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Effect of anhydride curing agents, imidazoles, and silver particle sizes on the electrical resistivity and thermal conductivity in the silver adhesives of LED devices

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ABSTRACT: This study investigated the preparation of silver adhesives applied to a light-emitting diode (LED) device as die-attach materials consisting of silver particles, on epoxy resin, curing agents, and accelerants for complete curing at 150 °C for 30 min. For the epoxy resin, this study used 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexanecarboxylate mixed with different types of anhydride curing agents such as 4-methylcyclohexane-1,2-dicarboxylic anhydride and hexahydrophthalic anhydride as well as imidazole accelerants such as 2-ethyl-4-methyl-1H-imidazole-1-propanenitrile, 2-phenylimidazole, 2-methylimidazole, 2-phenyl-2-imidazoline, and 1,2-dimethylimidazole. In addition, different size of silver particles and hybrid silver particles were used for the electrical resistivity and thermal conductivity of silver adhesives. Differential scanning calorimetric (DSC) measured conversion of silver adhesives based on different types and contents of the curing agents and accelerants under heating. The silver particles' distribution of silver adhesive also affected electrical resistance, as proved by scanning electronic microscopy (SEM) and four-point probe. The obtained results showed that the silver adhesive containing an 100 wt % of epoxy resin mixed with 85 wt % of hexahydrophthalic anhydride, 1.0 wt % (weight of epoxy resin) of 2-ethyl-4-methyl-1H-imidazole-1-propanenitrile, and 80 wt % (weight of epoxy resin) of hybrid silver particles (40 wt % 15 μm and 40 wt % 1.25 μm) was perfect, having the lowest electrical resistivity at 1.11×10^{-4} Ω·cm and good thermal conductivity at 3.2 W/m·K. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43587.

KEYWORDS: adhesives; crosslinking; differential scanning calorimetry (DSC); glass transition

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INTRODUCTION

Light-emitting diodes (LED) have been widely applied to illumination because they offer many advantages over traditional high-intensity discharge (HID) and fluorescent lights bulbs. For example, LED offers a longer lifetime; most LED bulbs have an average lifetime of 25,000–100,000 h of use.[1] LED also requires less heat than ordinary bulbs; many LED bulbs are actually cool when touched while in use. Finally, LED bulbs are energy savers, converting 80% of the electricity they use into light energy and the remaining 20% into heat.[2] Meanwhile, silver adhesives are usually applied to die-attach materials in LED devices,[3,4] being glued between the die and substrate. Such silver adhesives must possess low thermal resistance, good thermal conductivity, good reflectance and electrical conductivity, low heat degradation, and low temperature processing ability during assembly;[5] they should not produce any volatile organic compound (VOC) emissions, that damage the fluorescent powder and reduce the life time of LED devices.[6] The commercial silver adhesives applied to LED in the current study are shown in Table I. Among the available silver adhesives, 84-1LMI supplied by Ablebond Co. has lower electrical resistivity and higher thermal conductivity. In addition, silver adhesives have many advantages over conventional solder technology. Therefore, silver adhesives also have been used in isotropic conductive adhesives,[7,8] as an interconnecting material and in flip-chip assembly,[9] in liquid crystal display (LCD),[10] and in smart card,[11] radio frequency identification (RFID),[12] and solar cells.[12]

This project used 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexanecarboxylate as the aliphatic epoxy resin and anhydride curing agent in the LED packaging,[13] integrated circuit (IC) encapsulation,[14] and conductive ink paste[15] due to its lower viscosity and higher reaction rate and glass transition temperature. In addition, decreasing the curing temperature of the adhesive usually requires accelerating tertiary amines, imidazoles, or ammonium salts. However, most existing

Table I. Commercial Silver Adhesives' Characteristics

Brand/model	Electrical resistivity (Ω·cm)	Thermal conductivity (W/m·K)	Standard curing	Country of production
Ablebond/84-1LMI	5×10^{-4}	2.4	125 °C/60 min	The United States
Sumitomo/T-3007-20	-	1.2	150 °C/90 min	Japan
Ablestik/826-1DS	5×10^{-4}	2	150 °C/60 min	The United States
Eeedpool/FP-5053MV	1×10^{-3}	1.2	150 °C/60 min	Taiwan
Silver adhesive	1.11×10^{-4}	3.2	150 °C/30 min	This study

research has focused on the effect of reaction dynamics of anhydride[16,17] or imidazoles.[18,19] Only a few studies have discussed the effect of electrical resistivity for conductive adhesives. For example, Kim and Shi[9] reported the effect of curing time on the electrical resistivity of electrically conductive adhesives. Lin et al.[20] reported the effects of curing agents, such as dicyandiamide, boron–amine complex, and imidazole derivate, on the conductivity of isotropical conductive adhesives.

