cu particles

To investigate Cu particles modified by silane coupling KH550, FTIR was used to analyze the variation of functional group of KH550. Figure 2 shows the FTIR spectra of Cu particles before and after modified by silane coupling KH550 ($m_{KH550} : m_{Cu} = 2 : 100$) in the wavenumber range of 500–4000 cm^{-1}. It was clearly indicated that there was a strong adsorption band in the range of 800–1100 cm^{-1} appeared in the spectrum of Cu particles modified by KH550, which was probably attributed to the siloxane (Si—O—Si) asymmetric stretch mode.[25,26] When compared with the Cu particles modified by KH550, the intensity of characteristic absorption band between 3420 cm^{-1} and 3480 cm^{-1} (the O—H stretching mode) was slightly weaker, which was due to hydrolysis of Si—(OR)3 of silane coupling KH550 reacted with the adsorbed water on the surface of Cu particles.[27] This hydrolysis of Si—$(OR)_3$ produced some hydroxyl and was not complete. Anyway, we can find that Cu particles have successfully been modified by silane coupling KH550.

Figure 3 shows the SEM image of the conductive adhesives in which the mass ratio of Cu particles is 65%. Figure 3(b,d) indicated that the Cu particles modified by silane had a very good dispersion without forming aggregation. Figure 3(a,c) showed that micron Cu particles were randomly embedded in epoxy resin, and there were many interspaces between the Cu particles. Although, the Cu nanoparticles were right filled in those interspaces and integrated micron Cu particles to form the network structure in resin, which greatly increased the resistivity of conductive adhesives.

