UV-curable Encapsulants for LED

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ABSTRACT

UV cured epoxy systems represent complementary technology to the established heat cured epoxy systems for coating, adhesion and encapsulation of electronic devices. The UV cured epoxy systems offer significant benefits in terms of fast cure and thus very short production cycle time; low stress and better colour due to room temperature cure; process wise no mix ratio problem or anhydride handling issues and yet produce comparable or even better physical and chemical property than the more common heat cured systems. This paper deals with the evaluation and comparison among four different type of curing systems for LED encapsulants:
1. Free radical UV system with faster curing rate but only surface layer cure.
2. Cationic UV system with slower curing rate but deeper layer cure.
3. Hybrid of both free radical and cationic UV system.
4. Existing heat cure system.

Characterisation topics included the state-of-the-art LED package strength indicated by DMA modulus, TMA coefficient of thermal expansion, photostress, liquid nitrogen and ring washer crack test; outdoor performance indicated by heat age at 120 °C, 180 °C, atmospheric moisture absorption and boiling water absorption; solder heat resistance indicated by Tg, % cure and solder (TTW) delamination and last but not least the optical clarity indicated by % Transmission under UV-visible range and the refractive index.

Key Words: Free Radical, Cationic, Hybrid and LED Encapsulants.

INTRODUCTION

Incandescent, fluorescent and neon lamps have been used for decades in a wide variety of applications. The LED lamps has been gradually replacing these earlier devices in many applications due to their superiorities over the incandescent bulbs for the reasons as listed below:

1. LED need low currents and voltages to produce useful light output
2. The light emitting area of the LED can be defined precisely through the use of semiconductor photo-lithographic processes.
3. The LED device can be switched on at high speed

Most commercial LED lamps are manufactured by encapsulating an LED chip inside a plastic package with a len surface directly above the LED. The encapsulating plastic is most likely an epoxy system that has been specially formulated to give the maximum protection and maximum reliability to the LED device. The epoxy encapsulant must have the following minimum requirements :

1. Excellent optical clarity. This will enable the maximum transmission of light from the LED chip. The encapsulant must not turn yellow at high temperature and over a long period of time.

2. Good solder heat resistance. In most applications, the LED device is soldered onto a substrate or printed circuit board. The epoxy encapsulant must be able to protect the delicate LED chip and fragile electrical connections from the damaging effects of the high soldering temperature.

3. Good outdoor performance. LED devices are frequently used outdoors where they can be exposed to the harsh temperature extremes, sunlight and rain. The epoxy must be tough enough to withstand these elements.

4. Good package strength. The epoxy encapsulant glues the electronic parts together. The epoxy must provide very good adhesion and crack resistance to the thermal-mechanical handling.[1]

5. Ease of processing the material, fast cycle time, and low costs.

The heat cured epoxy system used for LED packaging is invariably anhydride-cured systems.

Generally, anhydride cured epoxy give high Tg, good heat stability in air, long pot life, low exhoterm during cures, and good electrical properties.[2]

However, acid anhydrides are hygroscopic materials and tend to pick up atmospheric moisture. They should not be allowed to remain exposed to air for extended periods. Absorption of moisture causes hydrolysis of the anhydride to acid.[3] This causes variable pot life of blends, lower Tgs, appearance of the insoluble acids, and reduced the crack resistance.[3] Certain anhydrides tend to sublime especially at elevated processing temperatures. This poses contamination issues which is concern in the electronics workplace where a clean production environment is required. Anhydride cure epoxies takes two hours or even more time to cure at high temperatures.[2] In the very competitive electronic industry, faster cycle time is continuously sought after to increase productivity and lower costs of production.

UV-curable powder coatings can be cured via both the cationic and the radical mechanisms. In radical cure systems various resins such as unsaturated polyester, polyurethane acrylate and maleate vinylether have been used. In the cationically cured systems, however, epoxy type resins including, bisphenol, novolac modified bisphenols, cycloaliphatic epoxides, glycidylmethacrylates and glycidyl acrylics have been dominantly used.[4]

One of the main components of UV curing system is photoinitiator, which must meet the following requirements:[5]

a) High photosensitivity in the range of wavelength 300-400 nm.

b) Good solubility and reactivity in the oligomer-monomer system.

c) Guarantee of the stability during storage and environmental tests.

A free radical cured UV material must be either very thin, clear or both in order to let sufficient amounts of UV radiant energy to penetrate through the material. In free radical polymerization, a monomer or oligomer joints with free radical and forms a large free radical. This larger free radical then acts upon another monomer or oligomer and forms an even larger molecules, and so on. The process is chain reaction that is endless until a polymer molecule is terminated[6]. In case of transparent thin films, free radical curing is very fast and, may react to completion in a millisecond or less. There are two types of photo-initiator[7] (1) Surface cure (Irgacure 184 and 651) and (2) through cure (Irgacure 819 and 907). It is known that the use of the mixture of some photo-initiator in the UV-adhesive give synergistic effects especially in the pigmented UV cure system[8].The wavelength area in the near UV between 370 nm and 430 nm play an important role for the effective curing in the white

pigmented system within 30 seconds without any cationic photo-polymerization mechanism[9].

