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Effect of epoxy and filler concentrations on curing behaviour of isotropic conductive adhesives

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Abstract Isotropic conductive adhesives (ICAs) are considered as the most promising replacement to lead-based solders due to relatively low melting point, simple processing and fine pitch capability. The study reports on the effect of volume fractions of silver flakes and particles on the curing reaction of ICAs. In addition, the thermal behavior of ICAs formulated with two types of polymeric adhesives: diglycidylether of bisphenol-A (DGEBA) and polyurethane (PU) was also investigated in this work. The increase in silver flakes concentration seem to reduce the melting temperature of the DEGBA and PU-based ICAs, which could be due to retardation of cross-linking of polymers due to silver flakes acting as barrier within the polymer matrix. In addition, the formulation of ICAs containing silver flakes and particles yielded a much higher reaction compared to conventional ICAs. The study showed that use of polyurethane (PU) as opposed to conventional Diglycidylether of bisphenol-A (DGEBA) showed a more stable system.

Keywords Isotropic conductive adhesives · Silver flakes · Differential scanning calorimetry · Nano-particles · Epoxy

Introduction

In recent years, extensive studies have been conducted for conductive adhesives in various areas such as joint reliability testing [1, 2], electrical properties and microstructure development [3] and joint residual stress analysis [4]. Electrically conductive adhesives consist of a polymer binder that provides mechanical strength and conductive fillers, which offer electrical conduction. Polymers are commonly classified as either thermosets (such as epoxies, polyimides, silicones, and acrylic adhesives) or thermoplastics. ICA formulations usually include epoxy resin as the polymer matrix due to their outstanding mechanical and thermal properties as well as processability. In addition, the epoxy resins have good resistance to moisture, solvents and chemical attacks [5]. More recently, a new class conductive adhesive, which is based on polyurethane (PU) materials have been developed [6]. The study has shown that the conductive adhesives have the properties of the polyurethane materials such as good adhesion and high toughness.

Silver (Ag) is the most commonly used conductive filler for isotropic conductive adhesives (ICAs) because of its high electrical conductivity, chemical stability and lower cost compared to other filler materials [6]. Unlike many other metals such as copper, that become non-conductive after being oxidised due to exposure to heat and humidity, silver oxides also show high conductivity. The silver fillers are typically fabricated into flakes and pretreated with organic lubricants to ensure the proper rheology of the ICAs [7, 8]. In addition, a mixture of silver flakes and particles with broad size distribution can offer improved conductance over narrow size distribution [9]. Flakes can provide improved conductivity by allowing the flake-like particles to overlap one another. On the other hand, the voids caused by the overlapping can be filled with the small particles. Other silver systems were also developed to improve the performances of silver-based conductive adhesives. Highly porous Ag was used as filler material for ICAs and researchers illustrated that the thermo-mechanical properties of the

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adhesives using porous Ag were improved because of the infiltration of the resin into the pores [10].

The physical, electrical and mechanical properties of conductive adhesives depend to a large extent on the degree of cure of the epoxy composition in the conductive adhesives. Most of the researchers concluded that a minimum degree of curing was needed to provide a certain level of mechanical and electrical performance in the adhesive joint. Below the critical degree of curing, the electrical resistance of the adhesive joint increased significantly due to absorption of a significant amount of moisture which in turn caused oxidation/hydration at the adhesive/substrate interface. In addition, below the critical degree of curing, the shear strength of the adhesive joint was found to be very poor compared with that of the adhesive joint which was cured above the critical degree of curing [9, 10].

This study reports the curing reaction of DGEBA epoxy and polyurethane (PU) base ICAs paste. In addition, the effect of silver flakes and particles into cure kinetics of the adhesives is also studied.

Experimental

Instrumental

DSC tests measurements were carried out with a Mettler Toledo DSC 823e calorimetry. Dynamic analyses at 10 °C/min heating rate in the temperature range from 25 to 300 °C under nitrogen purge gas (50 mL/min) were performed. The experiments were conducted under a nitrogen atmosphere in order to eliminate oxide formation during the process. The temperature is divided into three cycles: 25–300 °C, 300–25 °C and 25–300 °C, respectively. Small sample quantities were used (<5 mg). The samples were loaded in aluminium pans.