As Table I suggests, our study apparently demonstrated lower electrical resistivity and higher thermal conductivity as well as a shorter curing time at a curing temperature of 150 °C than studies using other commercial silver adhesives because we used suitable types and contents for the curing agent, accelerant, and silver particle sizes. Actually, the curing agents and accelerants are influenced by crosslink degree on adhesives under curing, and the silver particle sizes and shape have the efficiency of electrical resistivity and thermal conductivity on adhesives. When the particles have well connected to form the conduction path, the adhesives have lower electrical resistivity and higher thermal conductivity. We identified different types and contents of curing agents and accelerants that significantly affected the electrical resistivity of the silver adhesives. To date, no research has focused on anhydride curing agents or imidazole accelerants in the silver adhesives of LED devices. Thus, the current study adopts this approach to determine the effect of an anhydride curing agent, an accelerant, and hybrid silver particle sizes on the electrical resistivity of a cured silver adhesive.

EXPERIMENTAL

Materials

The epoxy resin (i.e., 3,4-epoxycyclohexyl-methyl-3,4-epoxycyclohexanecarboxylate), curing agents (e.g., hexahydrophthalic anhydride and 4-Methylcyclohexane-1,2-dicarboxylic anhydride), and accelerants (e.g., 2-ethyl-4-methyl-1H-imidazole-1-propanenitrile, 2-Phenylimidazole, 2-Methylimidazole, 1,2-Dimethylimidazolea, and imidazole) are shown in Table II. The dispersant as polyethylene glycol p-isooctylphenyl ether (X-100) was purchased from Dow Chemical Company Co., The United States. The various silver particles were supplied by Thin Tech Materials Technology Co., Ltd., Taiwan. The average particle size (D_{av}) was 1.25 μm of the spherical-like particle and, 15 and 25 μm of flake particles, whose tap density was 5.54, 4.01, and 3.25 g/cm^3 while their mass–median-diameter (D_{50}) was 1.87, 15.78, and 26 μm; and surface area was 0.68, 1.10, and 0.72 cm^2/g, respectively. For the substrates, sapphire was supplied by Mustec Corp. (Taiwan) while silicon carbide (SiC), aluminum oxide (Al_2O_3), and aluminum nitride (AlN) were supplied by Kallex Company Ltd. (Taiwan).

Preparation of Silver Adhesives

The formulation of silver adhesives is listed in Table III. The preparation of various silver adhesives was mixed with the help of an electric blender in room temperature for 2 h, and then was mixed via six millings in a milling process using a triple-roller mill (E-50, EXAKT, Germany) to form homogeneous silver adhesives. The silver adhesives cured were at 150 °C for 30 min.

Analysis of the Characteristics of Silver Adhesives

Differential scanning calorimetry (DSC) measurements were performed in air with a Mettler Toleo DSC822 that had been calibrated by standard procedures. The composite was heated at 10 °C/min from room temperature to approximately 300 °C. The total heat of reaction (ΔH_T) was estimated by drawing a straight line that integrated the area under the line that connected the baseline of the exothermal peak. The residual enthalpy of the cured composite (ΔH_R) was obtained by heating the composite at 100 °C/min from room temperature to 150 °C and keeping the temperature constant for 30 min in air. After 30 min, the sample was cooled rapidly to 30 °C in a DSC cell and then reheated at 10 °C/min to 300 °C. The conversion (α) was calculated by using the following equation[21]:

$$\alpha = \frac{\Delta H_T - \Delta H_R}{\Delta H_T}.$$

The silver adhesives were printed on aluminum oxide substrate using a 400-mesh, stainless-steel screen with an emulsion (thickness of 12 μm) buildup mounted on a frame that measured 24.3 × 29.7 cm. The dimensions of the pattern were 1.5 × 2 cm. The pattern was printed only in the forward direction using a squeegee that had a durometer hardness of 80. The pattern was used to measure the electrical resistivity of the cured silver adhesives using a four-point probe instrument manufactured (as shwon in Figure 1) by Everbeing International Corporation. The electrical resistivity, ρ, was calculated as follows: $\rho = 4.532t * (V/I)$,[22] where t is the thickness of the film, V is the voltage, and I is the DC electric current supplied by a power supply (Tektronix, DMM40506-1/2 Digit Precision Multimeter).

The microstructures of the cured silver adhesives were observed by JEOL JED 2300 field emission scanning electronic microscopy (SEM). The thermal conductivity coefficients of the cured silver adhesives were measured using a Hot Disk instrument (TPS2500S, Sweden), and the corresponding dimensions of the

Table II. The Chemical Structure of Epoxy Resin, Curing Agents, and Accelerants

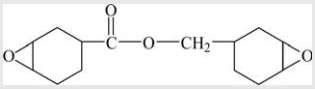
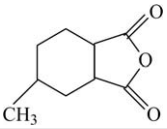
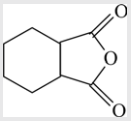
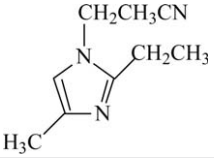
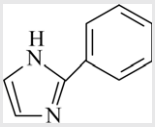
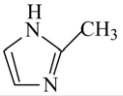
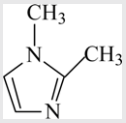
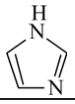
Chemical name (Code)	Chemical structure	Brand
3,4-epoxycyclohexyl-methyl-3, 4-epoxycyclohexanecarboxylate (UVR-6110)		Hubei Xinjing New Material Co., Ltd., China
Hexahydrophthalic anhydride (HHPA)		Fluka
4-Methylcyclohexane-1,2-dicarboxylic anhydride (4-MCHDA)		Sigma-Aldrich
2-Ethyl-4-methyl-1*H*-imidazole-1-propanenitrile (2-EMIP)		Sigma-Aldrich
2-Phenylimidazole (2-PhI)		Sigma-Aldrich
2-Methylimidazole (2-MI)		Sigma-Aldrich
1,2-Dimethylimidazole (1,2-DMI)		Sigma-Aldrich
Imidazole (Im)		Sigma-Aldrich