It is common to include another photo-initiator as photo-bleaching during the photo-initiation process. Due to the bad solubility of both the irgacure 819 and 907 when mixed in composition[10], additional heating is required (60^{0}C) to dissolve the photoinitiator. However, the composition turbidity and the deposit formation were observed during the compositions storage. Thus, we need to dissolve these photo-initiators into the monomer first. Many UV products cure at a wavelength of 365 nm (UVA), although some products cure at the visible end of the UV spectrum (400 nm-450 nm)[9]. The wet and tacky surface in acrylic systems due to the oxygen inhibition can be overcome by using intensive UVC light to ensure a rapid surface cure in the range of 100-400 mW/cm^2.[(11)]

Cycloaliphatic epoxide based cationic UV curable coatings offer the advantage of fast cure, low shrinkage, no oxygen inhibition[12], and good electrical properties. These characteristic make them ideal for microelectronic packaging materials[12]. Cationic photo-initiators, after UV exposure, spontaneously form cationic that trigger further cationic polymerization. Once the cationic polymerization has been started, cationic reactions can carry polymerization to completion in thicker, opaque materials or even in the dark (i.e. after radiant energy exposure stops)[9].

Due to the limited UV absorption of the cationic UV initiator using typical UV lamps, polynuclear aromatic compounds may be used as photosensitizers to extend the absorption of the system and subsequently to improve its UV curing rate and monomer conversion[13]. The sensitization is based on complex formation and electron transfer between the sensitizer and the photoinitiator[10]. Aryl iodonium and sulfonium salts are thermally stable photoinitiators for cationic polymerization. Photoinitiated cationic polymerization by photosensitization of diphenyliodonium and triphenylsulfonium salts is shown to proceed by two distinct electron transfer processes: (1) direct electron transfer from excited –state photosensitizers, and (2) indirect electron transfer from photogenerated radicals. The efficiency of the former process is attributed to instability of the

reduction products[13]. Our works aimed to compare the various UV-curable epoxy systems to conventional heat- curable epoxy systems for electronics application.

EXPERIMENTAL

Samples
a)   Cationic UV cure samples
b)   Free radical UV cure samples
c)   Hybrid UV cure samples
d)   Heat cure samples

Curing conditions
a)   UV curing samples

The curing process for the UV-curable LED encapsulants consists of a rapid polymerization induced by UV-reactive photo-initiators followed by a succeeding thermal polymerization either for free radical, cationic or hybrid curing samples. Casted samples were cured using the Efos ultracure 100SS Plus ultraviolet curing machine coupled with a medium pressure (1-2 atm) mercury arc lamp (Osram, Germany), with a light intensity approximately 300 mW/cm^2, over a wavelength range of 360-390 nm for 30 seconds at a distance of 3 cm . After uv curing, the post curing treatment was performed at 150°C for 30 minutes in convection blue M oven. Samples were stored in a desiccator at room temperature for at least 24 h before characterization of their properties.

Heat Cure system
Samples were cured in the blue M convection using the curing profile of 120^{0}C for 30 minutes followed by 125^{0}C for 2 hours.

Accelerated Tests for Yellowing
a)   Heat age at 180 C in Blue M box oven. This very high temperature heating was an accelerated test to stimulate the casted epoxies to yellow within 24 hours.
b)   Heat age at 120 C in Blue M box oven. This test was implemented to simulate the yellowing seen at temperature cycling during the reliability test.

Accelerated Tests for TMCL Cracks
Liquid nitrogen dip (-198 C) for 5 minutes

Table 1 : Comparison of The Evaluation Result For Heat Cure, Free Radical UV system, Cationic UV system and Hybrid UV system

