Ultraviolet Radiation Curable Epoxy Resin Encapsulant for Light Emitting Diodes

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ABSTRACT: Light-emitting diodes are currently encapsulated by thermally curable epoxy resins. Thermal curing systems require long curing cycles at high temperatures. Further, because of viscoelastic behavior of the resin, the resin tends to "creep" along the connecting wires (Weisenberg effect), which causes solderability problem. The cured resin should be removed manually, which is time consuming and labor intensive. These problems are solved by the ultraviolet radiation curable systems. UV curing is an ultrafast reaction and takes place at room temperature. No creep behavior occurs due to the rapidity of the curing. The UV curing technique can result in higher productivity and energy saving than the thermal process. This article presents results on the development of UV curable formulations based on cycloaliphatic diepoxide, diglycidyl ether of bisphenol A, and epoxidized novolac induced by cationic photoinitiators. "Mixture experimental design" was employed to arrive at the optimum composition, which meets the stringent demands of performance characteristics and durability. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1048–1056, 2006

Key words: light emitting diodes; epoxy resins; ultraviolet radiation curing; cationic photoinitiators

INTRODUCTION

Light-emitting diodes (LEDs), in recent times, have replaced incandescent, fluorescent, and neon lamps due to their ability to produce high luminosity at low currents and voltages, longer service life, and their compatibility with silicon-integrated circuits.

The LED lamps are encapsulated by a transparent polymers such as epoxy resins with refractive indices in the range 1.5–1.6. Epoxy resins are also noted for its good thermal stability and mechanical properties. Typical epoxy resins currently employed for encapsulation are thermally curable two-part liquid systems consisting of either diglycidyl ether of bisphenol-A or cycloaliphatic epoxide or their combinations cured thermally by an anhydride. However, there are several disadvantages such as high-temperature cure (>120°C), and long period of curing schedules requiring stringent process control to avoid failure of the devices. The two-part system has to be precisely in stoichiometric proportions. The resin-rich composition leads to lower glass transition temperature, while the hardener-rich composition may lead to discoloration of the product. Because of the limited pot life, the resin and hardener have to be mixed just before the encapsulation process. Another aspect of great significance is the "creep" of the liquid encapsulant during the thermal curing process. The creep is due to the viscoelastic response of the curing system during the thermal cure. Before the epoxy–anhydride system reaches the glassy cured state, it remains for a considerable time in the intermediate viscoelastic state for the "Wiesenberg" effect to be displayed. Accordingly, the resin creeps and remains on the leads of the LEDs, as illustrated in Figure 1. The epoxy creeping at the leads of the LEDs can result in solderability problems. The measure currently practiced involves scrapping manually the excess cured resin sticking to the leads. This is labor intensive and time consuming. All the problems associated with the thermal curing systems are totally eliminated due to the extremely rapid UV curing process. Further, the ultrafast ultraviolet curing increases productivity and saves space.

The objective of the present study was to develop suitable UV curable epoxide resin composition for the encapsulation of LEDs and to determine their performance characteristics. UV curable systems induced by cationic photoinitiators were chosen for the present study. Three different types of epoxy resin systems were chosen for the studies, namely cycloaliphatic diepoxide, bisphenol-A epoxy resin, and epoxidized novolac. It was believed that each resin system would contribute to a specific quality of the final product and also influence the cost. The curing behavior of the various compositions was assessed by determining the properties of the UV-cured films cast from these compositions. The following properties were identified as relevant to the LED'S:

1. Pendulum hardness, which will correspond to the surface hardness of the encapsulation.
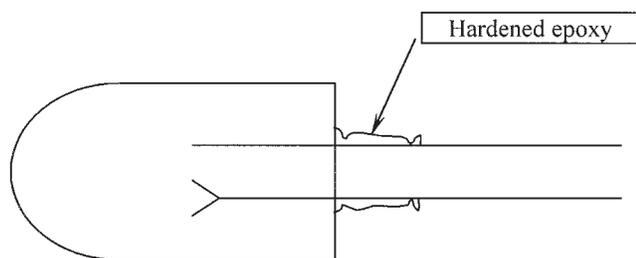
Figure 1 Illustration of epoxy creep on the leads of a LED lamp.

2. Tensile strength.
3. Yellowness index.
4. Glass transition temperature T_g.

To determine the unique composition, which would result in optimum performance characteristics of the resulting LEDs, "Mixture experimental design" was employed to determine the effect of resin composition on the properties of the UV-cured films. On the basis of these results, the actual LEDs were made in a pilot plant and tested.

As mentioned earlier, the UV curing of the epoxy resin encapsulant was carried out by employing cationic photoinitiator. A number of articles have been published[1–4] on the cationically induced UV radiation curing of cycloaliphatic diepoxide.