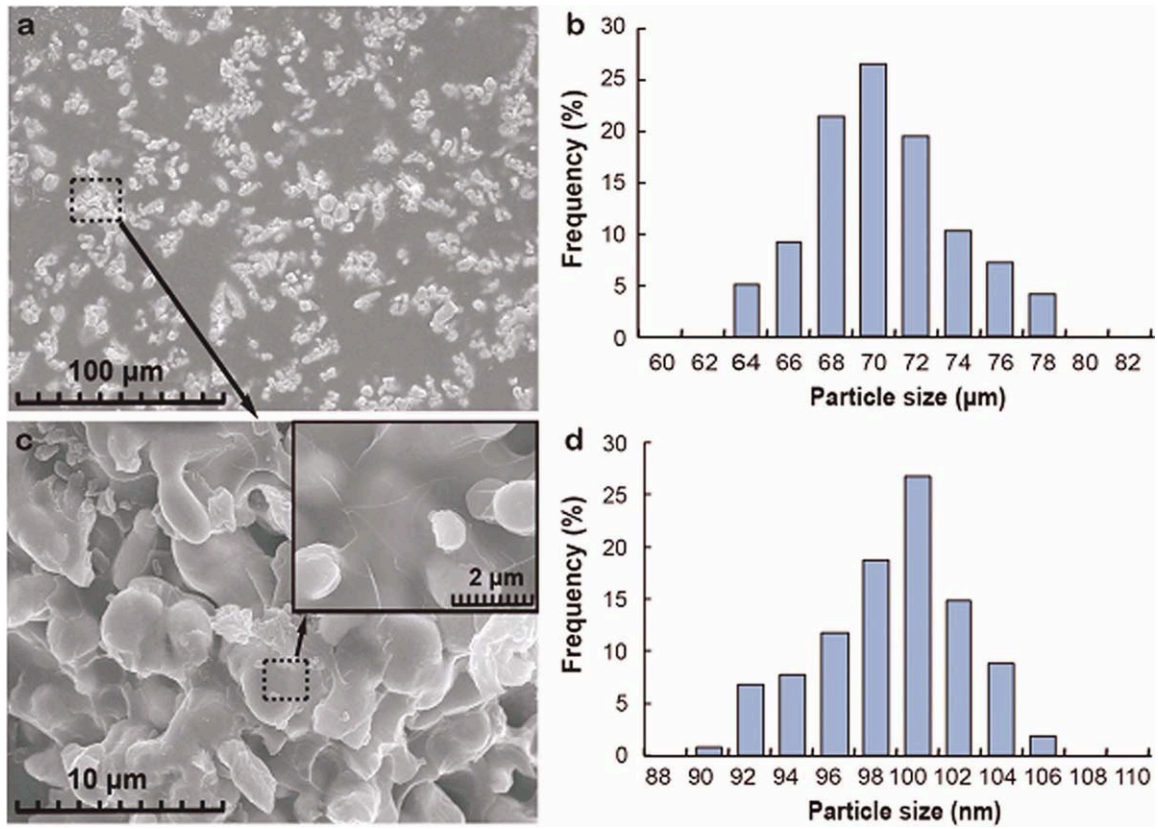

Figure 3 (a) SEM image of copper microparticles and nanoparticles in epoxy resin; (c) SEM image of copper microparticles and nanoparticles as marked by a black frame shown in panel (a); The size distributions of micron-sized (b) and nanosized (d) copper particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The curing process of polymeric matrix

We used FTIR to follow the curing process. Figure 4 showed the FTIR spectra of epoxy resin before and after curing in the wavenumber range of 550–4000 cm^{-1}. The strength for adsorption band at 915 cm^{-1} of epoxy substrates pronouncedly decreased, due to the consumption of epoxy substrates.[21,26,28,29] When the quality of curing agent (polyamide resin) was the half of the one of epoxy resin ($m_{E\text{-}51} : m_{PA} = 2 : 1$), conductive adhesive was just completely cured according to the intensity of the adsorption band at 915 cm^{-1}. The corresponding peak almost vanished after curing at 60°C for 4 h, indicating that epoxy resin had cured. Based on the analyses above, it was concluded that the conductive adhesive could be cured completely at 60°C for 4 h, and thus belonged to rapid curing adhesives at lower temperature.

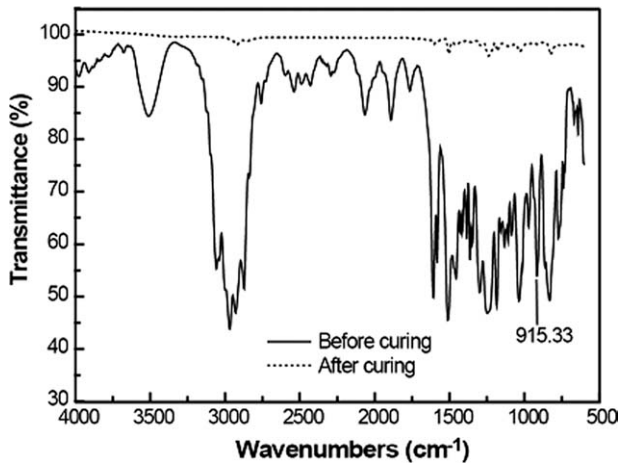

Figure 4 FTIR spectra of epoxy adhesives before and after curing.

Electrical characteristics

To investigate the effect of silane coupling KH550 on Cu particles and the long-term stability of bulk resistivity, the change of bulk resistivity during 100°C exposure is shown in Figure 5. The aging temperature is maintained at 100°C up to 1000 h. The bulk resistivity of conductivity adhesive filled by bare Cu particles was increased rapidly. This may be attributed to the severe oxidation at the surface of Cu particles, which leads to increased resistivity. However, Cu particles modified by silane coupling KH550 were filled in conductivity adhesive, the bulk resistivity was stabilized for 1000 h in high temperature.

