Research Article

Preparation and Characterization of Liquid Crystalline Polyurethane/ Al_2O_3 /Epoxy Resin Composites for Electronic Packaging

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Liquid crystalline polyurethane (LCPU)/ Al_2O_3 /epoxy resin composites were prepared by using LCPU as modifier. The mechanical properties, thermal stability, and electrical properties of the LCPU/ Al_2O_3 /epoxy resin composites were investigated systematically. The thermal oxidation analysis indicated that LCPU/ Al_2O_3 /epoxy resin composites can sustain higher thermal decomposition temperature. Meanwhile, coefficient of thermal expansion (CTE) was also found to decrease with addition of LCPU and nano- Al_2O_3 .

1. Introduction

Recently, the thermal conductive but electrical insulating polymer composites are extensively used in electronic packaging. Epoxy resin is widely used in electronic packaging industries due to their ease of processing, low cost and lower coefficient of thermal expansion. In microelectronic packaging, heat dissipation is becoming increasingly important, because of higher heat dissipation capability to promise electronic devices high performance, lower coefficient of thermal expansion, then avoid thermal stress, and lower dielectric constant to minimize signal delay [1–3]. Therefore, polymer composites filled with high thermal conductive filler emerge for solving thermal dissipation problem as low cost and available materials.

LCPU has many advantages such as anisotropic orientation, high heat resistance, high mechanical properties, low coefficient of thermal expansion, low dielectric constant, and good dimensional stability. Therefore, it can be used in various applications such as matrix for advanced composites, microelectronic packaging, structural adhesives, and optical materials [4]. In the present article, LCPU/ Al_2O_3 /epoxy composites were prepared by using LCPU as modifier and surface-modified Al_2O_3 by using KH-550 as high thermal

conductive filler, and the LCPU was used to improve mechanical properties, thermal property, and thermal conductivity of composites. The mechanical properties, thermal stability, and electrical properties were investigated systematically. Up to our knowledge, there is no research reported on this work.

2. Experimental

2.1. Materials. Epoxy resin (DGEBA, epoxy value = 0.51) was supplied by Yueyang Chemical Plant, China. Linear phenolic resin was purchased from Shanghai Chemical Reagent Company, China. The α - Al_2O_3 -nanosized powder used in this study which is untreated with the average diameter of 60 nm was purchased from Zhejiang Zhoushan Mingri Nanometer Materials Co., Ltd (China). γ -aminopropyltriethoxysilane (trade name: KH550) was provided by Liao Ning GaiZhou Chemical Industry Co. Ltd., China. LCPU was synthesized according to [5]; its molecular structure is shown in Scheme 1.

2.2. Surface Modification of Nano- Al_2O_3 . Into a 250 mL four-necked flask equipped a mechanical stirrer, a thermometer, a purger of N_2 , and a reflux condenser, 20.0 g of nano- Al_2O_3

SCHEME 1: The molecular structure of LCPU.

was charged, and atmosphere was replaced with N_2 gas. Then, 4.0 g of KH550 ethanol solution was sprayed onto the Al_2O_3 surface at 150°C under agitation at 400 rpm. After 30 min, unreacted KH550 and ethanol were removed under vacuum at 150°C . The resulting Al_2O_3 was dried and stored in vacuo at room temperature.

2.3. Preparation of LCPU/ Al_2O_3 /Epoxy Resin Composites. Epoxy resin was selected as matrix resin and linear phenolic resin as curing agent (EMC), and the weight ratio of epoxy and linear phenolic resin was 5 : 3. Accelerator (2 methylimidazole, 1 wt% of EMC) and liquid crystalline polyurethanes (LCPU, 5 wt% of EMC) were used as additives, and nano- Al_2O_3 was used as filler. This mixture was putted into a mould and hot pressed at 175°C under a pressure of 12 MPa at 180°C for 4 h.