EXPERIMENTAL

Materials

Cycloaliphatic diepoxide (Cyracure 6110), 3,4-epoxy-cyclohexylmethyl-3,4-epoxycyclohexene carboxylate (I) was obtained from Union Carbide. Bisphenol-A-type liquid epoxy resin was obtained for Dow chemical company (DER 331). The epoxidized-novolac was obtained from Dow Chemical (DEN 431). The cationic photoinitiators UVI 6974 and UVI 6990 were obtained from Union Carbide.

Cycloaliphatic diepoxide (ERL-4221) from Union Carbide had been used as a binder with photoinitiator in cationic UV radiation cured coating. It is capable of furnishing clear, shinning, and highly rigid coating when cured with onium salt photoinitiator.
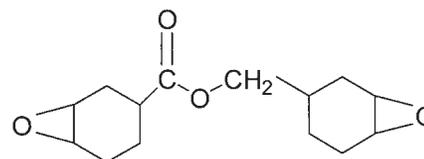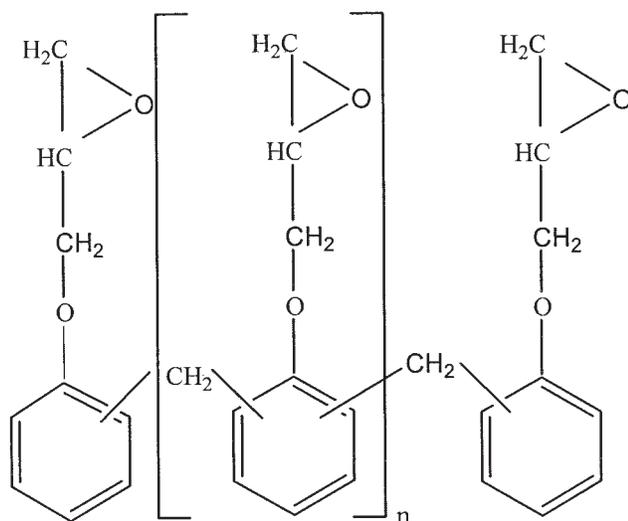

Cycloaliphatic diepoxide formula structure

(I)
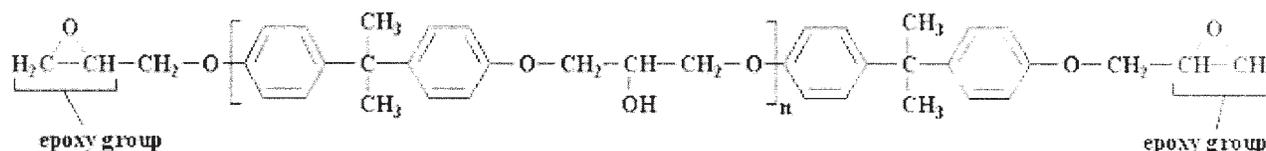
Bisphenol A Epoxy Resin


Epoxidized novolac

Equipment

Continuous UV irradiator

The curing equipment employed in the present investigation was specially designed and fabricated to ensure uniform cure of thick encapsulant. Simultaneous irradiation from both the top and the bottom was required for the complete curing of the LED device, since they have thick sections. The details of the equipment is reported elsewhere.[5]

The settings of the UV irradiator during the cure were as follows:

  i. Distance of the glass plate from the lamp was 16 in.
 ii. Line speed 1 cm/s.
iii. Lamp intensity was 125 W/in.
 iv. Total residence time in the oven was 38 s.
  v. Fan speed was 60 rpm.
 vi. The post curing condition was 15 min at 180°C.
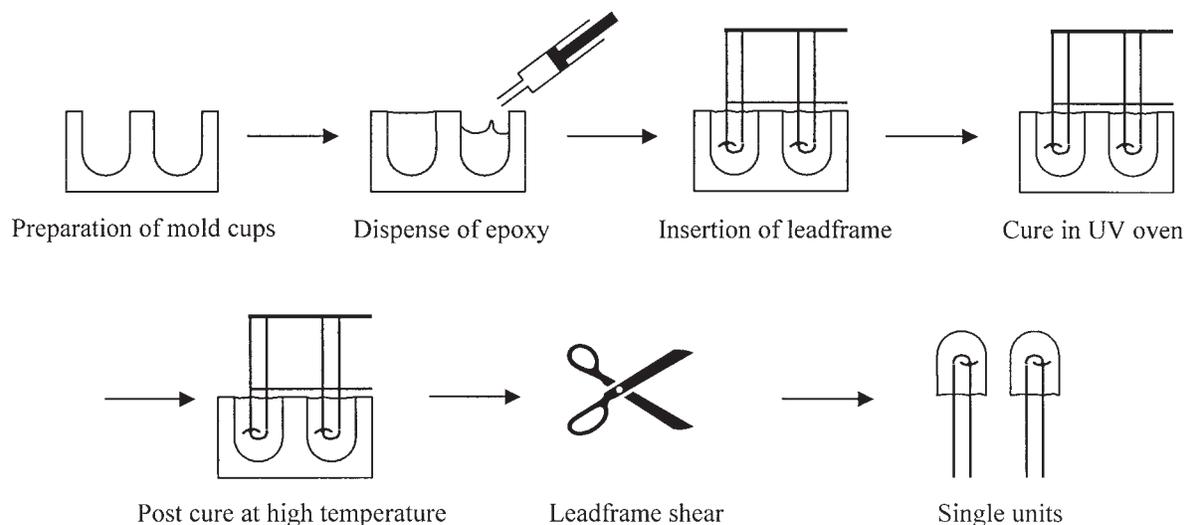
Figure 2 Production of LED Lamp.

