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Comparative Properties of Optically Clear Epoxy Encapsulants

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Abstract

Three epoxy systems were evaluated for physical and optical properties. The three systems chosen for the study were selected on the basis of their optical clarity, color and chemistry. Three distinctly different chemistries were chosen, aromatic epoxy- amine cured. Aromatic epoxy- anhydride cured and cycloaliphatic epoxy- anhydride cured. All three systems remained optically clear and water-white after full cure. The three selected systems were tested for physical properties, adhesion and light transmission properties. Light transmission was measured after thermal and humidity exposure. Adhesion was measured after humidity exposure only. Both of the epoxy-anhydride systems performed well in optical properties but poorer in adhesion as compared to the epoxy-amine system. The aromatic epoxy-amine system discolored badly during thermal exposure at 100 C.

Data generated from this work will be used in selecting clear encapsulating materials for photonics applications. No single system offers optimal performance in all areas. The best compromise material is the aromatic epoxy-anhydride system.

Introduction

The use of epoxy resins for the encapsulation of light emitting diodes (LED's) has been the standard material of choice for over 25 years. These materials have been characterized with that application in mind. Some of the key properties for the LED encapsulants are viscosity, clarity, glass transition temperature [T(g)], and coefficient of thermal expansion (CTE). In photonics applications, adhesion, refractive index and light transmission in the infrared (IR) region are also important. A direct comparison of these properties was conducted on three model epoxy formulations representing three different types of chemistry; aromatic epoxy-amine, aromatic epoxy-anhydride and cycloaliphatic epoxy-anhydride.

Methodology

Sample Preparation

Sample materials were selected from commercially available epoxy resins, hardeners and catalysts. The aromatic epoxy structure used was the diglycidal ether of bisphenol A (BADGE) and the cycloaliphatic epoxy, 3,4 Epoxy Cyclohexyl Methyl-3,4-Epoxy Cyclohexly Carboxylate Diepoxide CACE). The amine hardener was based on a family of polyoxypropylene diamines (POPDA). The anhydride hardener was Hexahydro-phthalic anhydride. Catalysts used to promote the epoxy-anhydride reactions were based on tertiary amines and metal salts. Test samples were prepared by mixing the epoxy resins with a stoichometric quantity of hardener. The resulting liquid materials were mixed under vacuum for 30 minutes, poured into 30 cc syringes and frozen at –40 C until use.

Test samples were prepared by thawing the premixed and frozen epoxy mixture for 1 hour at 25 C in a constant temperature water bath. Viscosity was determined using a Brookfield viscometer per ASTM D2393. Cured test specimens were prepared by casting the liquid epoxy mixture into steel molds previously treated with a silicone mold release. Cure schedules were based on using differential scanning calorimeter studies to determine reaction kinetics.

Material Identification

System A
BADGE – HHPA   Aromatic Epoxy-Anhydride
System B
BADGE – POPDA   Aromatic Epoxy-Amine
System C
CADE – HHPA   Cycloaliphatic Epoxy-Anhydride

Test Methods

The following test methods were used to obtain data reported:

- Glass Transition Temperature (T(g)) and Coefficient of Thermal Expansion (CTE) were determined using TA Instruments mode TMA 2940 per ASTM E1545.
- Flexural Strength, Modulus and Elongation were determined using an Instron model 5566 per ASTM D790.
- Water Absorption was determined after 96 hours exposure to saturated steam at 15 psi. (121 C) using a Napco 8100TD environmental chamber.
- Light transmission properties were determined on 25 mm thick castings from a 3 cm diameter circular mold. A Perkin Elmer Lambda 25 UV/Vis spectrophotometer was used to measure percent light transmittance over a range of 300 nanometers to 900 nanometers.

- Refractive index (I_R) was measured using an American Optical ABBE Refractometer per ASTM D542. A Variable Angle of Incidence Spectropscopic Ellipsometer (VASE®) was used to determine the refractive index over a wide spectral range. (Note: VASE® work was done by J.A. Woollam Co.; Lincoln, NE.)
- Thermal aging studies were conducted in a circulating air oven Blue M Model OV-500C Test temperature was 100 C.
- Humidity exposure testing was conducted in an Espec model LHU112 Temperature and Humidity chamber. Test conditions for light transmission were 60 C and 85% relative humidity. Adhesion testing was conducted after 85 C and 85% relative humidy.
- Die Shear Adhesion was determined on 25 mm square silicon die bonded to a glass microscope slide. A Dage Model 4000 die shear tester was used for testing.

