UV Modified Epoxy for LED Encapsulant

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Abstract. Light Emitting Diode (LED) packaging is important for the protection and enhancement of light extraction efficiency in LED. The most commonly used encapsulant is epoxy resin, which is the annealing cured. Multilayer time delayed aging of the epoxy resin causes delamination during packaging process. Ultraviolet (UV) modification is introduced in the curing process of epoxy resin to enhance the curing process of the epoxy. In this paper, the samples tested are either modified with UV or vice versa. Differential Scanning Calorimeter (DSC) is used for the analysis of the sample. Six samples are tested. Data analysis is based on the heat of reactions between the mixed materials; either the process is exothermic or endothermic when the temperature changes. The reaction between the materials determines its ability to crosslink, viscosity and temperature control for the whole reaction.

1. Introduction

1.1 Background
LED packaging involves processes such as wire bonds, die attach and encapsulation. Encapsulation is one of the important processes in LED packaging to provide environmental protection, good electrical resistance and light ray extraction \cite{1}. Epoxy resins are one of the popular materials as encapsulant because it possesses excellent chemical resistance, outstanding adhesion strength, high electrical resistance and able to cure at low temperatures \cite{2}. However, the dispensing and curing of epoxy resins on LED as encapsulant must be carried out immediately. Thus, multilayer time delayed aging epoxy resins causes delamination in LED. After the epoxy resins are mixed with curing agents, the curing process starts immediately and causes the mixed solution becomes more viscous and hardens at the same time. Modifications of epoxy resins was done to improve the curing temperature, humidity, viscosity and for other reasons during the curing process.

Most research focused on the modification of cycloaliphatic epoxy resins, but there is limited emphasis on the curing agents on UV curing \cite{3-5}. In this work, UV curing was applied to modify the curing process of epoxy resins. UV curing on the cycloaliphatic epoxy resins and the mixed solutions is used. Additionally, UV curing is also applied on the curing agents for seeking the potential that it may produce a better output from the theoretical analysis.

1.2 Epoxy Resins
Epoxy resins are crosslinkable materials that possess the same type of reactive functional groups, the oxirane or epoxy group. The epoxy group is characterized by its reactivity towards both nucleophilic...
and electrophilic species. Therefore, it is receptive to many types of curing agents or reagents. There are two types of curing agents, catalyst or hardener. Catalyst usually works with hardener in low concentrations on resins’ formulation. Carboxylic anhydrides, aromatic and aliphatic amines are common examples of hardener [6]. Epoxy resins are commonly used in various structural applications and coatings. There are many factors that affect the application of epoxy resin such as the adhesion strength, shrinkage, electrical resistance, environmental resistance and other factors that relate with the end application.

A cycloaliphatic epoxy resin was used in this work for its advantages of high glass transition temperature in the range of 200°C. Besides, it can be widely use as encapsulant for coils, transformers and other electronics devices. There are two types of structure of cycloaliphatic epoxy resins, which are the diglycidyl ester of hexahydrophthalic acid and 3,4 epoxycyclohexylmethyl-3,4 epoxy-cyclohexane carboxylate as shown in Figure 1 and Figure 2 respectively [6].

![Figure 1. diglycidyl ester of hexahydrophthalic acid structure [7].](image1)

![Figure 2. 3, 4 epoxycyclohexylmethyl-3,4 epoxy-cyclohexane carboxylate structure [7].](image2)

The curing agents for cycloaliphatic epoxy resins were hexahydrophthalic anhydride (HHPA) and methylhexahydrophthalic anhydride (MHHPA). HHPA is a solid at room temperature but melts to a low viscosity liquid between 35° and 37°C. At room temperature, MHHPA was a low viscosity that melts below -15°C. Lewis acid catalysts including both BF₃ and BCl₃ amine complexes are used to form single component systems with this epoxy resin. At room temperature, these formulations exhibit outstanding latency with fast cure rate at elevated temperatures [7].

2. Experimental

2.1. Samples Preparation

A commercial epoxy resin was used in this work. It consists of two parts, the cycloaliphatic epoxy resin (Part A) and the hardener (Part B). There were 6 samples tested with DSC and the mixing of the epoxy resins were carried out as followed: (a) Part A was mixed with Part B, (b) Part A was mixed with Part B and then left for 1 hour in room temperature (staging), (c) Part A was mixed with Part B and then UV irradiated for 2 minutes, (d) Part A was mixed with Part B and then shone with UV for 2 minutes plus another hour of staging, (e) Part A was shone with UV for 2 minutes and then mixed with Part B, (f) Part B was shone with UV for 2 minutes and then mixed with Part A. An EXECURE 3000 (100W) UV light source (Mercury-Xenon lamp) was used for UV curing in this paper. The UV spectrum of the Mercury-Xenon lamp is shown in Figure 3. The intensity of the UV light source can be adjusted from 0% to 100%. Figure 3 showed three different values of intensity of the UV light source, which are 30%, 50% and 80% respectively. The mixing ratio of Part A and Part B was 100:90. The mixed solution was then transferred to aluminium pan for DSC. The weight of the epoxy resin samples was recorded.
2.2. Thermal Profile
The sample size for DSC lies between 1mg–5mg and a drop of mixed solution was placed in aluminium pan and was weighed. The sample’s weights in this experiment were 0.57mg, 0.5mg, 1.0mg, 1.4mg, 1.2mg and 0.4mg from (a) to (f) respectively. DSC’s thermal analysis is based on an automatic thermal analyzer system, whereby the sample was sealed in aluminium pan and another empty sample sealed in the same way as a reference. The difference in the heat flow were recorded, when the temperature changes accordingly [6].

