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New flexibilized diallyl phthalate resins for encapsulating electronic display devices

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This research investigated diallyl phthalate encapsulating resins as a replacement for the moisture sensitive epoxies now used in light emitting diode (LED) displays. Consideration of display resin requirements led us to select for study the diallyl phthalate (DAP) polymer thermosetting system, which had most of the performance properties desired, but was excessively brittle. Flexibilizing co-monomers were evaluated including both vinyl and allylic types. A promising co-polymer of DAP with lauryl methacrylate (80/20) was defined that had most of the physical and performance characteristics desired, plus attractive inherent light diffusing properties. Allylic co-monomers such as diallyl adipate and triallyl citrate also formed interesting co-polymers and ter-polymers with DAP. DAP/epoxy interpenetrating polymer networks were also explored and found to be most suitable for LED application.

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1. Introduction

Casting is a process in which a plastic part is formed by pouring a liquid resin into a cavity (mould), where the monomer is allowed to polymerize to a solid material. The polymerized solid material is then removed from the mould. In encapsulation, the electrical or electronic component is surrounded or enclosed by a material, and the entire assembly need not be completely surrounded. Potting is similar to encapsulation; often the two terms are used interchangeably.

Plastic casting started about 1930 with phenolic resins. Potting and encapsulation of electrical units have been practiced since the discovery of electricity. Epoxies and polyesters are the most commonly used encapsulation materials. Improvements in these materials have resulted in greater utilization of electrical and electronic parts and equipment.

Electronic circuitry and housings containing electronic assemblies are encapsulated in plastics to provide electrical insulation, protection from environmental effects and handling abuses; and mechanical support to enhance the life cycle of such components.

Epoxy resin systems are the materials used most frequently in the electronics industry for encapsulation; among their advantages for use are their ease of handling, their broad application range in most extreme environments, their low polymerization shrinkage, and their good adhesion.

Epoxy-type encapsulating materials have several limitations in their use. Their most serious problem is the loss of mechanical properties after exposure to elevated temperature/high humidity environments. Another problem with the epoxies is their moisture sensitivity during the encapsulation of electronic parts. Absorbed moisture in the uncured resin can dramatically alter curing behaviour and hence the final properties.

Silicones, polyesters and polyurethanes are other materials used for encapsulation. The advantages and disadvantages of these widely used encapsulation materials are presented in Table I.

The encapsulating resin should contain chemical moieties that produce high heat and moisture resistance. Let us now consider what properties are obtained from specific chemical groups in a resin (see Table II). For low moisture absorption, a resin should contain low hydroxyl, amide, and ether linkages and high aromatic and alkyl groups.

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TABLE I Advantages and disadvantages of commonly used materials

Material	Advantages	Disadvantages
Epoxies	Wide range of formulation Low shrinkage Excellent adhesion	Moisture sensitivity Reversion on prolonged exposure to high temperature and humidity Loss of mechanical properties in elevated temperature/high humidity environments
Polyesters	Wide range of formulation Low cost Short cure cylce	High shrinkage High exotherm Thermal shock is poor
Silicones	Low exotherm Wide range of temperature usage (– 75° C to + 260° C) Flexible	High cost Poor adhesion to most materials Poor mechanical properties
Urethanes	Abrasion resistance Tough Flexible	Toxicity Limited temperature range (95° C maximum) Sensitive to moisture (reversion to liquid state)

For good adhesion properties it is important to have some hydroxyl, carboxyl, or nitrogen in the resin. A judicious choice of the various groups in a resin can lead to an encapsulation resin that will provide high retention of mechanical properties during prolonged exposure at 150° C in a very humid environment.

This paper describes the exploratory and development work that was performed on flexible diallyl phthalate (DAP) and DAP/epoxy interpenetrating polymer network encapsulating resins specifically useful for light emitting diodes (LED).

TABLE II Chemical groups and the physical properties associated with them for a resin

Group	Property obtained
Aromatic	Thermal and mechanical stability, stiffening effect
Cycloaliphatic	Thermal and mechanical stability, stiffening effect
Alkyl	Moisture and chemical resistance
Alkyl, long chain	Moisture resistance, plasticization, and toughening effect
Ether linkages	Chemical resistance, increased flexibility, and moisture sensitivity
Amide	Toughening and adhesion
Hydroxyl	Adhesion, moisture sensitivity
Di- and multi-functional vinyl	Curing, three-dimensional network. Increased thermal stability but also reduced toughness (increased brittleness)

2. Exploratory work on diallyl phthalate encapsulating resin

2.1. An ideal potting resin

An ideal potting resin should satisfy as nearly as possible the following requirements:

(a) High refractive index ($n_D^{25} > 1.50$ is essential and a value of 1.60 or greater is desirable for higher light output).