Results

Cure Rates

The relative cure rates of the three subject systems were determined using differential scanning calorimetery. A modified Bouschardt-Daniels equation was used to calculate the cure rates at various temperatures. Test samples were cured at twice the indicated time in order to allow for heat up and to assure the test samples were fully cured before test. Relative cure rates are indicated in Figures 1, 2 and 3.

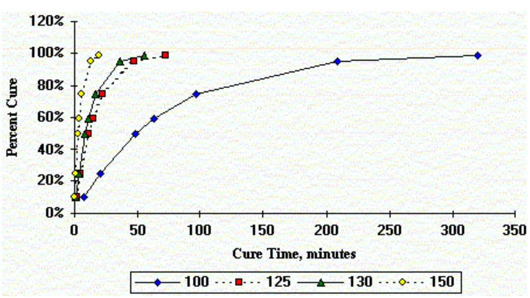

Figure 1 - Cure Rate of System A

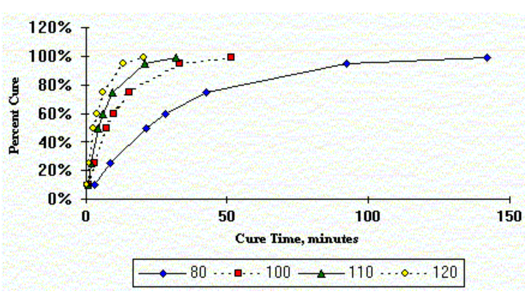

Figure 2 – Cure Rate of System B

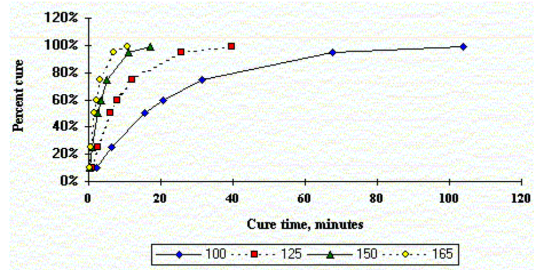

Figure 3 – Cure Rate of System C

Physical Properties

Physical properties of the subject materials are summarized in Table 1. The data indicates that System C, the cycloaliphatic epoxy-anhydride, provides the highest T(g) and System B., the aromatic epoxy-amine, the lowest. System A, the aromatic epoxy-anhydride system, offers the highest strengths and best water resistance.

Table 1 – Physical Properties

Property	System A	System B	System C
Viscosity	3250 cps.	350 cps.	1000 cps.
Cure	2 hrs @ 125 °C	4 hrs. @ 80 °C	1 hr @ a50 °C
T(g)	125 °C	87 °C	160 °C
CTE	66 ppm/ °C	73 ppm/ °C	74 ppm/ °C
Flex Modulus	2.9 Gpa	3.2 Gpa	3.5 Gpa
Flex Strength	133 Mpa	115 Mpa	103 Mpa
Elongation	5.9%	4.9%	3.0%
H_2O Absorp.	2.2%	4.6%	11.3%

Adhesive Properties

Die Shear strength properties are summarized in Figure 4. Each value represents an average of 5 specimens. Samples were tested immediately after exposure to 85 C/85 % RH. Initial adhesive strengths were similar for all three systems. After only 125 hours exposure, adhesive strengths for the two epoxy-anhydride drop dramatically. The apparent increase in adhesion of the epoxy-amine system is due to experimental error. The epoxy-amine system (B) does clearly out perform the two epoxy-anhydride systems. (A and C) This data illustrates that initial adhesion or bulk water absorption are not clear indicators of how well a material will perform in a humid environment.

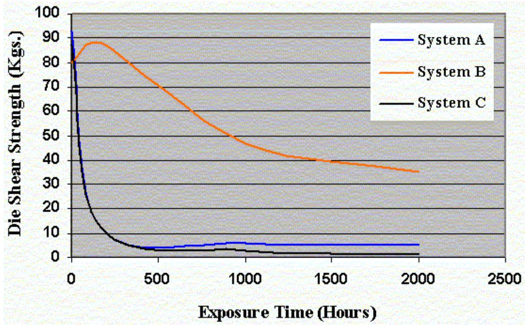

Figure 4 – Effects of 85/85 Exposure on Adhesion

Optical Properties

The refractive index of a optical media is an important consideration in the selection of that media. Refractive Index (I_R) is the ratio of speed of light in that media vs. the speed of light in air. Rayleigh scattering (losses) occur when light passes from one media to another with a different refractive index.