Formulation of isotropic conductive adhesives

Table 1 show the chemicals used in the formulation of ICAs, which was purchased from Sigma-Aldrich. The DGEBA/PU and silver particles/flakes were mixed according to the ratios shown in Table 2. Usually, the filler contents are determined by weight percentage. For example, for the formulation volume fraction of 0.2, 20% of metal filler (silver particle) is mixed with 80% diglycidylether of bisphenol-A.

Results and discussion

Characterisation of silver flakes and particles

An X-ray diffraction test was carried out on the silver flakes and particle; the phases in Fig. 1 show the existence of Ag only. Thus, it confirmed that the material is pure silver. The silver flakes/particle size were measured under scanning electronic microscope (SEM), where the silver flakes with a diameter approximately 5–10 μm and silver particles with a particle size ~200–250 μm.

Table 1 Chemicals used in the preparation of ICAs

Chemical functions	Chemicals
Resin	Diglycidylether of bisphenol-A (DGEBA) and polyurethane (PU)
Curing agents	Ethylene diamine
Fillers	Silver flakes and silver particles

Table 2 System investigated with different volume fractions of silver flakes, particles, DGEBA and PU

System	Parameters
S1	0.8-silver flakes/0.2-DGEBA
S2	0.6-silver flakes/0.4-DGEBA
S3	0.4-silver flakes/0.6-DGEBA
S4	0.2-silver flakes/0.8-DGEBA
S5	0.8-silver flakes/0.2-PU
S6	0.6-silver flakes/0.4-PU
S7	0.4-silver flakes/0.6-PU
S8	0.2-silver flakes/0.8-PU
S9	0.8-silver powder/0.2-DGEBA
S10	0.8-silver flakes + powder/0.2-DGEBA
S11	0.8-silver powder/0.2-PU
S12	0.8-silver flakes + powder/0.2-PU

Investigation of the curing process of silver-filled ICAs

As shown in Fig. 2, there is an exothermic peak observed before an endothermic trough. This observation suggested that crystallisation of epoxy, diglycidyl ether bisphenol A (DGEBA) occurs. When analysing crystallisation peaks by DSC, it is important to understand the kinetics of the crystallization process. Crystallization from the melt is a two-step process: firstly, nucleation (the rate-limiting step) must occur followed by rapid growth. In addition, most materials will exhibit some supercooling behavior. A supercooled liquid is a compound, which exists in the liquid state below its melting temperature resulting in an inherently unstable phase [1]. Unlikely, a crystallisation peak is not seen in polyurethane (PU) as shown in Fig. 3. This result suggested that the phase conversion of PU is more stable than that of DGEBA. Tabulation of melting temperature, T_m of ICAs is shown in Table 3. The melting point of DGEBA system is lower than that of PU system. This might be due to the crystallisation process in the

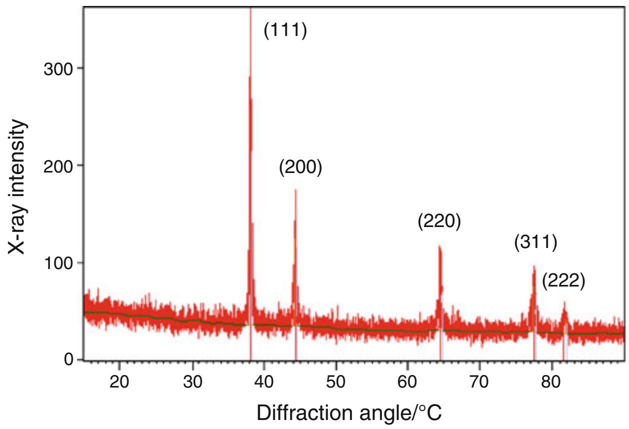

Fig. 1 X-ray diffraction pattern for silver (Ag)