Dynamic mechanical analyzer

The glass transition temperature of the cured samples was measured by Perkin–Elmer Dynamic Mechanical Analyzer (DMA).

Pendulum hardness tester

The extent of crosslinks caused by UV radiation was tested by determining the Konig pendulum hardness (DIN 53157) of the cured film cast on glass plate. Erichson Pendulum Tester Model 299/300 was employed.

Tensile strength of the cured films

The tensile strength of the cured films were determined in accordance with the standard ASTM D 882.

Yellowness index by gardner scale

This method covers the measurement of color of transparent liquids by comparison with arbitrary numbered glass standards by the ASTM-D1544–68(74).

Wishbone test

This is a specific component test and was performed to determine the strength of the LED lamp. The leads of the lamp were bent such that the leads are in a line. Tensile forces applied on the leads needed to break the encapsulant expressed as pound force (lbf) is recorded.

Batch UV irradiation

Batch irradiation of encapsulant of LEDs were carried out in a UV Portacure 1000 of the American Ultraviolet. UV lamp was 6 in. long, and the irradiation was carried out at 125 W/in.

Methods

Encapsulation process

Typical encapsulation of the LED with various UV-curable formulations was carried out, as shown in Figure 2. The curing of the encapsulant was carried out either in a batch irradiator (as in the case of exploratory trials) or in a continuous irradiator (in the case of systems selected for reliability studies). In the case of batch curing, the irradiation was possible only from the top. To ensure that the mold cup containing the UV-curable resin-mix is uniformly exposed to radiation, irradiation procedure, as shown in Figure 3, was adopted in the case of batch process. On the other hand, in the continuous process, the curing equipment was designed for uniform exposure to radiation from top and bottom.

Screening experiments

On the basis of several exploratory investigations, the following systems namely, mixture of cycloaliphatic, bisphenol-A, and novolac together with polycaprolactone polyol warranted detailed studies.

Experiments with cycloaliphatic epoxide, DGBA epoxy, and epoxidized novolac

To evaluate the performance and optimize the compositions suitable for LED encapsulation, "mixture
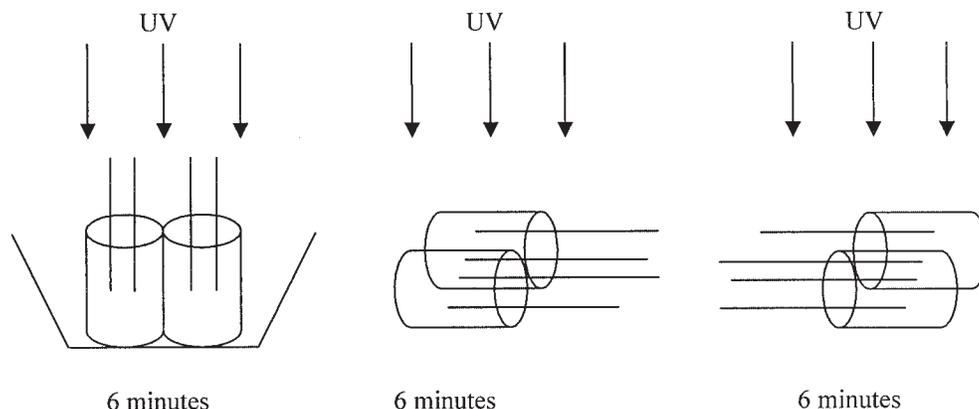
Figure 3 Curing procedures using American Ultraviolet.

experimental design"[6−8] was adopted. The objective of the experimental design was to (a) develop the mathematical models that quantify the effect of compositional variables on the product performance, (b) identify the interaction of factors that affect the product/process, and (c) interpret the results using response surface methodology and arrive at the optimum conditions for the best performance.

For this purpose, "D-Optimal design" available in the Design Expert software[9] was employed, which enabled the appropriate choice of functional relationships to be chosen from among the "canonical polynomials" given in Table I. The graphical representation of the data and optimization were also possible from the software.

Accordingly, 14 different three-component mixtures distributed in the simplex space were altogether generated by the software. These data points are shown in Table II. Twenty percent caprolactone polyol (TONE 0310) and 1% triphenyl hexafluoro antimonate (Cyracure 6974) were also incorporated uniformly to each of the aforementioned compositions.