The I_R for the test materials was measured at 640 nm at 25 C:

System A Aromatic epoxy-anhydride	1.53
System B Aromatic epoxy-amine	1.51
System C Cycloaliphatic epoxy-anhydride	1.49

Figure 5 illustrates the effect of wavelength on the refractive index. The sample used for this testing was a transfer grade epoxy-anhydride molding powder prepared by Dexter laboratories in Olean, NY. A similar response is expected with the subject test materials based on the similarity of the base epoxy chemistry. Actual values were not determined on the test materials in order to save the time and expense.

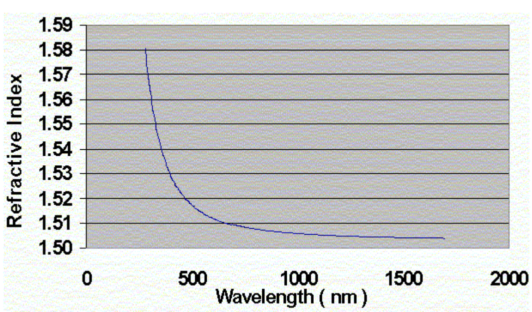

Figure 5 – Refractive Index vs. Wavelength

Light transmission properties are a critical performance factor. Initial light transmission and retention of light transmission after thermal and humidity exposure are important factors. The three subject materials were selected because of their color and clarity. Effects of environmental exposure remained to be determined. Two environmental exposure criteria were selected for study. They were thermal exposure at 100 C and moisture exposure at 85 % RH and 60 C.

Light transmission is wavelength dependent and will vary with the extent of discoloration that occurs during cure and environmental exposure. Figure 6 illustrates the effects of thermal aging on light transmission. As the material thermally ages and becomes yellow in appearance, a reduction in transmission at the lower wavelengths in evident.. Transmission at the higher wavelengths remains unchanged.

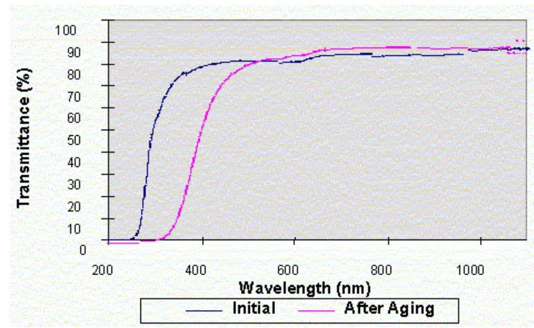

Figure 6 – Transmittance vs. Wavelength

Using the fact that light transmission at the lower wavelengths decreases with the amount of yellowing, and is unchanged at the higher wavelengths, a "yellowing coefficient" can be determined by measuring the transmittance at 800 nm and 400 nm and dividing the transmittance at 400 nm by the transmittance at 800 nm. Figure 7 illustrates the effects of thermal aging at 100 C on the yellowing of the subject materials. This data indicates superior thermal aging properties are obtained with the epoxy-anhydride systems.

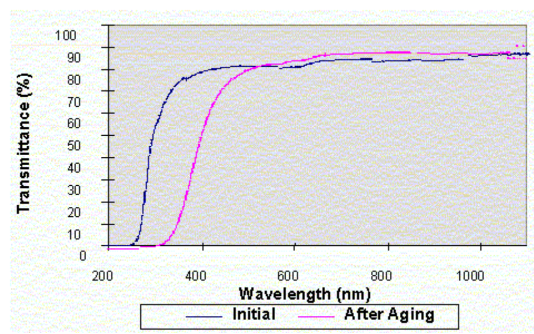

Figure 8 – Effect of Thermal Aging on Yellowing

Effect of humidity exposure on transmission was determined using a single wavelength, 640 nm. This wavelength was chosen because it represents the range at which the transmission properties remain constant with aging and is well within the visible range. Figure 8 illustrates the effect of 85% RH exposure at 60 C on the light transmission of the subject materials. All three systems performed well under these test conditions. Some slight yellowing was observed in the epoxy-amine system (B). Examination of the cast samples used to determine water absorption (Figure 1) for the three systems did however indicate severe degradation of the cycloaliphatic epoxy-anhydride system (C) resulting in surface crazing and nearly complete loss of light transmission properties. The aromatic epoxy systems, A and B did not exhibit crazing and retained optical transparency.