Table III. Formulation of Silver Adhesives

	Material									
Code	Silver particle (1.25 μm)	Epoxy	HHPA	MCHDA	2-EMIP	2-PhI	2-MI	1,2-DMI	Im	X-100
A	85	100	85	-	1	-	-	-	-	-
B	85	100	-	85	1	-	-	-	-	-
C	85	100	25	-	1	-	-	-	-	1
D	85	100	50	-	1	-	-	-	-	1
E	85	100	85	-	1	-	-	-	-	1
F	85	100	100	-	1	-	-	-	-	1
G	85	100	85	-	1	-	-	-	-	1
H	85	100	85	-	-	1	-	-	-	1
I	85	100	85	-	-	-	1	-	-	1
J	85	100	85	-	-	-	-	1	-	1
K	85	100	85	-	-	-	-	-	1	1

The values of all material are expressed weight percentage (wt %) to weight of epoxy resin.

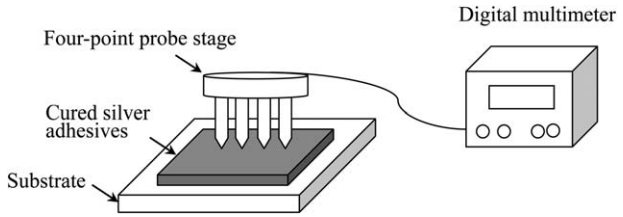


Figure 1. Schematic of four-point probe configuration.

sample specimens were 30 × 30 × 0.8 mm. In addition, adhesion strengths of the silver adhesives were measured by a pull tester, which adheres to the ASTM D897 standard. The silver adhesive glue on the two ends of the substrates (10 × 10 mm) was kept under 150 °C curing for 30 min as specimen. Then the specimen was attached on to the two steel bars (top bar is 15 mm diameter and 30 mm high, and down bar is 15 mm diameter and 50 mm high) and connected to a pull tester (Al-7000-S purchased from Gotech Testing Machines INC, Taiwan) as shown in Figure 2 for adhesion strength measurement at the pull rate of 20 mm/min. For each type of silver adhesive, the pull test was repeated five times.

RESULTS AND DISCUSSION

The Effect of the Curing Agent on Electrical Resistivity

The formulation of silver adhesives containing different types of curing agents is shown in Table III as A and B. The results indicated that the cured silver adhesive containing HHPA demonstrated lower electrical resistivity than that containing MCHDA, as shown in Table IV. Compared with the reactivate of these two curing agents, the enthalpy (ΔH) of the silver adhesive containing HHPA was higher than that containing MCHDA, as shown in Figure 3, which indicates that silver adhesive containing HHPA has higher crosslink density. The results concur with those of Tao *et al.*[23] During the curing process, a conductive adhesive was cured through the crosslink effect and shrunk simultaneously. The higher crosslink density of the silver adhesive form a shrinkage increase of adhesives resulting in a dense structure that caused between silver particles content more in the adhesive, which form the electrical flow more content points and increased the electrical conductivity.[9,24] However, the structure of the MCHDA curing agent incorporates a methyl group substitution that can be attributed to electron-donating. The results might increase the electron density of the anhydride and subsequently reduce the electrophilic addition to the oxirane ring of epoxies that cause the crosslink reaction decrease.

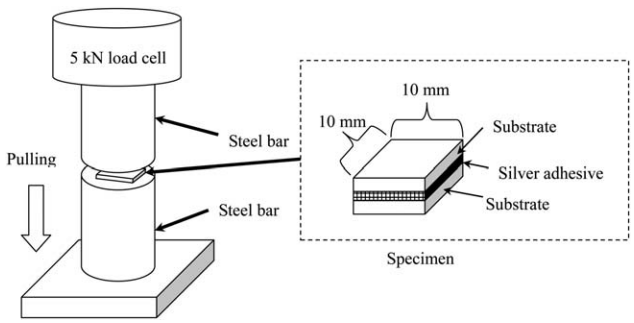


Figure 2. The test scheme of adhesion strength and specimen.