(b) Good form stability at elevated temperature. The resin should be capable of withstanding ~ 85° C/85% relative humidity (r.h.) for prolonged time periods.

(c) Good high-temperature performance, as well as some degree of flexibility (toughness-with-rigidity), so as to relieve strains in the LED part resulting from temperature variations.

(d) Hydrolytic stability and low moisture sensitivity.

(e) Good clarity. (However, if a resin component functions as a diffuser in a controlled manner, any self-diffusing functionality may be an asset.)

(f) Good initial colour, and no or only slight colour drift during service life.

(g) An easy and straightforward polymerization (curing) process.

(h) No gaseous products produced during curing.

(i) Low shrinkage ($< 8.0\%$) in undergoing the transition from the liquid state to the solid cured state.

(j) A tough and preferably infusible cured resin.

(k) No interference with the delicate electronic parts by the resin during manufacture and service life.

(l) Good adhesion to the display cap (housing) and good wetting of the metallic components.

(m) Resistance to thermocycling over the extreme temperature conditions anticipated in use (e.g. 0 and 100° C).

(n) Resistance to polymerization or de-polymerization under normal ambient conditions. This will nearly insure constant physical and electrical characteristics of the resin throughout the entire life of the LED.

(o) Consistency in replication of properties under identical processing conditions so as to reduce the proportion of rejects formed in production.

(p) Non-corrosive.

2.2. Flexibilized diallyl phthalate resin

There are only two resins which are clear, easily polymerizable, and have a high refractive-index: DAP and styrene. Besides having a high refractive index, DAP has other advantages; it has a good colour, excellent heat resistance and form stability at elevated temperatures, good hydrolytic stability, excellent electrical properties, low vapour pressure, and is free from handling hazards.

Styrene, having a high vapour pressure, requires long polymerization cycles and is limited to a closed processing system.

The excellent properties of polymerized diallyl phthalate are well known. Neat DAP monomer, however, tends to crack during polymerization. To avoid cracking, a mineral or fibre filling is commonly used in DAP moulding compounds. Both during and after curing the mineral or fibre functions as a cushion and terminator of microcracks. In a clear potting resin, fibre or mineral filling is prohibited unless the filler has the same refractive index as the resin. Therefore, the use of a plasticizing monomer appeared to offer a possible means of eliminating cracking while retaining optical clarity.

Fujio *et al* [1] report co-polymerization of DAP (80–90 mol%), acrylates (10–70 mol%), and other vinyl monomers (0–60 mol%) by emulsion polymerization to give latexes useful for coatings, adhesives, and mouldings. A U.S. patent [2] describes moulding compounds that retain high impact resistance over a range of temperatures. They are prepared from 45–95 wt% methyl methacrylate, 3–15 wt% dialkyl phthalate, and 3–40 wt% ethylene co-polymer and cured in two stages at 55–80° C and 120° C in the presence of mixed free radical initiators. Other work on DAP-related polymerization is described by Lorkowski and Pfeiffer [3], Thomas [4], Yaralov *et al.* [5] and Matsumoto and Oiwa [6].

On polymerization, DAP yields a cross-linked structure to give a heat- and chemical-resistant product of outstanding electrical resistivity and dielectric strength. Unmodified DAP potting resin is too brittle and tends to crack. Work was performed to determine which modifying co-monomers could be used to plasticize DAP so as to produce an outstanding potting resin. The co-monomers tested were: styrene, methyl methacrylate (MMA), butyl methacrylate (BMA), *n*-octyl methacrylate (OMA), 2-ethylhexyl methacrylate (EHMA), isodecyl methacrylate (IDMA), lauryl methacrylate (LMA), stearyl methacrylate (SMA), hydroxypropyl methacrylate (HPMA), diallyl adipate (DAA), and triallyl citrate (TAC).

2.2.1. Co-polymerization of DAP with alkyl methacrylates

The reactivity ratios (r_1, r_2) for butyl methacrylates to polymerize with DAP are not known but can be calculated from Q (a measure of the resonance stability of a monomer) and e (polar factors) values. Using this procedure we have calculated $r_1 = 2.78$ and $r_2 = 0.0332$. These unfavourable ratios r_1 and r_2 make the low-temperature preparation of uniform co-polymers difficult or impossible, except in very specific, narrow ranges of composition. However, at higher polymerization temperatures the difference in monomer reactivity ratios will become less and a somewhat wider range of co-polymers can be made. This conclusion has been drawn from temperature dependence and activation energy considerations.