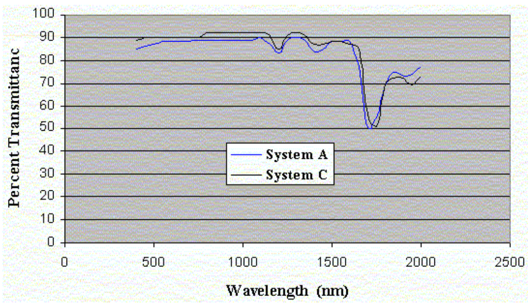

Figure 9 – Effect of Humidity Exposure on Light Transmission at 640 nm

Based on thermal stability, the two epoxy-anhydride systems (A and C) were chosen for further light transmission studies. Both were examined for transparency in the infrared region. These wavelengths are of interest because of the efficiency of optical data transmission in the infrared. Figure 9 illustrates the transmission properties of systems A and C over the entire visible and infrared region.

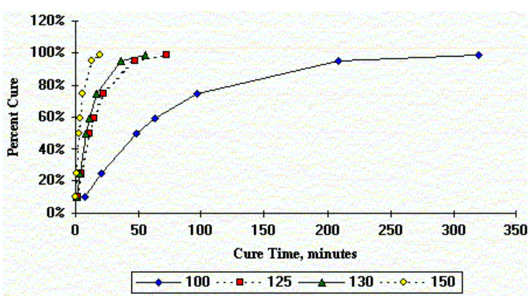

Figure 9 – Transmittance vs. Wavelength

Figure 10 examines closely the region between 1350 and 1550 nm. The cycloalipatic epoxy-anhydride system C is consistently higher in transmission than the aromatic epoxy-anhydride system A.

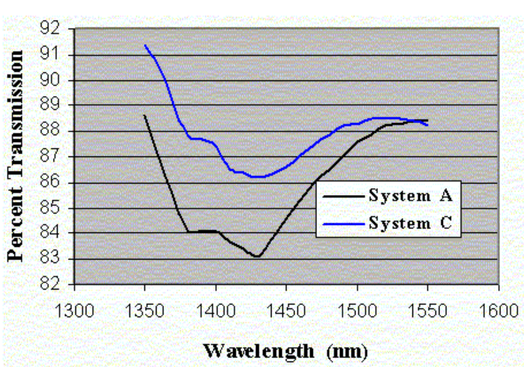

Figure 10 – Infrared Transmission vs. Wavelength

Conclusions

Critical factors in the successful use optically transparent materials are matching the properties of the encapsulant to the critical performance requirements for the application.

Test data indicates:

1. The epoxy amine system has better adhesion retention after humidity exposure than either of the anhydride cured systems .
2. The anhydride based systems have significantly better color stability during thermal aging at 100 C as evidenced by the reduced "Yellowing Index" values.
3. The aromatic epoxy systems have better water resistance than the cycloaliphatic based systems as evidenced by lower water absorption values and better clarity after exposure to high humidity, temperature and pressure.
4. The epoxy-amine system cures at lower temperatures than the anhydride based systems while the cycloaliphatic epoxy is faster curing than the aromatic epoxy.
5. All systems retain their optical clarity in 85 % RH exposure.
6. The Refractive Index is higher with the aromatic epoxy systems.
7. Both the aromatic epoxy and the cycloaliphatic epoxy systems have good optical clarity in the nfrared region up to 1500 nm.
8. The material properties of the aromatic epoxy-anhydride system, low modulus, low coefficient of thermal expansion, high elongation and high strength are the better of the three systems tested.

As with most materials there are trade-offs in properties that must be considered when making the proper selection. From the data presented, the aromatic epoxy-anhydride system offers the best overall performance of the materials tested. When lower cure temperatures or better adhesion are required, the aromatic epoxy-amine system is recommended. When very high temperatures are encountered the cycloaliphatic epoxy-anhydride system should be used.

Acknowledgements
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