Table IV. The Electrical Resistivity and Enthalpy of Different Types of Curing Agents

Sample	Electrical Resistivity (Ω·cm)	ΔH (J/g)
HHPA	3.254×10^{-4}	−974.2
MCHDA	7.204×10^{-4}	−60.5

In addition, the formation of silver adhesive containing the different contents of the HHPA curing agent is shown in Table III as C to F. Figure 4 shows that the electrical resistivity of the cured silver adhesives decreased as the quantity of the curing agent increased from 25 to 85 wt %. Figure 5 and Table V show the results obtained for the different quantities of the crosslinking and different enthalpy (ΔH) resulting from the adhesive that contained different amounts of the curing agent when heated from room temperature to 300 °C. The obtained results about the extent of the crosslinking reaction that produced a value of ΔH are as follows: 85 wt % > 50 wt % > 100 wt % > 25 wt %. The silver adhesives containing 50 and 85 wt % of the curing agent were heated at 150 °C for 30 min to complete curing, which did not generate any residual heat obtaining $\alpha = 1$. However, the silver adhesives containing 25 and 100 wt % of the curing agent had residual enthalpy (ΔH_R) of −4.9 J/g and α of 0.87 and ΔH_R of −4.2 J/g and α of 0.95, as shown in Figure 6. The results obtained for these two silver adhesives were incomplete for curing when they were heated at 150 °C for 30 min. Therefore, the results depicted in Figures 5 and 6 suggested that the different contents of the curing agent lead to a different degree of curing, which affects the electrical resistivity. According to the results, silver adhesive containing 85 wt % of the HHPA curing agent had the largest ΔH (−974.16 J/g) when they cured; thereby suggesting the greatest enthalpy, which produced the lowest electrical resistivity at 2.76×10^{-4} Ω·cm.

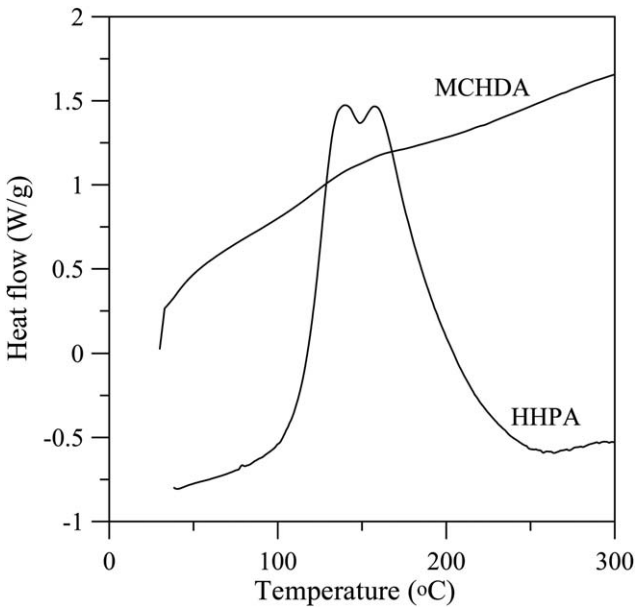


Figure 3. DSC curves of silver adhesives for different types of curing agents during a dynamic cure on heating rate of 10 °C/min.

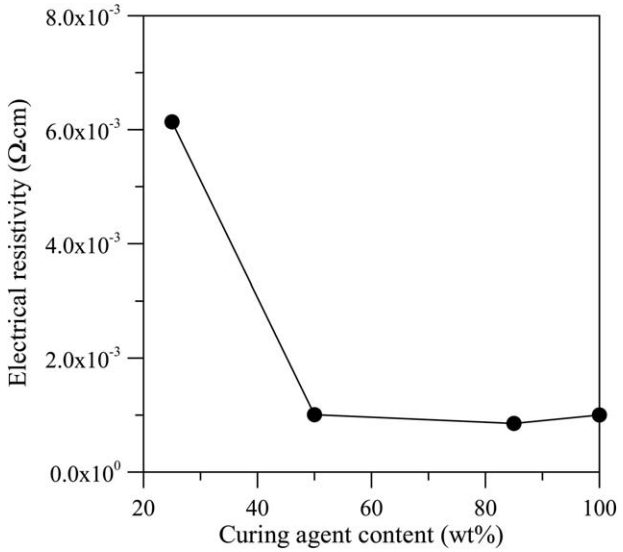


Figure 4. Electrical resistivity of the cured silver adhesives for different contents of the HHPA curing agent.

However, when the silver adhesive contained 100 wt % of HHPA, the electrical resistivity of the cured silver adhesive slightly increased to 1.00 × 10^{-3} Ω·cm, which was higher than the 85 wt % of HHPA. This was due to the fact that silver adhesive containing 100% of HHPA has lower ΔH (−85.24 J/g) than the one containing 85 or 50 wt %. The excessive amount of curing agent could be related to the nonreacted curing agent molecules hindering crosslinking reaction of the silver adhesive form a smaller ΔH value, causing a higher electrical resistivity phenomenon. It is also possible that an excessive amount of curing agent covered the surface of the silver particle, resulting in increased resistance to tunneling from a higher electrical resistivity.