RESULTS AND DISCUSSION

Both the direct as well as the synergistic effect of the compositional variables on the following properties of the UV films as well as cured LEDs were determined:

1. Pendulum hardness.
2. Tensile strength.
3. Glass transition temperature.
4. Yellowness index.

These results are shown in Table II.

Effect of compositional variables on the pendulum hardness

The following quadratic model adequately fitted the data for pendulum hardness with statistically insignificant "lack of fit."

$$\text{Hardness} = 154.66x_1 + 150.77x_2 + 132.57x_3$$
$$+ 116.34x_1x_2 + 132.32x_1x_3 + 75.77x_2x_3 \quad (1)$$

where x_1 = cycloaliphatic epoxide; x_2 = bisphenol-A epoxide; x_3 = epoxidized novolac.

Since the coefficient of $x_1 > x_2 > x_3$, cycloaliphatic epoxide exerts the highest influence on the hardness of the cured film. In addition, binary blends are synergistic in all cases.

The results are shown as contour plots in Figure 4. It can be noticed that a maximum hardness can be obtained at the following composition: forty-one per-

TABLE I
Canonical Polynomials

Linear	$E(Y) = \sum_{i=1}^{q} \beta_i x_i$
Quadratic	$E(Y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{q}^{i=1} \sum_{i<1}^{i<j} \beta_{ij} x_i x_j$
Cubic	$E(Y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \sum_{i<j}^{q} \beta_{ij} x_i x_j + \sum_{j=1}^{q} \sum_{i<j}^{q} \delta_{ij} x_i x_j (x_i - x_j) + \sum_{k=1}^{q} \sum_{j<k}^{q} \sum_{i<j}^{q} \beta_{ijk} x_i x_j x_k$
Special Cubic	$E(y) = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \sum_{i<j}^{q} \beta_{ij} x_i x_j + \sum_{k=1}^{q} \sum_{j<k}^{q} \sum_{i<j}^{q} \beta_{ijk} x_i x_j x_k$

TABLE II
Experimental Compositions According to D-Optimal Mixture Design

| Std	Run	Block	Factor A: cycloaliphatic	Factor B: DGEBA	Factor C: novolac	Response pendulum hardner	Response tensile strength (kg/ cm^2)	Response T_g (°C)	Response yellowing index Gardner
9	1	1	0.17	0.17	0.67	179	78.9	70	9.55
11	2	1	0.00	1.00	0.00	152	213.3	66	9.04
12	3	1	0.50	0.00	0.50	175	88.32	141	8.89
6	4	1	0.00	0.00	1.00	132	77.8	5	10.35
4	5	1	0.00	1.00	0.00	149	191	63	8.63
10	6	1	0.33	0.33	0.33	179	76.1	86	9.15
1	7	1	1.00	0.00	0.00	153	50	153	8.91
5	8	1	0.00	0.50	0.50	154	107.2	65	9.19
14	9	1	0.00	0.00	1.00	130	109.43	65	10.51
7	10	1	0.67	0.17	0.17	176	57.8	130	8.05
2	11	1	0.50	0.50	0.00	181	56.1	84	8.6
3	12	1	0.50	0.00	0.50	175	100.5	135	9.21
8	13	1	0.17	0.67	0.17	179	106.1	72	9.07
13	14	1	1.00	0.00	0.00	159	66.7	158	8.91

cent cycloaliphatic diepoxide, 26% diglycidyl ether of bisphenol–A, and 34% epoxidized novolac.

The effect of individual resin on the hardness can be seen from trace plots (Fig. 5). The vertical axis is the predicted hardness values, and the horizontal axis is the incremental change made in each component from the standard composition namely the centroid. The strong nonlinear effect of all the three resin systems on the hardness can be observed. The film hardness increases initially as the cycloaliphatic diepoxide (x_1) increases, and after reaching a maximum value, the hardness decreases. The cycloaliphatic epoxide resins have more compact structure than the bisphenol A or the epoxidized novolac types and thus gives cured products in which the crosslinks are closer together. After reaching a maximum, the hardness values decrease, since the film hardness is very sensitive to the influence of the other two resins in which the crosslink density are not as close as in the case of cycloaliphatic epoxide.

