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Electrical and mechanical properties of electrically conductive adhesives from epoxy, micro-silver flakes, and nano-hexagonal boron nitride particles after humid and thermal aging

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ABSTRACT

In this study, we incorporated micro-silver flakes and nano-hexagonal boron nitride (BN) particles into a matrix resin to prepare electrically conductive adhesives (ECAs). The humid and thermal aging results under a constant relative humidity level of 85% at 85 °C revealed that the aged ECAs containing 3 wt% of nano-hexagonal BN particles had high reliability. The contact resistance was low and the shear strength high. Nano-hexagonal BN particles have a good effect on the reliability of ECAs that can be used to improve the properties of ECAs.

1. Introduction

As an environment friendly alternative to lead bearing solders, electrically conductive adhesives (ECAs) have many advantages, such as few processing steps to reduce fluxing and cleaning of the components to lower the processing cost, low processing temperatures to enable the use of heat-sensitive and low cost components and substrates, fine pitch interconnection capability, etc. [1–8]. However, compared to the mature soldering technology, ECAs still have some shortcomings—relatively low conductivity, unstable contact resistance, and relatively bad reliability—that limit the application fields to a certain extent [9–13]. In addition, the reliability is very important to the electronic products, which require that the electronic packaging materials have good electrical, mechanical, and thermal properties [14–24]. In humid and thermal surroundings, the electrochemical corrosion at the contact interface caused by the water gain of polymer matrixes, the internal hydrolysis of colloids themselves, the stress concentration caused by the surrounding changes, the delamination between devices, etc., all are likely to increase the electrical resistance and reduce the bonding strength, and thus cause the failure of electronic devices [14–24]. Therefore, the reliability of ECAs in the humid and thermal surroundings has been a hot research focus all the time. In this study, the electrical and mechanical properties of ECAs after a humid and thermal aging were investigated.

In our previous studies, a matrix resin composite of a functional epoxy, a reactive diluent, a silane coupling agent, and a curing agent was fixed, and a formulation of ECAs containing 25 wt% of matrix resin and 75 wt% electrically conductive fillers was optimized. These ECAs were cured completely at 150 °C for 30 min, had a high pyrolysis temperature above 350 °C and a high glass transition temperature at 180 °C [25–28]. In addition, some high performance uni-modal, bi-modal, tri-modal, flexible, and fast curing ECAs were also developed from the matrix resin, micro-silver flakes, micro-silver spheres, nano-silver spheres, and carbon nanotubes [29–34]. In this study, the matrix resin and the formulation described above were still used. We then incorporated micro-silver flakes and nano-hexagonal boron nitride (BN) particles into the matrix resin to prepare ECAs, the electrical and mechanical properties of which we investigated under a constant relative humidity level of 85% at 85 °C (85 °C and 85% RH) for 500 h.

2. Experiment

2.1. Samples

ECAs were a composite of matrix resin, micro-silver flakes, and nano-boron nitride particles. The matrix resin contained a functional epoxy (N, N-diglycidyl-4-glycidyloxyaniline, Sigma-Aldrich, MO, USA) as the main resin, a reactive diluent (2-ethylhexyl glycidyl ether, Sigma-Aldrich, MO, USA), a silane coupling agent

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Table 1
Design of ECAs and ECA-BN samples.

	Matrix resin (wt%)	Micro-silver flakes (wt%)	Nano-hexagonal BN (wt%)
ECA	25	75	–
ECA-BN-A	24.5	75	0.5
ECA-BN-B	23.5	75	1.5
ECA-BN-C	22.5	75	2.5
ECA-BN-D	22	75	3
ECA-BN-E	20	75	5

(3-glycidoxypropyltrimethoxysilane, Sigma-Aldrich, MO, USA), and a curing agent (1-cyanoethyl-2-ethyl-4-methylimidazole, Shikoku Chemicals, Chiba, Japan). Their ratios were 75 wt%, 23 wt%, 1 wt%, and 1 wt% respectively in the matrix resin. The size of the micro-silver flakes was 4–8 μm and the thickness was 0.5 μm (Silcoat AgC-A, Fukuda Metal Foil & Powder, Kyoto, Japan). The size of the nano-hexagonal BN particles was less than 100 nm (CWnano, Shanghai, China). As Table 1 shows, the micro-silver flakes were fixed at 75 wt%, the matrix resin at 20–25 wt%, and the nano-hexagonal BN particles at 0–5 wt%. To fabricate these ECAs, the matrix resin was prepared first: the functional epoxy, reactive diluent, silane coupling agent, and curing agent were mixed together using a 78-1 magnetic mixer (Lantian, Hangzhou, China) until they became homogeneous; then the micro-silver flakes and nano-hexagonal BN particles were incorporated into the matrix resin using a MIX500D SLOPE solder cream mixer (Smtech, Shenzhen, China) with a speed of 3000–4000 rpm and a time of 10–20 min. After the fabrication, the obtained ECAs (Table 1, Fig. S1) were stored at −20 °C. For testing, they were taken out to room temperature, thawed for about 30 min, and stirred strongly for about 5–10 min to make sure the fillers were distributed more evenly.