2.2.2. Co-polymerization of DAP with styrene

Bledzki *et al.* [7] reported successful bulk polymerization of styrene and DAP using benzoyl peroxide initiation and continuous mixed monomer feed. This procedure would not be applicable to single charge bulk casting. Ito *et al.* [8] reported that DAP could be used to cross-link styrene using an azo catalyst. We have found experimentally, however, that DAP and styrene do not co-polymerize or even homo-polymerize in the presence of each other even under vigorous free radical initiation conditions. The two monomers appear to inhibit the polymerization of each other and this is attributed to fundamental differences in the mechanisms of vinyl and allylic polymerization.

2.3. Development of DAP encapsulating resins

2.3.1. Selection of co-monomer

MMA, because of its low boiling point and high vapour pressure, was eliminated early in the work. BMA polymerizes quite readily with DAP but proved too volatile to be useful in open vessels. EHMA did plasticize DAP but some monomer loss was encountered during curing. IDMA, LMA and SMA were found to polymerize satisfactorily with DAP. On co-polymerization with DAP, IDMA gave clear products and LMA and SMA gave resins varying from clear to opaque depending on the amount of co-monomer and on the polymerization conditions. At an equal level, SMA produced a greater opacity in the DAP resin than did LMA. Thus, LMA offers a better plasticizing and diffusing co-monomer than SMA in the DAP resin. LMA was therefore selected for co-polymer optimization.

Various ratios of DAP to LMA, different types and amounts of catalyst, and various methods of preparing the potting resin were investigated. The preferred mixture was found to be 80 parts by weight DAP, in the form of a viscous syrup, and 20 parts by volume LMA monomer.

Another composition which was studied in some detail was based on DAP/EHMA/HPMA (85 wt %/10 wt %/5 wt %). Hydroxypropyl methacrylate co-polymerizes readily with DAP, and it was thought that the hydroxyl groups would contribute to the increased adhesion.

2.3.2. Syrup preparation methods

The very early work on flexibilized DAP was performed using mixtures of monomers. It was found that the use of syrup was superior to the direct use of a monomeric mixture.

Three methods of syrup preparation were investigated: In bottle polymerization, viscosity was difficult to control from batch to batch, and occasionally gelation was encountered during syrup preparation; another disadvantage of the bottle method is that the prepared syrup drifts up in viscosity due to catalyst residue remaining in the syrup. Use of solid DAP pre-polymer with DAP monomer produced straw coloured syrups, and therefore this method of syrup preparation was abandoned. The resin kettle method was found to be a reproducible resin preparation method.

The kettle method was found to be most suitable for the preparation of DAP/EHMA/HPMA syrup from the monomer mixture. DAP/LMA syrup was made by first preparing a high viscosity DAP syrup and then diluting it sequentially with LMA monomer. A slightly more uniform co-polymer was made from DAP monomer with a delayed and slower addition to LMA to a heated and stirred DAP. A 5-litre flask was charged with 1600 g DAP monomer (optical grade) and 3.29 g benzoyl peroxide. The polymerization, conducted under nitrogen blanket and with stirring, was performed at 80 ± 2° C. In about 5 h, the viscosity of DAP reached approximately 10 Pa sec. At this point, the contents were quickly cooled by a cold water bath to less than 45° C and then 400 g lauryl methacrylate was sequentially added and mixed. This DAP/LMA (80 wt %/20 wt %) syrup of about 1.13 Pa sec viscosity was stored in either 4 or 8 fl oz glass bottles.

2.3.3. Encapsulation with DAP/LMA syrup

2.3.3.1. Catalyst type and concentration. A number of catalysts, alone or in combination, were investigated at various levels for the DAP/LMA (80 wt %/20 wt %) potting resin. It should be pointed out that catalyst(s), catalyst level(s) and curing cycle(s) are all interdependent in providing final results.

Vazo* catalysts, as typified by azobisisobutyronitrile and various Luazos from Pennwalt, are low-temperature catalysts and were not found to be suitable for DAP/LMA and other DAP potting resins. Peroxide catalysts (e.g. benzoyl peroxide and dicumyl peroxide) looked more promising.

With a combined low and high temperature curing cycle (e.g. 90° C followed by 125° C) it was found essential to use a combination of benzoyl peroxide (Bz_2O_2) and dicumyl peroxide (DiCup).

Catalyst levels of 0.03, 0.06, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 1.0% each of benzoyl peroxide and dicumyl peroxide were investigated. Low levels of catalysts were less than satisfactory in that complete curing was not achieved. Three-

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*Du Pont Ltd.

tenths of a per cent each of Bz_2O_2 and DiCup were found to be most effective for the low and high curing temperature cycles. The higher catalyst levels produced problems with cracking during or after curing.

From a production view-point, a programmed curing cycle is not desirable. It was found possible to effect curing of DAP/LMA (80 wt %/20 wt %) at a single 125° C curing temperature without cracking during curing and after polymerization. At 125° C, a combination of 0.3% each of Bz_2O_2 and DiCup was found suitable. Later, it was experimentally shown that curing at 125° C could be best effected with 0.3% DiCup only. Elimination of benzoyl peroxide also reduced resin shrinkage.