2.4. Measurements. The impact strength was tested according to China National Standard GB1043-79 on a JC-25. The tensile strength was examined according to China National Standard GB1040-92 on an electron omnipotence tester RGT-5. Thermogravimetric analyses (TGAs) were carried out using netzsch STA449 under nitrogen. The volume resistivity (ρ_v) was tested according to PC68 Digital Megger under 250 V. Coefficient of thermal expansion was tested according to netzsch DIL402C thermal expansion instrument. Heat-conducting property was carried out with a unithermtm model2022 conductometer. Dielectric constant (ϵ_r) and dielectric loss were performed using a type agilent 4294A analyzer.

3. Results and Discussion

3.1. Mechanical Properties. The effect of the different nano- Al_2O_3 particles content on the mechanical properties is summarized in Table 1. From Table 1, it can be seen that the system which is modified with LCPU only (c) can achieve more superior impact strength than that of the pure epoxy system (a). However, the impact strength of LCPU/ Al_2O_3 /epoxy composites slightly decreases with nano- Al_2O_3 content increasing. This can be attributed to the uniform dispersion of the nano- Al_2O_3 in epoxy resin, which resulted in some aggregates and made tough and fracture resistance properties decreased [6].

3.2. Thermogravimetry Analysis (TGA). TGA was applied to evaluate the thermal stability of LCPU/ Al_2O_3 /epoxy composites. From Figure 1, the TGA curve clearly shows that the initial decomposition temperature of composites is relatively higher than that of the pure epoxy resin by adding only nano- Al_2O_3 or LCPU, which is $5\text{--}10^\circ\text{C}$ higher than that of the

- (a) EP/LCPU/ Al_2O_3 = 100/0/0
- (b) EP/LCPU/ Al_2O_3 = 100/0/60
- (c) EP/LCPU/ Al_2O_3 = 100/5/0
- (d) EP/LCPU/ Al_2O_3 = 100/5/50

FIGURE 1: The TGA curves of composites.

unmodified epoxy resins. The reasons for the improvement in thermal stability of the composites are probably attributed to the high thermal stability of rigidity mesogenic groups and the existence of the strong interaction between the urethane linkage of LCPU and the polymer matrix.

3.3. Thermal Conductivity. The different content of nano- Al_2O_3 influence on thermal conductivity of packaging materials was shown in Table 2. It was observed that the thermal conductivity in the composites increases with Al_2O_3 loading, and the higher thermal conductivity of Al_2O_3 filled thermal composites is possibly due to higher intrinsic thermal conductivity of Al_2O_3 fillers (30 W/m K). The intrinsic thermal conductivity of the epoxy resin matrix is as low as 0.221 W/m K; however, the addition of Al_2O_3 and LCPU filler resulted in a steady increase of the thermal conductivity by about 3-4 times at the volume fraction from 50% to 70%. The increasing of the volume fraction of the Al_2O_3 filler will result in the formation of a steadier network and, thus, increases the thermal conductivity greatly. The results of Table 2 show that the thermal conductivity of the composites also improved when LCPU content is about 5 wt%; this is because that the highly ordered structure of LCPU molecule would be expected to suppress phonon scattering so that the resin should have high thermal conductivity [7].

3.4. Electrical Properties. The different content of nano- Al_2O_3 influence on electrical properties was shown in Table 3. It is found that the volume resistivity (ρ_v) and dielectric constant (ϵ_r) of composites were increased with the increasing content of nano- Al_2O_3 or LCPU. This is because that a great amount of interfacial areas formed between the nano- Al_2O_3 and the epoxy matrix, and the chain of epoxy

FIGURE 2: SEM micrographs of fractured surface of the composites: (a) pure epoxy; (b) EP/LCPU = 100/5; (c) EP/LCPU/Al₂O₃ = 100/5/50; (d) EP/LCPU/Al₂O₃ = 100/5/70.

TABLE 1: Influence of Al₂O₃ contents on mechanical properties for the epoxy resin systems.

Sample (wt%)	Impact strength/(kJ/m ²)	Tensile strength/(MPa)	Tensile modulus/(MPa)
(a) EP/LCPU/Al ₂ O ₃ = 100/0/0	8.26	49.63	4980
(b) EP/LCPU/Al ₂ O ₃ = 100/0/60	6.13	31.57	5010
(c) EP/LCPU/Al ₂ O ₃ = 100/5/0	9.37	56.02	4595
(d) EP/LCPU/Al ₂ O ₃ = 100/5/50	8.51	50.71	5430
(e) EP/LCPU/Al ₂ O ₃ = 100/5/60	8.12	47.58	4990
(f) EP/LCPU/Al ₂ O ₃ = 100/5/70	7.64	30.39	4915

TABLE 2: Thermal conductivity of the composites.