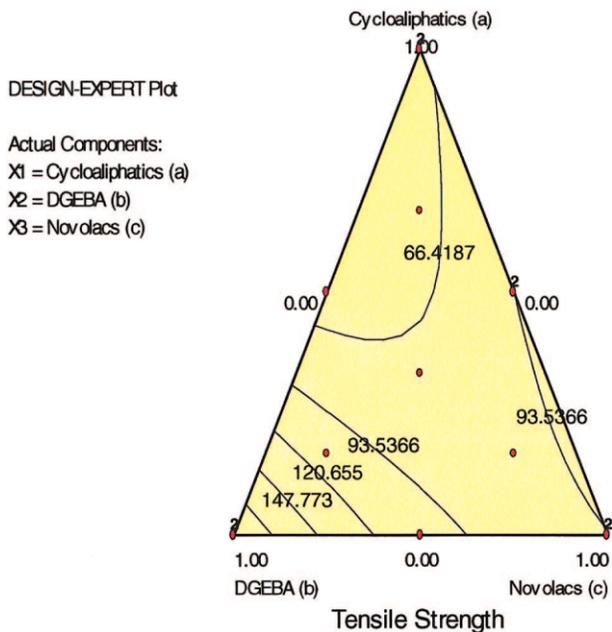### Effect of compositional variables on the tensile strength of the films

The following quadratic model adequately represents the observed data of Table II.
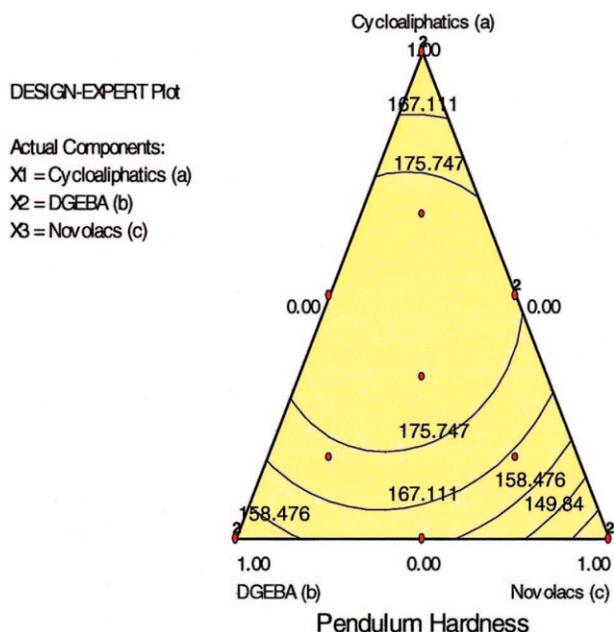
Figure 4 Effect of composition on hardness-contours. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
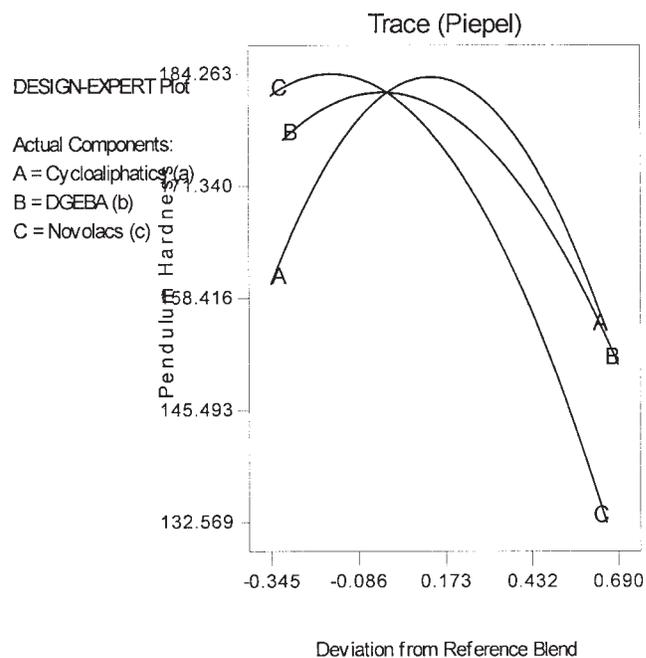
Figure 5 Trace plots for hardness.

Figure 6 Effect composition on tensile strength. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 Trace plots for tensile strength.

$$\text{Tensile strength} = 58.72x_1 + 202.01x_2 + 92.88x_3$$
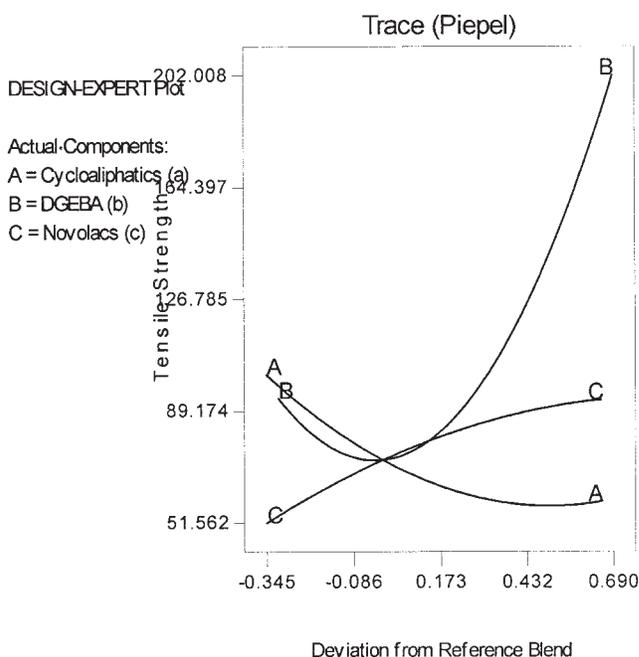$$- 300.46x_1x_2 + 70.37x_1x_3 - 173.18x_2x_3 \quad (2)$$