Table V. The Reaction Enthalpy, Residual Enthalpy, and Crosslink Conversion of a Silver Adhesive Containing Different Contents of the HHPA Curing Agent

Curing agent content (wt %)	ΔH (J/g)	ΔH_R (J/g)	α
25	−36.54	−4.9	0.87
50	−732.34	0	1.00
85	−974.16	0	1.00
100	−85.24	−4.2	0.95

Effect of Accelerant on Electrical Resistivity

The formation as G to K in Table III was shown silver adhesives containing the different type accelerants such as 1,2-DMI, 2MI, 2-PhI, Im, and 2-EMIP. The electrical resistivities and enthalpy of various silver adhesives are shown in Table VI and Figure 7. The results demonstrated that the effects of different types of accelerant on the electrical resistivities of cured silver adhesives were ordered as follows: 1,2-DMI > 2MI > 2-PhI > Im > 2-EMIP. First, we compared the four accelerants (i.e., Im, 2-MI, 2-PhI, and 1,2-DMI) because they have a similar chemical structure. The temperature (T_g) of the cured silver adhesives (Table VI) was as follows: 2-PhI > Im > 2-MI > 1,2-DMI. Due to the T_g of adhesives increase as the crosslink density increases.[25] Meanwhile, the volume shrinkage can be determined by comparing the T_g, which the higher the T_g have the higher the volume shrinkage.[25] However, the results in Table VI indicate that the electrical resistivity of a silver adhesive containing 2-PhI was higher than Im, although the T_g of a silver adhesive containing 2-PhI was higher than Im. According to the results, we can consider another factor that the silver adhesive containing 2-PhI was subjected to incomplete curing, as it had ΔH_R of −0.94 J/g after being heated at 150 °C for 30 min. As 2-PhI is a weaker base than Im because the benzene ring

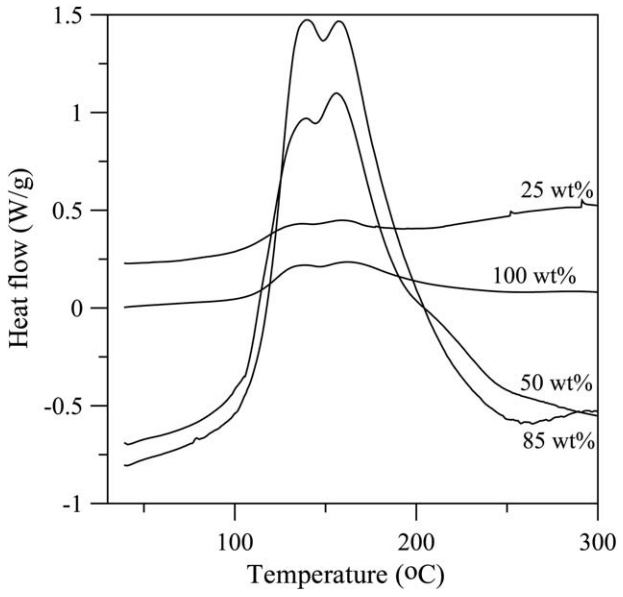


Figure 5. DSC curves of silver adhesives for different contents of the HHPA curing agent during a dynamic cure on heating rate of 10 °C/min.

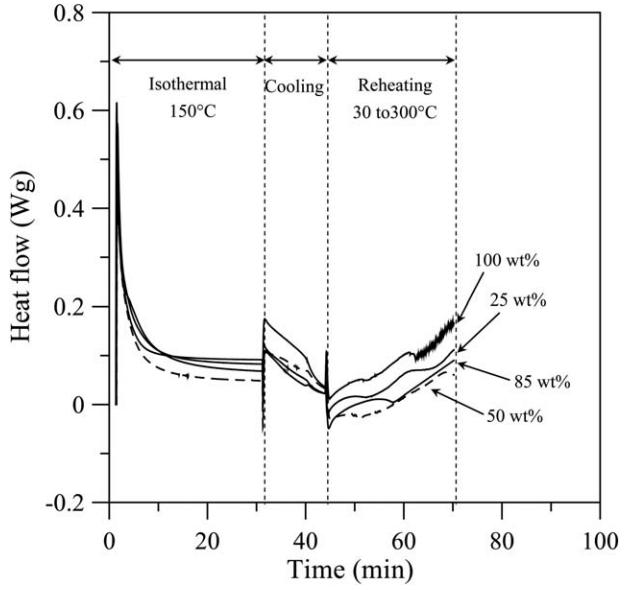


Figure 6. DSC curves of the silver adhesives containing a 0.25 to 1 weight ratio of the HHPA curing agent when subjected to isothermal reaction at 150 °C, cooling, and reheating steps.

Table VI. The Electrical Resistivity, Enthalpy of Reaction, Residual Enthalpy, and T_g of Silver Adhesive Containing Various Accelerants

Accelerant type	Electrical resistivity (Ω·cm)	ΔH (J/g)	ΔH_R (J/g)	T_g (°C)
Im	0.29	−101.90	0	139.3
2-PhI	0.88	−89.60	−0.94	145.5
2-MI	1.36	−96.20	−2.77	137.5
1,2-DMI	1.89	−74.00	0	123.0
2-EMIP	2.76×10^{-4}	−83.93	−0.36	112.5

is an electron withdrawing group, attracting electron density away from the nitrogen lone pair on structure will form lower polymerization than Im. That means silver adhesive containing 2-PhI achieved to complete curing needs more time, and the results are same as those reported by Ham *et al.*[19] The incomplete curing of the adhesive's capsulate covering the surface cause higher electrical resistivity.