![Figure 4. Temperature against time for the curing process of epoxy resin in DSC.](image)

The aluminium pan was placed in DSC to obtain the thermal profile of the sample. The curing temperature set up for the sample was shown in Figure 4. The temperature of DSC was ramp up from room temperature to 125°C and then stays isothermal for two hours. Then, it ramp up another 25°C to 150°C and then stays isothermal for an hour. The samples were then cooled down to room temperature.
before the next experiment is carried out. Data of heat flow against temperature was obtained and plotted in graphs as shown in Figure 5, 6 and 7.

3. Results and Discussion

Generally, the DSC results showed two exothermic curve and endothermic curve except the last sample (only showed two endothermic curve). The first endothermic peak represents the solid-solid transition between two crystalline phases, whereas the second peak indicates the melting of crystallites [5]. On the other hand, the first exothermic peak show the initiation of polymerization and the second peak is the initiation of polymerization by thermal decomposition [9]. The samples were named (a)-(f) respectively and they are stated as followed:

(a) Part A was mixed with Part B
(b) Part A was mixed with Part B and then left for 1 hour in room temperature (staging)
(c) Part A was mixed with Part B and then UV irradiated for 2 minutes
(d) Part A was mixed with Part B and then shines with UV irradiated for 2 minutes plus another hour of staging
(e) Part A was irradiated with UV for 2 minutes and then mixed with Part B
(f) Part B was irradiated with UV for 2 minutes and then mixed with Part A.

The positive heat flow values indicates the occurrence of endothermic reaction, while the negative heat flow values indicates the occurrence of exothermic reactions. The exothermic peaks represent the energy before the reactions. As the heat flow values increased, the atoms required more energy to break the bonds. In other words, the higher the exothermic reaction, the higher the activation energy required for chemical bondings. Figure 5 showed three samples without staging condition. From the graph, it is observed that there were two endothermic peaks (indicates by red rectangle) and exothermic peaks (indicates by green rectangle). For un-staged samples, the four peaks of heat flow for sample (a) is -1.58, 1.56, -2.06 and 0.37 respectively, while -1.22, 2.09, -1.35 and 0.40 for sample (c) and -1.57, 0.77, -1.32 and 0.28 for sample (e). The first endothermic peak occurred at the same temperature for all sample, but the second endothermic peak occurred at 125°C for sample (a) and 150°C for sample (c) and (e) respectively. By comparison from these three peaks, sample (c) exhibit the best results as the negative heat flow value was optimum, which means that a lesser activation energy is required to break the bonds.

Figure 6 showed DSC results for two staging samples. The first exothermic peak occurred at 63°C before it achieved isothermal temperature (125°C) for both sample. Another exothermic peak for sample (b) occurred at 125°C whereas it occurred at 144°C for sample (d) before it achieves isothermal temperature (150°C). The epoxy resin, after aging has vigorous exothermic reaction that up to -4.10 and -4.04 respectively. The first endothermic peak occurred at the same temperature for both sample, but the second endothermic peak occurred at 138°C and 149°C for sample (b) and sample (d) respectively. The effect of UV modification was not effective on the staging of epoxy resin because the phase transition of crystalline reduces after UV curing on the staging samples.
Figure 5. Graph of heat flow against temperature for non-staging condition.

Figure 6. Graph of heat flow against temperature for one hour aging condition.
Figure 7 showed without staging condition’s sample. This sample’s exothermic peak is small and can be assumed as 0, which also means that the reaction between epoxy resins and curing agents was not initiated before the temperature ramp up to 125°C. However, the first endothermic peak occurred at 122°C and the second endothermic peak occurred at 150°C, which also indicates that after UV curing of part B, the initiation of solid-solid transition between two crystalline process in this sample decrease to 122°C, while the following curing temperature remains the same. When UV light is irradiated on the curing agents, the electrons gain addition energy and excited from lower energy level to higher energy level by light absorption. Thus, the donor needs more energy to activate the crosslink of the epoxy resins and delayed the reaction between epoxy resins and curing agents.

![Heat Flow against Temperature](image)

**Figure 7.** Graph of heat flow against temperature.

Sample (f) showed the best results among all the samples for the application as LED encapsulant as the negative heat flow values is close to zero, little activation energy required to break the chemical bonds. Sample (f) still has two endothermic peaks as per required in the curing process, which means that the UV curing does not modify the bonding structure of epoxy resins. On the other hand, it improves the curing process of the epoxy resins.

### 4. Conclusion

In conclusion, modification of epoxy resins by using UV is possible. Sample (f) showed the best results among all the samples in this paper as application for LED encapsulant, for the following reasons, the polymerization and polymerization by thermal decomposition does not initiate during the temperature ramp up process, which also indicates that the viscosity of the epoxy resin remains the same before the real curing process happens at its respective temperature. Hence, the reaction between the epoxy resins and the curing agents can be delayed by UV curing. In other words, delamination occurring during the LED packaging process able to be solve by this method.
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