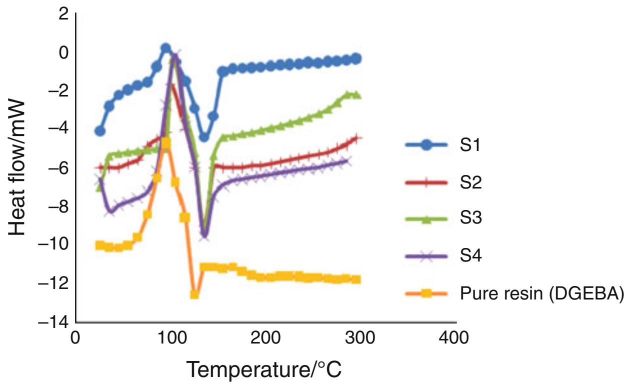

Fig. 2 Dynamic DSC curves of silver flakes–DGEBA epoxy systems

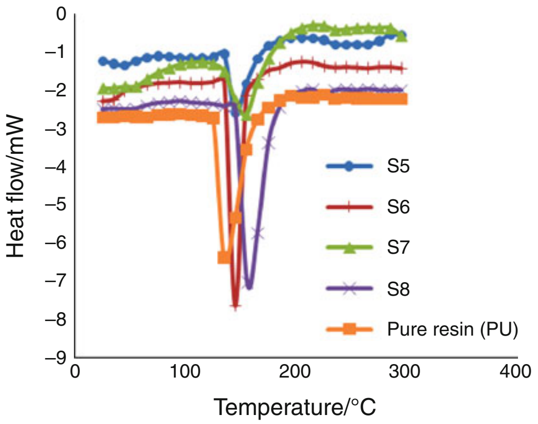

Fig. 3 Dynamic DSC curves of silver flakes–PU systems

DGEBA epoxy which is a rapid and energetic process which results in a fast return to a steady state (solid) when the crystallisation process is complete. On the other hand, the rate of cure for PU is slower. However, it can be seen in Figs. 2 and 3, the DGEBA epoxy has a wider endothermic trough than PU. This might be due to an inconsistency in the mixture of polymer–filler system [11]. The width of the peak or trough is used as an industrial measure of the quality of a paste and may indicate the tendency of the paste to have mushy or non-equilibrium behavior [12, 13]. In overall, the results suggested that PU is a more stable thermosetting polymer material.

Effect of volume fraction (silver loading) on the thermal properties of ICAs

By comparing the differential scanning calorimetry (DSC) curves of ICAs of all filler's (silver flakes) volume fraction with that of the corresponding unfilled polymer resin as shown in Figs. 4 and 5, it can be seen that the unfilled adhesives has a lower melting temperature, T_m. Thus, the cure reaction of the unfilled adhesives occurs at a lower temperature range. This implies that the silver flakes in the conductive adhesives increase the energy barrier of the cure reaction to a certain extent [14]. In addition, this indicates that the curing agent catalyses the reaction more efficiently in the unfilled adhesives. It could be caused by the fact that the silver flakes in the ICAs diffuse in between the polymer molecules and the curing agent could not contact with the epoxy as easily as it does in the unfilled polymer systems.

As the volume fraction of filler silver flakes increased for both DGEBA (S1–S4) and PU (S5–S8) adhesives, the melting temperature of the filler–polymer system is decreased, as shown in Table 3. For the DGEBA epoxy, the highest exothermic reaction, ΔH (mJ) and total heat (Jg^{-1}) was observed for volume fraction of 0.2. As the volume fraction is increased to 0.4 and 0.6, there is a drop in reactions rate and followed by an increase at 0.8. A similar trend was also observed for the PU adhesives with a much higher exothermic reaction and total heat, as shown in Table 3. Silver flakes added seems to act as a barriers between the cross-linked polymer chains and retard the polymer from further cross-linking reaction. On the other hand, the rate of reaction is increased due to the decrease in the amount of adhesive that surrounds the silver flakes. As a result, there is an increase in surface reaction due to free surface areas and surface energy between contacting silver flakes.