Sample (%)	Thermal conductivity (W/m K)
(a) EP/LCPU/Al ₂ O ₃ = 100/0/0	0.221
(b) EP/LCPU/Al ₂ O ₃ = 100/0/60	0.677
(c) EP/LCPU/Al ₂ O ₃ = 100/5/0	0.246
(d) EP/LCPU/Al ₂ O ₃ = 100/5/50	0.675
(e) EP/LCPU/Al ₂ O ₃ = 100/5/60	0.736
(f) EP/LCPU/Al ₂ O ₃ = 100/5/70	0.748

matrix activity, free volume, and the carrier ion mobility greatly reduced, so that electrical conductivity decreased, and the volume resistivity increased. Generally low losses in a material are required. From Table 3, the $\tan \delta$ of the samples decreases with increasing the Al₂O₃ particles. As to

coefficient of thermal expansion (CTE), it can be seen that the CTE of the composites was decreased with increasing Al₂O₃ particles in epoxy matrix. The reduction in CTE may be attributed to the segmental motions of the epoxy chains that are restricted.

3.5. Microstructure Analysis. Figure 2 showed morphologies of impact fracture surface of the composites. There can be seen from Figure 2(a) the smooth glassy fractured surface with crack in different planes in case of pure epoxy; this is an indication of brittle fracture. As for the modified with LCPU system as shown in Figure 2(b), the fracture surface shows branches and appears rougher than that of the pure epoxy, and its impact strength gets considerable improvement correspondingly. The impact fracture surface of Al₂O₃ particles and LCPU (5 wt%) composites were shown in Figures 2(c) and 2(d), fracture surfaces present more large

TABLE 3: Electrical performance of the composites.

Sample (wt%)	ρ_v (Ω cm)	ϵ_r	($\tan \delta$) ($\times 10^{-2}$)	CTE ($\times 10^{-5}$ K $^{-1}$)
(a) EP/LCPU/ Al_2O_3 = 100/0/0	3.63×10^{14}	4.72	6.65	6.675
(b) EP/LCPU/ Al_2O_3 = 100/0/60	1.71×10^{16}	5.15	6.38	5.640
(c) EP/LCPU/ Al_2O_3 = 100/5/0	2.29×10^{16}	5.28	5.58	6.203
(d) EP/LCPU/ Al_2O_3 = 100/5/50	2.35×10^{16}	6.21	5.55	6.153
(e) EP/LCPU/ Al_2O_3 = 100/5/60	2.39×10^{16}	7.98	3.88	4.683
(f) EP/LCPU/ Al_2O_3 = 100/5/70	3.63×10^{16}	7.80	4.93	4.601

and deep cavities, which can be explained as that the LCPU was originated to form anisotropic microfibril during curing, and microfibrils acted as bridge combining both sides of the crack to induce crazing and transmit load and led to some plastically deformed materials. The resulted microstructural analysis corresponds to the mechanical properties, and no phase separation can be observed, which indicated that LCPU, Al_2O_3 particles, and EP have good compatibility.

4. Conclusions

Liquid crystalline polyurethane (LCPU)/ Al_2O_3 /epoxy resin composites were prepared by using LCPU as modifier, and the microstructure of the composites was characterized by SEM. The dependence of the mechanical properties, thermal conductivity, and electrical properties on alumina and LCPU content was studied. The following conclusions can be drawn from the results obtained in this work.

- (1) The LCPU can act as an effective toughening modifier for the epoxy resin. But the mechanical properties of composites modified with LCPU and Al_2O_3 slightly decrease with Al_2O_3 particles content increasing.
- (2) The volume resistivity, coefficient of thermal expansion, and $\tan \delta$ show a little decline, while the dielectric constant of the composites increases with the increase of Al_2O_3 loading. The difference could be attributed to the significant interfacial zone between the epoxy and the Al_2O_3 particles.

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