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ARTICLE

# Influence of Curing Procedures on the Electrical Properties of Epoxy-Based Isotropic Conductive Adhesives

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**Abstract:** A typical isotropic conductive adhesives (ICAs) composed of an epoxy-based binder containing micro-sized silver flakes was prepared and the effects of different curing procedures on the electrical properties of the ICAs were investigated. The results show that there is greater influence of the curing temperature on 55wt% silver loading, the volume resistivity of ICAs decreases to $4.5 \times 10^{-3}\ \Omega\cdot$cm from $5.2\times10^{-2}\ \Omega\cdot$cm cured at 250 and 180 ºC, respectively. However, there is almost no effect on the high silver loading. The variations in electrical resistance of the ICAs with 65wt% silver loading was in situ monitored during the curing process, and it is found that the resistance reaches to $1.99 \times 10^{6}\ \Omega$ at 180 ºC after cured for 27 min, $1.39 \times 10^{-3}\ \Omega$ for 40 min, and 18.8 Ω for 60 min and the cooling process has almost no effect on the electrical resistance of the ICAs. The reasons for the dependence of the bulk resistivity on temperatures were also discussed in terms of the dispersing of the silver flakes in ICAs by SEM.

**Key words:** isotropic conductive adhesives; curing; volume resistivity; silver flakes

Electrical conductive adhesives (ECAs) as a potential substitution of lead-bearing solders have recently received a lot of attention from the researchers in electronics industry[1-5]. Compared with conventional tin-lead solders, the ECAs possess many advantages, such as environmental friendliness, finer pitch printing, lower temperature processing and more flexible and simpler processing[3-8]. However, complete replacement of soldering by ECAs is yet not possible owing to several limitations of ECAs which are mainly related to reliability aspects like limited impact resistance, unstable contact resistance, low adhesion, and conductivity.

Isotropic conductive adhesives (ICAs), the major type of ECAs, are composed of polymeric binders (which provide mechanical strength) and conductive fillers (which act as channel for charge transport). The characteristics of an ICA are essentially the result of its two components. Epoxy resin is one of the common materials used as polymer matrix in the ICAs. The interconnect properties and reliability of conductive adhesives are determined by the state of cure of the binder[9-14]. Therefore, an understanding of factors that affect the relationship between the curing states and the interconnect properties is essential to enable correct choice of curing conditions for conductive adhesives in order to achieve high reliability. Some of the work in literatures detailed the effects of the thermal history on electrical properties of an epoxy-based ICAs, and indicated the curing and post-heating treatment impacted the internal stress of the ICAs, which had a significant effect on the electrical resistivity of the ICAs[9-14]. However, academic reports concerning the effects of the curing states still remain inconsistent.

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In the present work, we prepared a typical ICAs composed of an epoxy-based binder containing micro-sized silver flakes and discussed the reasons for the dependence of bulk resistivity on curing procedures.

## 1 Experiment

Diglycidyl ether of bisphenol A (R-128) was purchased from Guangzhou Hongchang Co., Ltd. 4-methylhexahydrophthalic anhydride (MHHPA) and 2-ethyl-4-methylimidazole (2E4MZ) were supplied by Guangtuo Chemical Co., Ltd. Micro-sized silver flakes (SF1023K, $D_{50}$<5 μm, $D_{90}$<7.0 μm, $D_{10}$<1.0 μm) were purchased from Guangdong Fenghua Advanced Technology Group Co., Ltd.

The ICAs were prepared based on the following procedure: R-128, MHHPA and 2E4MZ with a mass ratio of 1:0.85:0.05 were put in a small beaker, and was sonicated for 30 min. Then, the silver flakes were incorporated into the polymer matrix with sonication for another 30 min to make the fillers uniformly dispersed in mixture. Two strips of polyimide tape were applied onto a pre-cleaned glass slide with a gap width of 1 cm. The formulated composite was bladed into the space between the two strips. The polyimide tapes were removed before curing at the desired temperature and time. The thickness of the cured film was controlled by the polyimide tapes.

Heat generation of ICAs during curing reaction was studied with a differential scanning calorimeter (DSC Q100 V9.5 Build 288) from TA Instruments. An approximately 10 mg sample of an adhesive was placed in a hermetic aluminum DSC pan. In a nonisothermal cure study, the samples were heated in the DSC cell from 25 ºC to 300 ºC at different heat rates of 5, 10, 15 and 20 ºC /min in nitrogen.

All scanning electron microscopy (SEM) images were taken on a JSM-6460. The resistivity of the ICAs was measured using a DMR-1C four-point probe meter (Nanjing Daming instrument Co., LTD). The resistivity, $\rho$, was calculated using the following Eq.(1):

$$\rho=R_L\omega \quad (1)$$

where, $R_L$ and $\omega$ are square resistance and thickness of sample, respectively. The thickness of samples was measured by the micrometer gauge.

## 2 Results and Discussion

Fig.1 shows the DSC of the ICAs filled with 65wt% silver flasks at different heat rates of 5, 10, 15 and 20 ºC /min. The initial curing temperature, the peak exothermic temperature, curing end temperature and the heat rates are abbreviated to $T_i$, $T_p$, $T_e$ and $\beta$, respectively[12]. With increasing of the heat rates, the initial curing temperature, the peak exothermic temperature and curing end temperature all become higher, and the range of curing temperatures becomes wider. The optimal curing conditions can be obtained by the relationship of the cure temperature of the cure reaction with the heat rates, so the optimal conditions of the ICAs could be estimated from linear extrapolation at heat rate $\beta$=0 K/min, which are also given in Fig.2 and Table 1. It is well known that the curing time actually decreases with the increase of the curing temperature. The optimal curing temperature of the cure reaction is impacted by the heat rates, so it is very important to control the heat rates during the curing procedure.

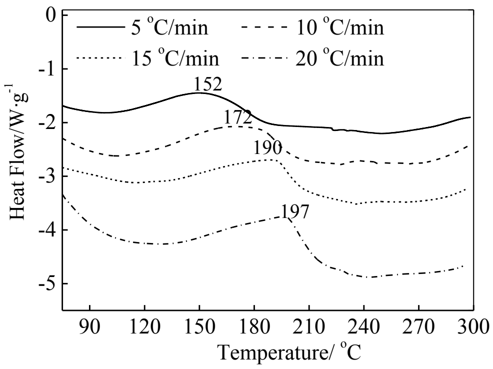


Fig.1 DSC curves of ICAs at different heat rates in nitrogen

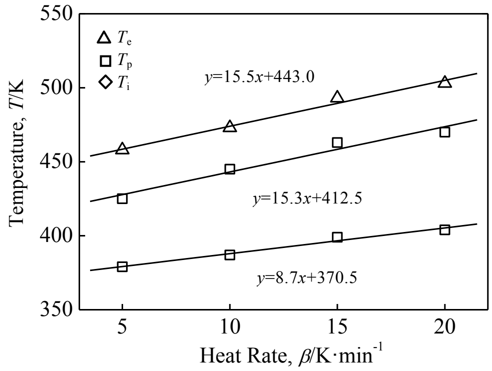


Fig.2 Linear fit curves of the relation between curing temperatures $T$ and heat rates $\beta$

**Table 1 DSC results of nonisothermal curing of ICAs at different heat rates**

| $\beta$/K·min$^{-1}$ | $T_i$/K | $T_p$/K | $T_e$/K |
|---|---|---|---|
| 5 | 379 | 425 | 458 |
| 10 | 387 | 445 | 473 |
| 15 | 399 | 463 | 493 |
| 20 | 404 | 470 | 503 |
| 0 | 370 | 412 | 443 |