In electronic assembly environment, the commercial ICAs will usually be formulated at volume fraction of 0.8 in order to optimise on the electrical conductivity of the samples. In light of this, four samples (S9–S12) were formulated using the DGEBA and PU adhesives but with mixture of silver flakes and particles (S10 and S12), as shown in Table 3. The reaction rate and total heat of sample S10 and S12 are higher when compared to S9 and S11. In addition, a mixture of silver flakes and silver particles system has a higher melting point than the silver

Table 3 Curing reaction temperatures of formulated ICAs

System	Parameter	Melting point/°C	Exothermic heat, Δ*H*/mJ	Heat per mass of the pastes/J g^{-1}
S1	0.8-silver flakes/0.2-DGEBA	134.81	166.24	48.75
S2	0.6-silver flakes/0.4-DGEBA	134.99	70.56	18.56
S3	0.4-silver flakes/0.6-DGEBA	135.27	60.49	16.94
S4	0.2-silver flakes/0.8-DGEBA	135.82	207.84	56.79
S5	0.8-silver flakes/0.2-PU	144.89	352.89	100.54
S6	0.6-silver flakes/0.4-PU	144.99	193.10	53.25
S7	0.4-silver flakes/0.6-PU	154.88	188.12	53.44
S8	0.2-silver flakes/0.8-PU	155.75	523.71	141.93
S9	0.8-silver powder/0.2-DGEBA	129.86	33.59	8.93
S10	0.8-silver flakes + powder/0.2-DGEBA	154.87	317.42	92.48
S11	0.8-silver powder/0.2-PU	134.90	256.32	82.64
S12	0.8-silver flakes + powder/0.2-PU	136.73	448.91	122.32

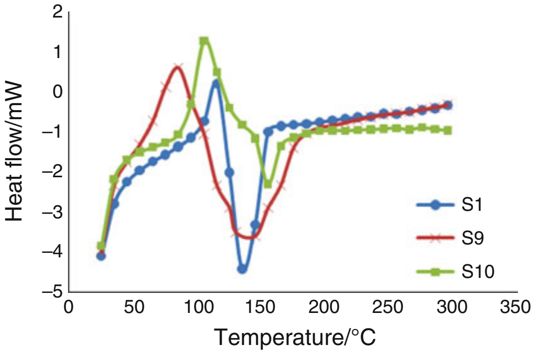

Fig. 4 Dynamic DSC comparison of silver flakes and particles mixtures in DGEBA epoxy systems

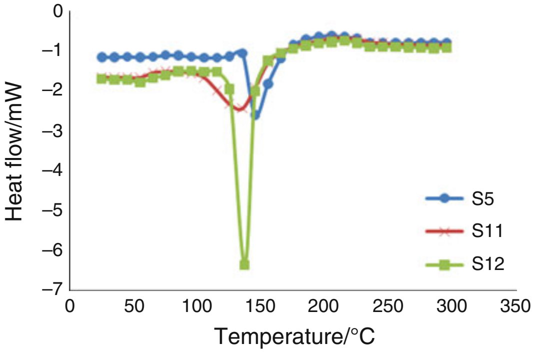

Fig. 5 Dynamic DSC comparison of silver flakes and particles mixture in PU systems

particles-based ICAs system. The results also seem to show that the use of PU adhesive as opposed to DGEBA produce high amount heat energy during the cross-linking process. Dispersion of smaller size silver flakes into broad size silver particles is seen to have a higher melting point than the monodisperse of broad size silver particles system itself. This might be due to the dispersion of smaller size filler particles filled in the space in between the broad size filler particles causes a stronger attraction force to the epoxy, and hence more energy is needed to break the bond.

Conclusions

In the curing studies, it was found PU showed a more stable phase conversion as opposed to DGEBA, which indicates the good interracial reaction of PU in the polymer–filler systems. As the volume fraction of silver flakes increases, the melting point is seen to decrease. This could be due to the silver flakes/particles acted as barrier between the cross-linked polymer chains and prevented the polymer from further reaction. The ICAs with silver flakes and particles seem to produce a higher reaction rate compared with silver flakes or particles. It is desirable to added more silver flakes/particles or combination of the both to achieve good electrical conductivity. However, the reduction in the polymer may affect the overall mechanical properties of the electrical joint.

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