The dependence of electrical resistivity of conductive adhesive was shown in Figure 6. The concentration of the filler, when internal conductive network

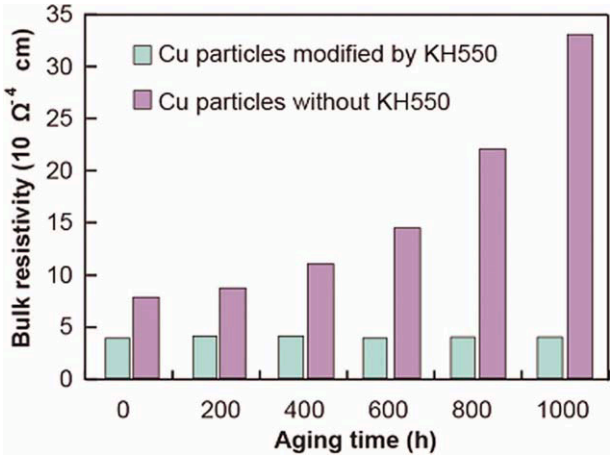

Figure 5 Bulk resistivity shift of conductive adhesive with copper powder and copper powder modified by silane coupling KH550 as conductive filler during 100°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of particles was formed within the polymeric matrix and the material becomes electroconductive, is called percolation concentration.[22] A number of factors had been identified as being important for the formation of conductive networks in the filled polymers. In this study, we researched the relationship between electrical resistivity and the weight fraction of conductive fillers to find the percolation concentration in the Cu particles/epoxy resin filled conductive adhesive. The data in Figure 6 were the average value of three samples for each formulation. The bulk resistivity of conductive adhesives decreased slowly as the Cu particles content increases, and it decreased sharply when the Cu particles in the whole system is 50–60 wt %, then the decreasing trend becomes slow again with increasing Cu particles content. When the Cu particles content was 60 wt %, the bulk resistivity of conductive adhesive could be

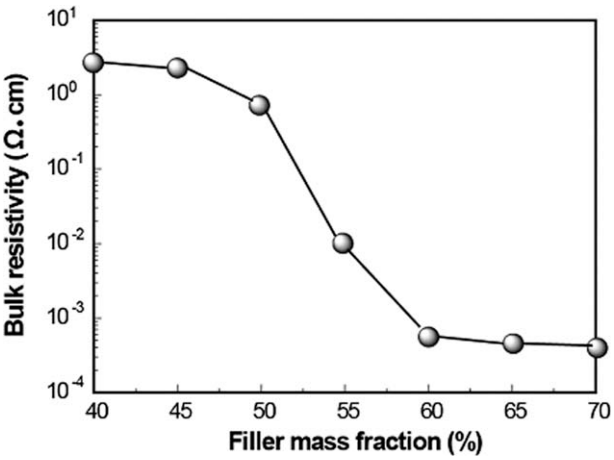

Figure 6 Relationship between the resistivity and the content of conductive filler.

TABLE I
The Tension and the Bulk Resistivity of Conductive Adhesive

No.	Conductive filler content (wt %)	m_m/m_n	Bulk Resistivity (10^{-4} Ω cm)	Tensile strength (MPa)
1	60	3/7	5.1	18.9
2	60	5/5	4.2	18.0
3	60	7/3	4.5	17.6
4	65	3/7	3.9	17.3
5	65	5/5	3.7	16.7
6	65	7/3	4.1	16.3
7	70	3/7	3.2	16.0
8	70	5/5	3.0	15.8
9	70	7/3	3.1	15.6

m_m/m_n is the mass ratio of Cu microparticles and nanoparticles.

4.2×10^{-4} Ω cm. When the Cu particles in conductive adhesive reached to some content, they could interconnect and form conductive channels, and therefore, the bulk resistivity was very low.