Because $x_2 > x_3 > x_1$, it can be concluded that the cycloaliphatic epoxide (x_1) produces films with lowest tensile strength. Furthermore, coefficient of x_{13} is positive indicating "synergistic blending" of cycloaliphatic epoxide and novolac epoxide. Blending of cycloapliphatic epoxide (x_1) and the diglycidyl ether of bisphenol A (x_2) is antagonistic due to negative coefficient. Contour plot of eq. (2) (Fig. 6) shows that maximum tensile strength can be obtained with 35% cycloaliphatic diepoxide (x_1), 33% diglycidyl ether of bisphenol A, and 33% epoxidized novolac.

It can be noticed (Fig. 7) that after reaching a maximum tensile strength value, the tensile strength decreases on further increase. As stated earlier, the tensile is also very sensitive to the influence of the other two resins in which the crosslink density are not as close as in the case of cycloaliphatic epoxide.

## Effect of compositional variables on the glass transition temperature

The following quadratic model adequately represents the experimental data:

$$T_g = 156.97x_1 + 65.91x_2 + + 65.59x_3 - 109.5x_1x_2$$
$$+ 98.46x_1x_3 - 26.47x_2x_3 \quad (3)$$

Because $x_1 > x_2 > x_3$, the T_g value is essentially determined by the quantity of the cycloaliphatic diepoxide (x_1) in the ternary mixture. All the binary mixtures containing component x_2 (diglycidyl ether of bisphenol A) have antagonistic blending effect. The quadratic model is represented as contour plots in Figure 8. The optimum composition as computed is 97% cy-
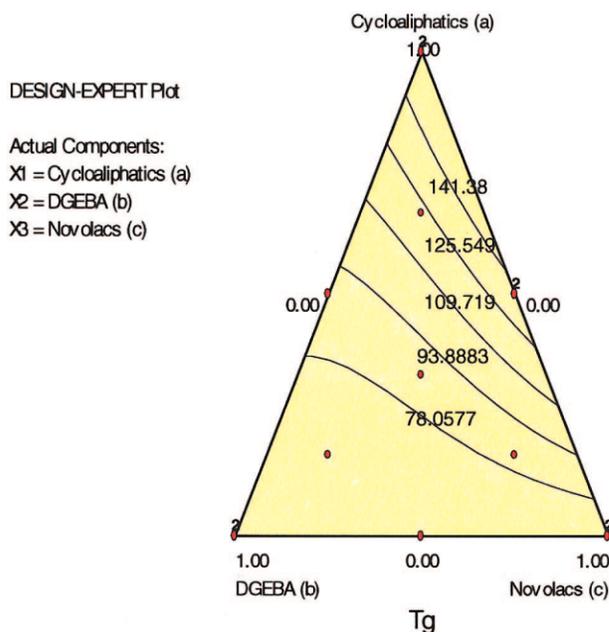
Figure 8 Effect of composition on T_g-contours. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 9   Trace plots for T_g.