The silver adhesive containing the 2-EMIP accelerant had the lowest electrical resistivity at 2.76×10^{-4} Ω·cm. Although it also had the lowest T_g, the chemical structure of 2-EMIP at the first position showed a strong electron withdrawing from the cyano group (—CN).[26] It has a smaller band gap as well as high change mobility,[27,28] and it was expected to show good intrinsic conductivity.[29]

In addition, the silver adhesive containing different amounts of 2-EMIP accelerant influenced the electrical resistivity, ΔH and ΔH_R (Figure 8, Table VII, and Figure 9 for results). When they were heated at 150 °C for 30 min, the silver adhesive without the accelerant had the largest electrical resistivity at 7.43×10^{-4} Ω·cm. The adhesive with the largest ΔH_R (−41.26 J/g) and lowest α (0.45), after being heated at 150 °C for 30 min, indicated that the silver adhesive was incompletely cured. When increasing the

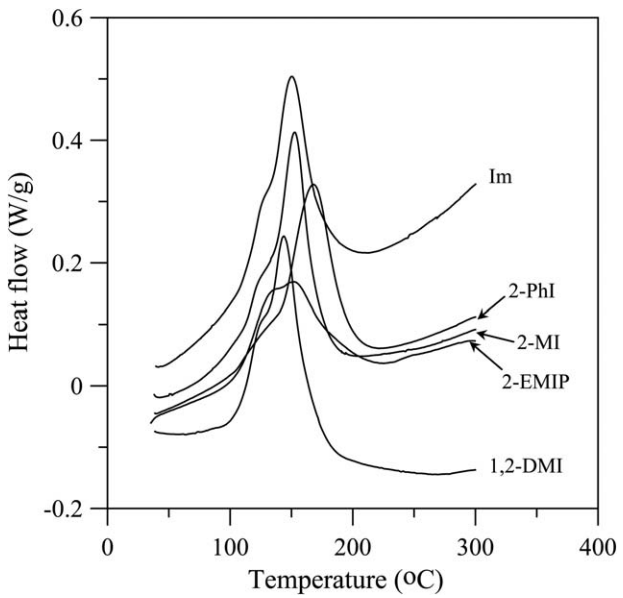


Figure 7. DSC curves of the silver adhesives containing different types of accelerant on heating rate of 10 °C/min.

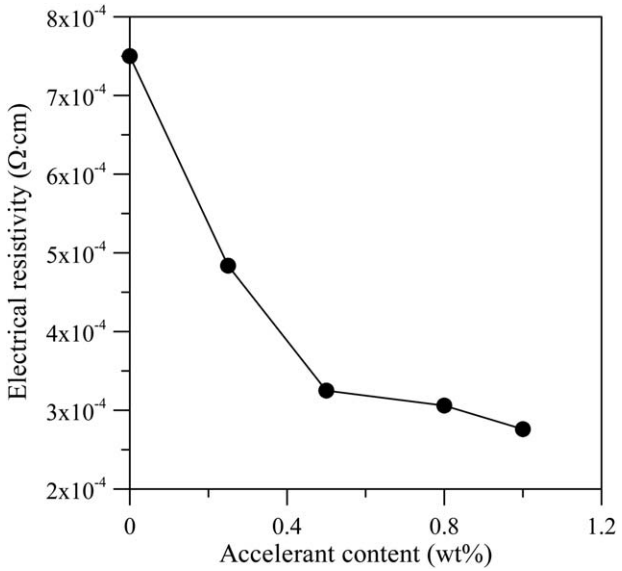


Figure 8. Electrical resistivity of the cured silver adhesives for different contents of 2-EMIP accelerant.

Table VII. The Reaction Enthalpy, Residual Enthalpy, and Crosslink Conversion of Silver Adhesive Containing Different Contents of 2-EMIP Accelerant

Accelerant content (wt %)	ΔH (J/g)	ΔH_R (J/g)	α
0	−74.78	−41.26	0.45
0.25	−65.80	−4.90	0.93
0.50	−96.59	−1.73	0.98
0.80	−83.93	0	1.00
1.00	−80.40	0	1.00

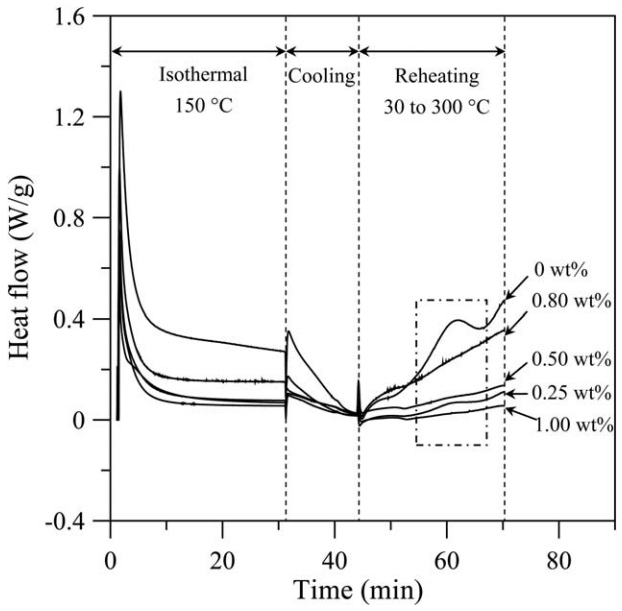


Figure 9. DSC curves of the silver adhesives containing 0.25–1.00% of the 2-EMIP accelerant when subjected to isothermal reaction at 150 °C, cooling, and reheating steps.