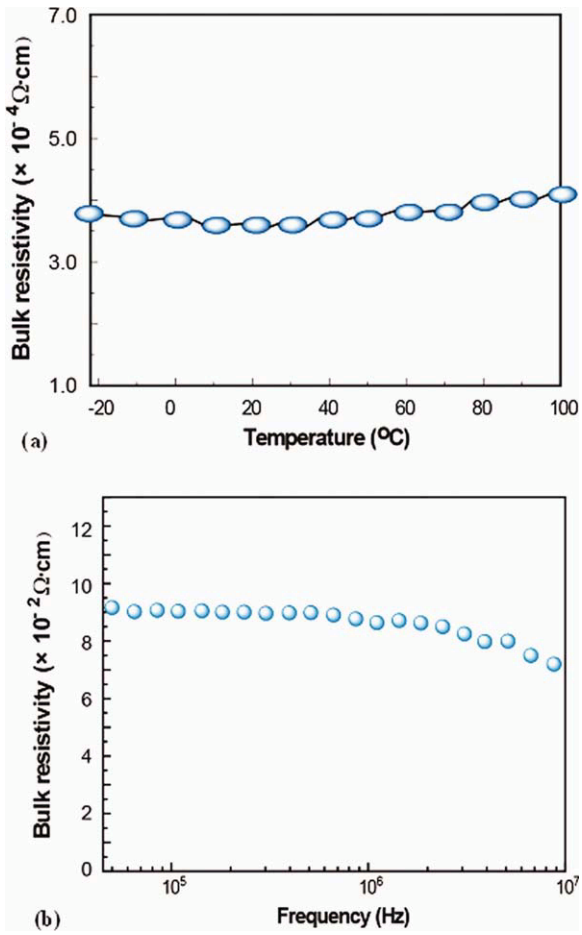

Figure 7 The curve of electrical resistivity with the change of temperature (a) and frequency (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

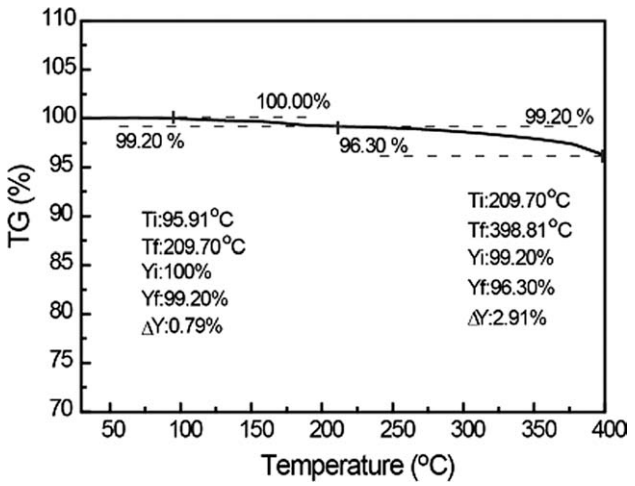

Figure 8 The TGA spectra of copper powder filled conductive adhesive.

Mechanical property

Adhesive joint for mechanical properties detection was obtained by bonding two Al plates with Cu particles filled conductive adhesive. The data of the tension in different conductive filler content (C) in the whole concentration and the mass ratio ($m_m : m_n$) of Cu microparticles and nanoparticles was shown in Table I. Considering the tension and bulk resistivity, we chose 65 wt % as filler content and 1 : 1 as the mass ratio of Cu microparticles and nanoparticles. At this point, the tension and the bulk resistivity were 16.7 MPa and 3.7×10^{-4} Ω cm, respectively.

Thermal property

In practice, conductive adhesive may be used in the conditions of high temperature or high frequency. To prove that conductive adhesive can still maintain good performance, electrical resistivity was investigated with the change of temperature from −20°C to 100°C and frequency from 10^2 to 10^7 Hz. The results were shown in Figure 7. Clearly, by heating the conductive adhesive after curing to a higher temperature, the resistivity increased slightly. The ratio of variation in resistivity was orders of magnitude smaller than 20% [Fig. 7(a)]. However, the effect of frequency on resistivity was greater than the one of temperature. When the frequency reached 10^6 Hz, the resistivity was decreased by 25% [Fig. 7(b)]. Overall, the resistivity affected by these two factors was relatively weak, which had been met the practical application.