Figure 10   Effect of composition on yellowness index-contours. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
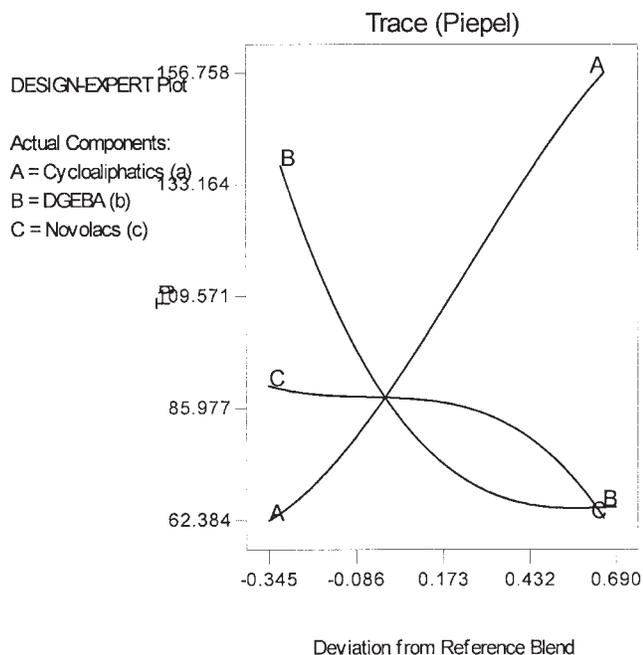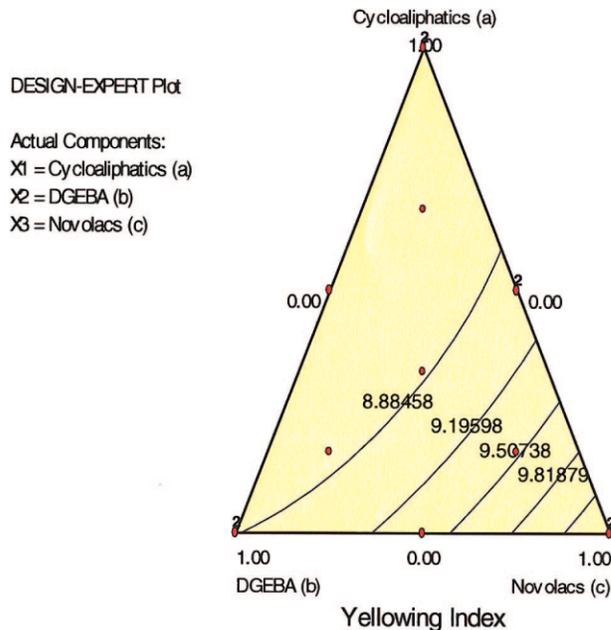
coaliphatic diepoxide and 3% epoxidized novolac. The trace plots for the T_g (Fig. 9) shows that cycloaliphatic resin has a very strong effect. This is again due to the compact structure and closeness of the crosslinks of the cured material leading to higher heat distortion temperature[10] than the bisphenol A-based resins.

Effect of compositional variables on yellowness index

The data fits a quadratic model given below

Yellowness index $= 8.89x_1 + 8.84x_2 + 10.41x_3$

$$- 0.42x_1x_2 - 2.18x_1x_3 - 1.07x_2x_3 \quad (4)$$

Thus, epoxidized novolac resin produces films with the highest yellowness index. The cycloalipahtic epoxide and DGEBA-based resins produce cured product with lesser yellowness index, and hence, desirable to produce acceptable products. The effect of the compositional variables on the yellowness index is shown as contours plots in Figure 10.

A composition consisting of 83% cycloalipahtic diepoxide and 17% of DGEBA-based epoxy resin should give a cured product with minimum yellowness index within the range of composition studied.

From the trace plots of yellowness index (Fig. 11), it can easily be observed that novolac resin exerts a very strong positive effect due to aromaticity of the epoxidized novolacs. The epoxidized novolac employed is based on phenol, which normally contains oxidized products that impart color.[11] Further, the novolac res-

ins may contain traces of quinine methides, which may impart dark color to the resin[10] and hence not desirable if acceptable clarity in the cured products is essential. Addition of cycloaliphatic is desirable. DGBA-based resin does not influence the yellowness index.
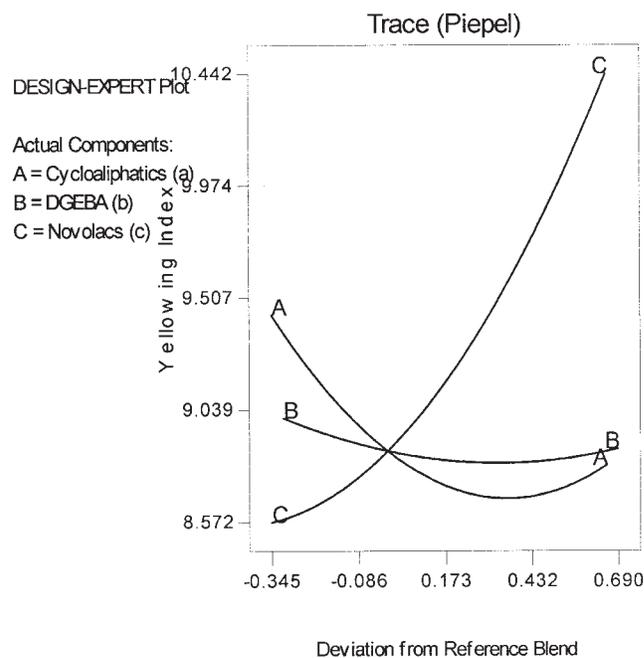

Figure 11   Trace plots for yellowness index.

TABLE III
Suggested Solutions for the Resin-Optimized Formulation

Solution	Cycloaliphatic resin	DGEBA resin	Epoxidized novolaks	Predicted response			
				Hardness	Tensile	T_g	Yellowing
1	0.73	0	0.27	174.6	1.37	151	8.7
2	0	1	0	150.8	3.64	66	8.7
3	0.1	0.9	0	162.1	2.92	65	8.7

Optimization of composition with compromise of different properties and reliability tests on the optimum composition

When several process variables control a wide range of properties of a product, a compromise or trade off is always inevitable. A scale of importance (constraint) is assigned to each property based on practical considerations, thus ranking in the present case is: T_g > yellowness > hardness > tensile strength. Based on this, optimization of suitable composition was attempted to maximize the following properties namely T_g, tensile strength, and hardness and minimize the yellowness index.