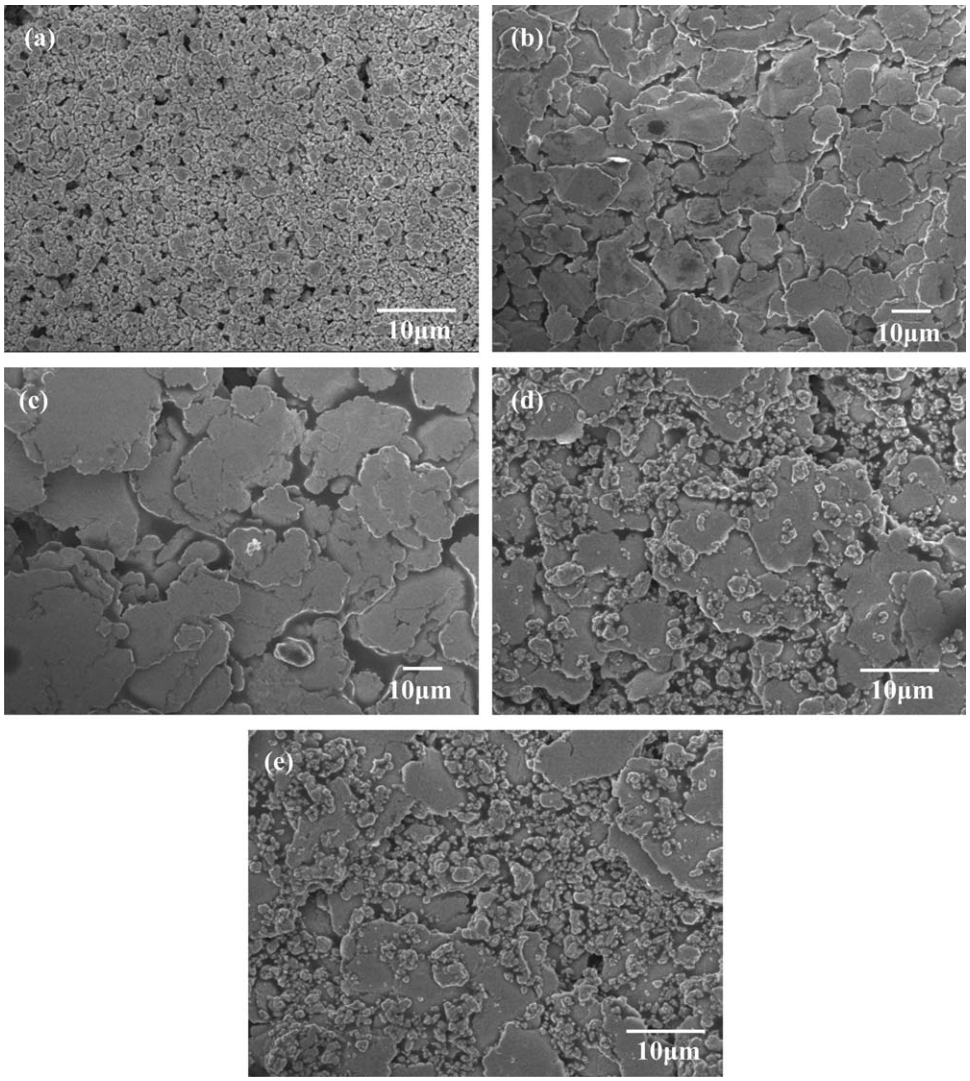


Figure 10. SEM images of cured silver adhesives for different types of silver particles (a) 1.24 μm, (b) 15 μm, (c) 25 μm, (d) 50% 15 μm and 30% 1.24 μm, (e) 40% 15 μm and 40% 1.24 μm.

amounts of 2-EMIP accelerant in the silver adhesives, it helped to enhance α and ΔH_R simultaneously and decreased the electrical resistivity. Therefore, a silver adhesive added 1.00 wt % of 2-EMIP accelerant, which has the lowest electrical resistivity at $2.76 \times 10^{-4}\,\Omega$·cm.

The Effect of Silver Particles' Different Particle Size on Electrical Resistivity and Thermal Conductivity

The silver adhesives consisted of 100 wt % of epoxy resin and 85 wt % of HHPA, 1.00 wt % (weight of epoxy resin) of 2-EMIP accelerant, 1.0 wt % (weight of epoxy resin) of X-100 and 85 wt % (weight of epoxy resin) of the 1.25, 15, and 25 μm silver particles, and 80 wt % of hybrid silver particles, which affected the electrical resistivity and thermal conductivity of the cured silver adhesives (as shown in Table VIII). The results indicated that silver adhesives containing 15 μm silver particles had the lowest electrical resistivity and better thermal conductivity than those containing 1.25 and 25 μm silver particles at the same 85 wt % content. The SEM images showed that the cured silver adhesives containing 1.25 and 25 μm silver particles had larger holes than those containing 15 μm silver particles, as shown in Figure 10(a–c). A lot of holes can cause the electrical throughput not to be continuous, thereby forming higher electrical resistivity. However, the 15 and 25 μm silver particles have larger particle sizes and are flake-shaped, which have more content area between particles than 1.25 μm silver particles (sphere-like shape), thereby contributing higher thermal conductivity to the cured silver adhesives.