No	Evaluation Parameter	Heat Cure System	Free Radical UV cure System	Cationic UV Cure System	Hybrid UV Cure System	
1	Viscosity, cps					
	a) Resin	2850	-	-	-	
	b)Hardener	130	-	-	-	
	c) Mix	1400	1040	1260	900	
2.	Refractive Index					
	a) Resin	1.5440	-	-	-	
	b) Hardener	1.4788	-	-	-	
	c) Mix	1.5114	1.517	1.527	1.523	
3	Specific Gravity					
	a) Resin	1.1799	-	-	-	
	b) Hardener	1.1593	-	-	-	
	c) Mix	1.1730	1.0756	1.2114	1.1474	
4	Gel Time,					
	a) Convection Oven 120 °C 7 Minutes		-			
	b) UV 300 mW/cm^2	-	3 Seconds	18 Seconds	10 Seconds	
5	Optical Transmission, %, $\lambda =$ 400 - 900 nm (Thickness ~ 10 mil)		> 92	> 92	> 92	> 92
6	DSC					
	a) Tg , °C Precure	125 (120°C / 30 Minutes)	133 (300mW/cm^2 / 30 Seconds)	100 (300mW/cm^2 / 30 Seconds)	112 (300mW/cm^2 / 30 Seconds)	
	Post Cure	142 (125°C / 30 Minutes)	149 (150°C / 30 Minutes)	144 (150°C / 30 Minutes)	156 (150°C / 30 Minutes)	
	b) Cure, % Precure	94 (120°C / 30 Minutes)	100 (300mW/cm^2 / 30 Seconds)	94 (300mW/cm^2 / 30 Seconds)	93 (300mW/cm^2 / 30 Seconds)	
	Post Cure	98 (125°C / 30 Minutes)	100 (150°C / 30 Minutes)	98 (150°C / 30 Minutes)	99 (150°C / 30 Minutes)	
7	Material Price, Rm / Kg	X	1.5 X	2.0 X	2.0 X	
8	Boiling water resistance, wt gain %					
	24 Hours	2.13	1.46	1.24	1.15	
	72 Hours	2.44	2.03	1.55	1.38	
	168 Hours	2.58	2.36	1.81	1.55	
9	a) Yellowing at 120°C, Gardner					
	1)	2 Days	1	1	1	1
	2)	4 Days	2	1	1	1
	3)	6 Days	2	1	1	1
	4)	8 Days	2	1	1	1
	5)	10 Days				

			2	1	1	1
	b) Yellowing at 180⁰C, Gardner					
	2)	0 Hour	1	1	1	1
	3)	24 Hours	2	2	1	1
	4)	48 Hours	3	3	1	1
	5)	72 Hours	4	4	1	2
10	Cracked Resistance, T1 3/4 Lamps					
	Liquid Nitrogen, 5	8.33	10	0	0	
	3)	Minutes (%)				
11	TGA					
	Decomposition Temperature	> 300 ºC	> 300 ºC	> 300 ºC	> 300 ºC	

Epoxy samples were cured into T1 ¾ (5 mm) LED lamps. 5 to 10 units of lamps were immersed in liquid nitrogen in a thermos flask for 5 minutes. The epoxy might crack around the leadframe because of differential contraction between mild steel and epoxy.

Boiling Water Absorption Test

The slabs (15mm x10 mm x 5 mm) were weighed accurately and immersed in water and reflux for a period of one week. The slabs were wiped using tissues paper and weighed again, percentage of water absorption was determined using the equation below:

$$\text{Water absorption (\%)} = \frac{(\text{Weight after immersion} - \text{weight before immersion})}{\text{Weight before immersion}} \times 100$$

Optical Transmission

Visible absorption spectra were recorded by visible spectrometer (Jasco V-530, US). Glass plate were cleaned and dried, then film approximately 10 mil in thicknesss were cast onto the plate with aluminium spacer. The films were treated as per procedure 3.2 curing conditions .

TG : DSC

For the DSC (Perkin-Elmer 7, England) study, about 10 mg of sample was placed in the aluminium pan , sealed properly and scanned from temperature 30 to 250 ºC at a heating rate of 10 ºC min^{-1} under the nitrogen atmosphere (flow rate is 30 ml min^{-1}). The instruments was calibrated with indium standards before measurements.

TGA

The dynamic thermogravimetric analysis of the samples were carried out at a heating rate of 30 ºC min^{-1} under nitrogen atmosphere (flow rate is 30 ml min^{-1}) in the temperature range of 25-600 ºC.

Viscosity

The viscosity of the products was measured with Brookfield viscometer RVF at the speed of 100 rpm using the Spindle # 3 at 25 ºC using a 50 ml plastic container .

Refractive Index

Refractive index was measured with Atago Abbe Refractometer NAR- 1T

RESULTS AND DISCUSSION

From Table 1,the mix viscosity of UV curing system is lower than the heat cure system. This would facilitate the degassing process, minimize bubbles trapped during dispensing and improve the visual defects or dome defects. No mixing is required since UV curing is one part system. The gelling time for UV cure system is shorter within seconds at room temperature.Tg and percentage cure for UV cure is higher than heat cure system, this means more resistance for thermal shock or temperature cycling.Cationic and hybrid UV cure is more resistance for yellowing especially significantly reduce yellowing at 180 C. UV cure system seems resist to cracking.This will be confirm by Modulus. Boiling water resistance was better for hybrid UV system compared to the heat cure system.

The percentage of weight gain at 168 Hours is 1.55 % for Hybrid UV cure whereas for heat cure is 2.58 %. This indicated that hybrid cured epoxy have better resistant to hydrolysis.

CONCLUSION

Generally, UV cure system especially the cationic and hybrid curing system give better yellowing, moisture and crack resistance compared to heat curing system. Shorter curing time at room temperature is more economical in energy. Other physical properties of UV cure system were maintained and comparable to heat cure system. Cationic UV cure system is recommended for the best yellowing resistance

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