Table III gives the software-derived solutions. Among the three desirable solutions, only one (solution 1) was practically feasible. Solutions 2 and 3 had the difficulty of improper cure. This shows that the mathematical solutions obtained from the software may not truly be feasible in real applications. However, the results from the software could provide several alternate solutions to investigate further for a final practical solution.

From the various response functions (eqs. (1)–(4)), it is obvious that the film-hardness was mostly contributed by cycloaliphatic and DGEBA resins while the DGEBA resins contributed to tensile strength. Antagonistic blending effect of DGEBA resins and epoxidized novolac resin on the tensile strength exists as shown by "−3.66 BC" term in the response equation for tensile strength. Further, epoxidized novolac also causes high discoloration (high yellowness index) to the system. High-T_g is favored only by cycloaliphatic resins because of their more compact structure than the bisphenol A-epichlorhydrin resins and this in turn gives products in which the crosslinks are closer together.

Thus, the final solution named "solution 4" was adopted, and the predicted responses are shown in Table IV. These responses were compared with two control formulations, one consisting of novolac resin and the other consisting of 50% DGEBA and 50% cycloalipahatic epoxide.

To improve the color of the cured components, it was decided to add antioxidants, since they would prevent the oxidative degradation during the post cure. Several antioxidants were tried, and triphenyl phosphite was found to be very efficacious. Accordingly, triphenyl phosphite was incorporated in formulations corresponding to solutions 4, 5, and 6, shown in Table IV. The optimization of the quantities of antioxidants and photoinitiators were carried out by a separate set of experiments so as to maintain optimum cure response. This would ensure in turn optimum cure rate and crosslink density of the final product. Initial experiments also showed that 10% caprolactone polyol as a flexibilizer was ideal. Based on these experimental facts, the final compositions for reliability experiments contained caprolactone polyol, antioxidants, and photoinitiator in accordance with the amounts given in Table V.

All the three formulations, given in Table V, were cured in the mold cups for lamps, and the T_g, "wishbone" test, and the Gardner yellowing index values were recorded and shown in Table VI.

Reliability test, temperature cyclic test, and operating life test

All the three formulations listed in Table VI were dispensed into the moldcups inserted with real electronic circuits and diodes. The following tests were performed on the LEDs cured with different formulations, according to the internal standard test methods at the Agilent laboratories.

1. Reliability test.
2. Temperature cyclic test.
3. Operating life test.

Two other types of commercial encapsulations were tested in parallel as a control. These results showed that the UV-cured components behaved identically as the control.

TABLE V
Formulations with Antioxidants

Solution	Hexafluoroantimonate (%)	Triphenyl Phosphite (%)
4	0.5	0.5
5	1	1
6	1	1

TABLE IV
Formulations and Predicted Properties of the Resulting Polymer

Solution	Cycloaliphatic resin	DGEBA resin	Epoxidized novolaks	Predicted response			
				Hardness	Tensile	T_g	Yellowing
4	0.73	0.27	0.00	176.55	0.34	110.80	8.74
5	0.39	0.39	0.22	183.84	1.31	90.43	8.88
6	0.50	0.39	0.00	181.80	0.95	84.07	8.73

CONCLUSIONS

UV-curable formulations based on a mixture of cycloalipahtic diepoxide, bisphenol A epoxide, and epoxidized novolac were successfully developed in the laboratory and tested in a pilot plant scale for encapsulating light-emitting diodes. UV curable process was found to be superior to the thermal curing systems currently employed in the electronic industry due to ultrafast reaction, avoidance of creep of the resins on the connecting wires, saving of the space and energy. Cationic photoinitiators were found to be ideal for effecting the UV curing. Optimization of the composition of the resin system for the encapsulant was achieved by employing "Mixture experimental design," an efficient statistical method. Functional relationship between the response variables and the compositional variables was determined. From these mathematical functions represented as response surfaces and perturbation plots, the effects of the individual resins on the final properties (responses) were interpreted on a molecular basis. The system involved multiple responses (T_g, tensile strength, hardness, and yellowness index), and it was not possible to maximize all the responses simultaneously. A compromise or "trade off" of some of the properties was needed to obtain overall acceptable final performance characteristics of the LEDs. This involved carrying out "optimization with constraint" and was achieved by the use of the Design Expert Software.

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TABLE VI
Laboratory Scale Test Results

Solutions	T_g (°C)	Wishbone strength (lbf)	Gardner scale
4	141	3.8	2
5	173	5.5	4
6	180	6.6	4