In addition, silver adhesives containing hybrid silver particles, such as 15 and 1.25 μm, have lower electrical resistivity and higher thermal conductivity of cured silver adhesives (containing 40 wt % 15 μm and 40 wt % 1.25 μm or containing 50 wt % 15 μm and 30 wt % 1.25 μm silver particles) than silver adhesives containing 80 wt % of 15 μm silver particles. The results were also similar for silver adhesives containing 85 wt % of 15 μm silver particles. Some parts of the smaller particle-sized 1.25 μm silver particles filled the hole positions between the 15 μm silver particles, which contributed more content area between silver particles, as shown in Figure 10(d,e), and caused

Table VIII. Electrical Resistivity and Thermal Conductivity of Cured Silver Adhesives for Different Silver Particle Sizes and Hybrid Silver Powders

Silver particles	Electrical resistivity (Ω·cm)	Thermal conductivity (W/m·K)
85 wt % 1.25 μm	2.76×10^{-4}	2.9
85 wt % 15 μm	1.32×10^{-4}	3.3
85 wt % 25 μm	4.96×10^{-4}	3.3
80 wt % 15 μm	2.54×10^{-4}	2.3
40 wt % 15 μm and 40 wt % 1.25 μm	1.11×10^{-4}	3.2
50 wt % 15 μm and 30 wt % 1.25 μm	1.64×10^{-4}	3.3

the silver adhesives to have better electricity conducting and thermal conductivity properties. Therefore, the silver adhesive containing 80 wt % of hybrid silver particles can use fewer silver particles and decrease the cost of adhesives while maintaining the same quality as 85 wt % of 15 μm silver particles.

Effect of Adhesion Strength on Different Substrates

The substrates (e.g., sapphire, SiC, Al_2O_3, AlN) provided higher thermal conductivity and good properties of disappearing thermals, which are often applied in LED devices. The silver adhesives need good adhesion strength for these substrates of the LED device, which enhances the LED device's durability. Therefore, we examined silver adhesives containing 40 wt % 15 μm and 40 wt % 1.25 μm silver particle glued on different substrates (i.e., sapphire, SiC, Al_2O_3, AlN), which resulted in the average adhesion strengths of 736.0, 510.6, 506.7, and 735.0 N/cm^2, respectively (as shown in Figure 11). These substrates could be ranked in the following order: sapphire ≈ AlN > SiC ≈ Al_2O_3. The results indicated that the silver adhesives have better adhesion strength for sapphire and AlN substrates. It is hypothesized that increasing the number of hydroxyl groups on the surface would lead to an improvement in the strength of the bond between the ceramic and an adhesive.[30]

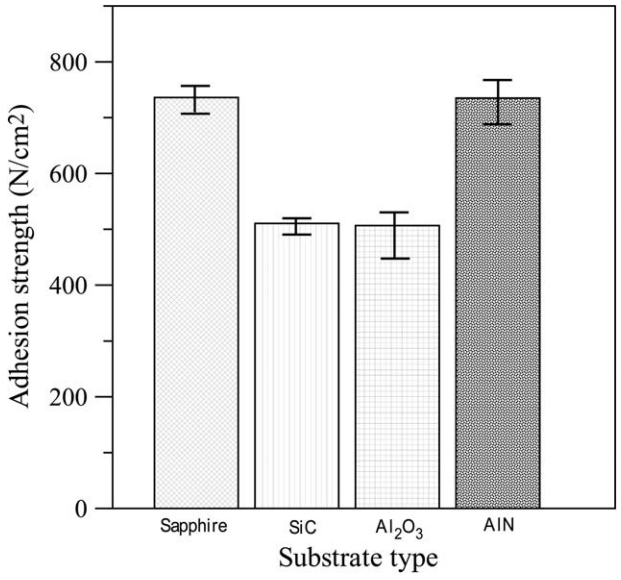


Figure 11. Adhesion strengths of the silver adhesives for different types of substrates.

CONCLUSIONS

This study successfully prepared silver adhesives to meet LED device requirements electrical resistivity $\leq 5 \times 10^{-4}$ Ω·cm and a thermal conductivity greater than 1 W/m·K. These properties are also better than those of commercial silver adhesives. Preparing low electrical resistivity and high thermal conductivity of silver adhesives depends on choosing the appropriate type and content of the curing agent, accelerant, and silver particles.

The study demonstrated that a silver adhesive containing a HHPA curing agent has higher crosslink density, causing increased particle contact; this increase in closeness results in higher electrical conductivity. The silver adhesive containing the 2-EMIP accelerant had the lowest electrical resistivity. In addition, the larger particle sizes and flake-like shape of silver particles allowed for more content area between particles, which led to higher thermal conductivity for silver adhesives. When silver adhesives used a hybrid of different particle sizes of silver particles, smaller particles filled the holes between larger particles, resulting in more content area between silver particles. This result also formed higher thermal conductivity for the cured silver adhesives. In summary, the best silver adhesive demonstrates a lower electrical resistivity at 1.11×10^{-4} Ω·cm and good thermal conductivity at 3.2 W/m·K.

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