2.2. Characterization

The humid and thermal aging of samples was conducted using a MCU-800 constant temperature and humidity experimental box (Minch Technology, Taiwan) at 85 °C and 85% RH for 500 h. This equipment adopts the surface evaporative humidification and stainless steel cooling-heating systems to control the temperature and humidity. To obtain the contact resistance, the samples were prepared according to Fig. S2(a). A FR-4 printed circuit board (PCB) had a metal coating of Au/Ni/Cu on the lap-joints and the Cu coating contacted with ECAs; the 1206 chip resistor had a surface metal coating of Ag/Ni/Sn and the Sn coating contacted with ECAs (Fig. S2 (b)). After aging at 85 °C and 85% RH, the contact resistance of samples was obtained using a Hewlett & Packard HP-34401A (HP, CA, USA) to measure the voltage (U) and an Agilent E3631A Triple Output DC Power Supply (HP, CA, USA) to measure the supply current (I). Each test point was repeated 50 times. To obtain the shear strength, the samples were prepared according to Fig. S3(a). Another FR-4 PCB substrate (50 mm × 8 mm × 2 mm) with a metal coating of Au/Ni/Cu on the lap-joints was used. The ECAs were printed on the lap-joints using a mask. The thickness of cured ECAs was about 0.1 mm. After aging at 85 °C and 85% RH, the shear strength of samples was obtained using an Instron 5548 Microtester (Instron, MA, USA) at a tensile rate of 5 mm min^{-1} (Fig. S3(b)). Five samples were tested for each value. The shear strength (σ, MPa) was calculated by

$$\sigma = \frac{F}{BD}$$

where σ (MPa) is the shear strength, F (N) is the maximum load, and B (mm) and D (mm) are the length and width of fracture region respectively. The water absorption of samples was obtained at 85 °C and 85% RH. The ECAs were printed onto an aluminum foil using a mask. The thickness of the mask was 0.1 mm and the size of the mask holes was 2 mm × 2 mm. Five samples were tested for each value. The water absorption (φ, %) was calculated by

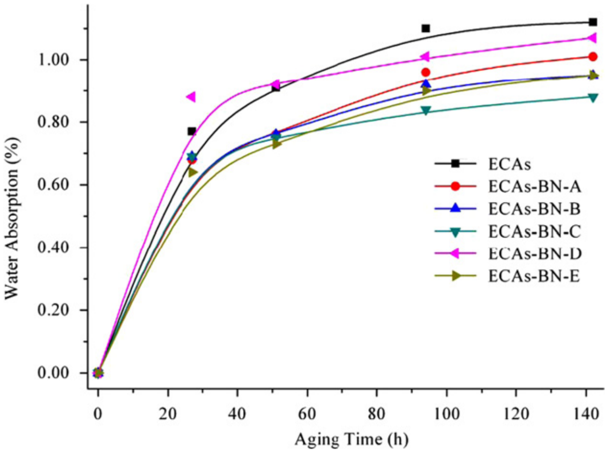

Fig. 1. Water absorption of ECAs and ECA-BN vs aging time.

$$\varphi = \frac{m_t - m_0}{m_0} \times 100$$

where m_0 (g) is the weight of samples before aging and m_t (g) is the weight of samples that absorbed water. The separation and delamination of samples was observed using a PVA TePla SAM400 Quad (QUESTAR, Guangzhou, China).

3. Results and discussion

During the humid and thermal aging, ECAs absorbed water vapor, which gathered on the surface of ECAs firstly, and then penetrated, diffused in ECAs, and saturated eventually, as the aging time increased. There were three factors influencing the water absorption. Firstly, the hydrophilic matrix resin of ECAs increased the water absorption. Secondly, the nano-hexagonal BN particles had a good dispersion in water showing their hydrophilicity [35–38], which increased the water absorption also. Finally, there were voids and gaps in the cured ECAs because of the incorporation of micro-silver flakes, which were helpful for the penetration and diffusion of water vapor in ECAs, while the incorporated nano-hexagonal BN particles filled and occupied some of them to delay and reduce this penetration and diffusion that coincided well with the dual mode sorption theory [39–43]. As Fig. 1 shows, the water absorption increased sharply from 0 h to 40 h, showing that the water vapor penetrated and diffused quickly in ECAs during the initial 40 h [29,44,45]. Thereafter, as the aging time lengthened from 40 h to 130 h, the water vapor continued to penetrate and diffuse in ECAs slowly, leading to saturation eventually.

As described above, the hydrophilic matrix resin, hydrophilic nano-hexagonal BN particles, and the voids and gaps in cured ECAs caused the water absorption mainly. As the nano-hexagonal BN particles increased from 0 wt% (normal ECAs) to 2.5 wt% (ECA-BN-C), the matrix resin decreased and some voids and gaps were filled and occupied, which both combined together to decrease the water absorption; increasing nano-hexagonal BN particles increased the water absorption. However, the decrement had a more significant effect than the increment, so the water absorption decreased from normal ECAs to ECA-BN-C, as shown in Fig. 1. As the nano-hexagonal BN particles increased to 3 wt% (ECA-BN-D), the decreasing matrix resin continued to decrease the water absorption and the