TGA is the most favored technique for rapid evaluations in comparing and ranking the thermal stability of various polymer composites. In this study, TGA was used to test thermal stability of Cu particles filled conductive adhesives after curing.[30] The TG thermogram was shown in Figure 8, it was divided into two stages of thermal decomposition. The weight of conductive adhesive began to decrease slightly from 95 to 209.7°C, which was the first phase of thermal decomposition. It was mainly due to the water loss. The temperature of weight loss in the range of 209.70–398.81°C was the second phase. The weight loss was 2.91%, which was attributed to

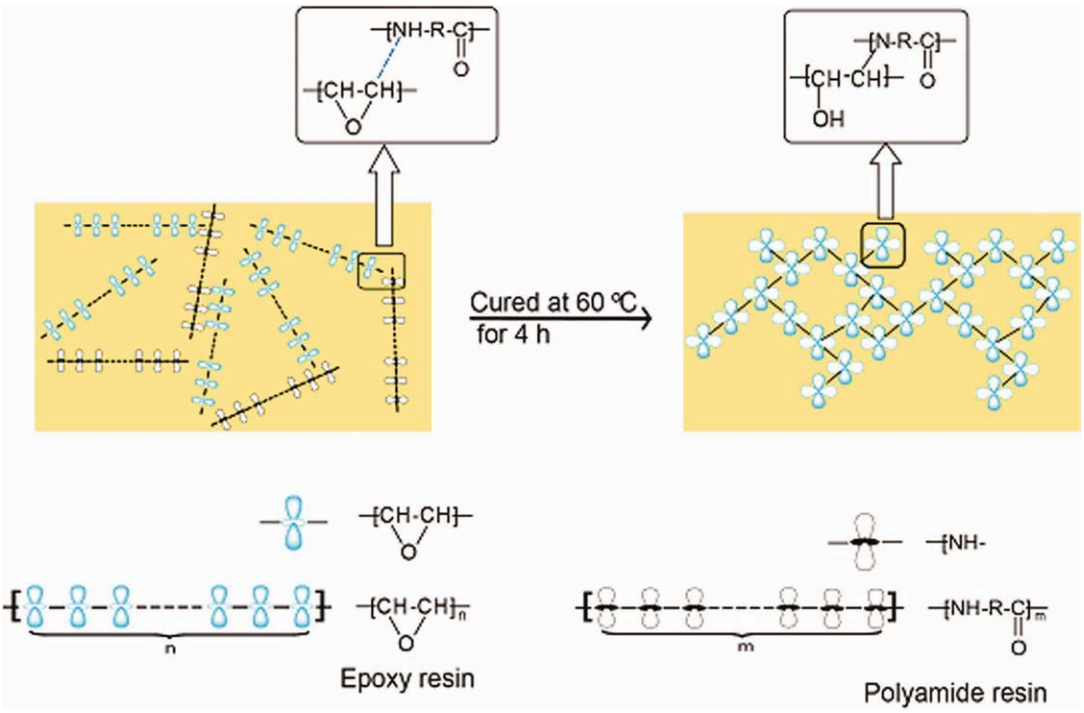

Figure 9 The curing mechanism of epoxy resin and polyamide resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the thermal decomposition of a small amount of polymer. The above results showed that the Cu particles filled conductive adhesive displayed the high thermal stability and can be used in the current electronics industry.

Curing mechanism

Polyamide resin can reacted with epoxy resin, at 60°C, and form cured epoxy resin. The curing mechanism was shown in Figure 9. Both polyamide resin and epoxy resin are long-chain polymers, the secondary amine in a monomer of polyamide resin can make nucleophilic attack to the carbon atoms of epoxy rings in a monomer of epoxy resin. The secondary amine would form a tertiary amine after the reaction, and the etherification of a hydroxyl group with epoxy may occur. As a result, a crosslinked polymer network is generated between epoxy and secondary amine.[31]

CONCLUSIONS

The low-cost conductive adhesive was prepared with antioxidized Cu particles. The nanosized and microsized Cu particles modified by silane coupling KH550 exhibited excellent antioxidation ability. Polyamide resin of low formula weight as curing agent was used to improve the content of Cu particles and further decrease the resistivity. According to testing, the optimal ratio of the main composition was determined. High-performance conductive adhesive was obtained, which could be cured completely at 60°C for 4 h. The electrical resistivity of the conductive adhesive decreased to 3.7×10^{-4} Ω cm and the tensile lap strength remained at a high level (about 16.7 MPa). The change rates of bulk resistivity were less than 15% at high temperature (100°C).

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