The combination low and high temperature cure lasted for 24 h. The curing time was brought down to 12 h by using a 125° C curing temperature and 0.3% DiCup. Increasing the DiCup level to 1.0% reduced the curing time to 4 h but caused slightly more shrinkage of the resin.

2.3.3.2. De-bubblers evaluated. In the encapsulation process, de-gassing is essential to assure filling of the segments of "eight" (display window, 8). Degassing also eliminates any accidental air bubbles remaining in the display cap cavity. Although the surface activity of LMA provides de-bubbling in DAP/LMA (80 wt %/20 wt %) syrup, inclusion of 0.1 wt % Mazu DF 110S (1% silicone de-foamer from Mazer Co.) was seen to help both in degassing and in modifying other surface characteristics.

2.3.3.3. Stabilizers. Kovar integrated circuit frames, although flash-coated with silver, tend to discolour the DAP potting resin during curing. This undesirable discolouration is attributed to generation of unsaturated aldehydes which, on complexing with Fe^{++} (from Kovar), results in a brown discolouration.

To minimize or eliminate the discolouration caused by the aldehyde, a room- or low (70° C)-temperature reducing agent would seem to be the answer. Hypophosphorous acid (HPA), at a level of 500 ppm was found effective in completely eliminating the discolouration.

2.3.3.4. Catalyst concentration and cycles. The following curing cycles were developed for DAP/LMA (80 wt %/20 wt %) and other DAP syrups.

(a) Slow cycle (in air and using 0.2 wt % each of Bz_2O_2 and DiCup catalyst): 90° C/12 h + 130° C/12 h.

(b) Medium fast cycle (in nitrogen and using 0.2 wt % each of Bz_2O_2 and DiCup catalyst): 90° C/2 h + 100° C/1 h + 110° C/1 h + 120° C/2 h + 130° C/2 h (total curing time = 8 h).

(c) Medium fast cycle (in air and using 0.3 wt % each of Bz_2O_2 and DiCup): 125° C/12 h.

(d) Medium fast cycle (in air and using 0.3 wt % DiCup): 125° C/12 h.

(e) Fast cycle (in air and using 1 wt % DiCup): 125° C/4 h.

Of these, the medium fast cycle in air using 0.3 wt % DiCup and cured at 125° C/12 h seemed best suited for the DAP/LMA (80 wt %/20 wt %) syrup. Bz_2O_2, in the combination catalyst (0.3 wt % each of Bz_2O_2 and DiCup), did not contribute to curing at 125° C. In fact, a slight increase in shrinking was observed in going from syrup to cured resin.

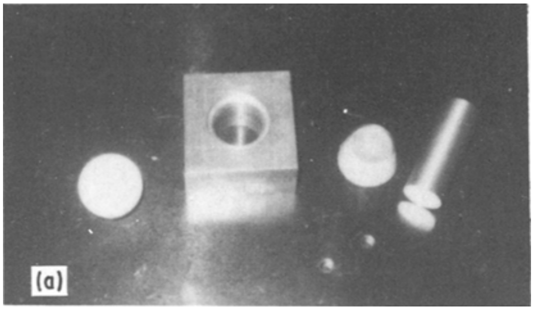
2.3.3.5. De-taping. One aim of the potting resin work was to incorporate the feature of de-taping the display units (removing the back adhesive tape which holds the liquid resin in the perforated cap) in 3 h. To determine if early de-taping of displays potted with DAP/LMA and DAP/EHMA/HPMA is possible, a statistically designed experiment was run. Catalyst level and curing temperatures were investigated as a function of de-taping time. It was concluded that DAP/EHMA/HPMA resin does not lend itself to early de-taping, whereas such de-taping is both possible and practical with DAP/LMA. DAP/LMA could be de-taped after 125° C/3 h but DAP/EHMA/HPMA could not for the following two important reasons:

(1) DAP/LMA cures at a faster rate than DAP/EHMA/HPMA, at least initially;

(2) LMA, due to the fatty nature of the lauryl group, has low surface energy, particularly in a semi- and fully-cured state and, because of this inherent nature, smooth-surfaced parts were obtained with DAP/LMA but not with DAP/EHMA/HPMA.

2.3.3.6. Effect of syrup viscosity on de-taping and curing. The effect of the DAP/LMA syrup viscosity on de-taping and curing was studied. It was concluded that the viscosity of the DAP/LMA syrup should be in the range of 0.85 to 1.15 Pa sec.

Several DAP/LMA syrups were evaluated with 0.3 wt % benzoyl peroxide, 0.3 wt % DiCup,



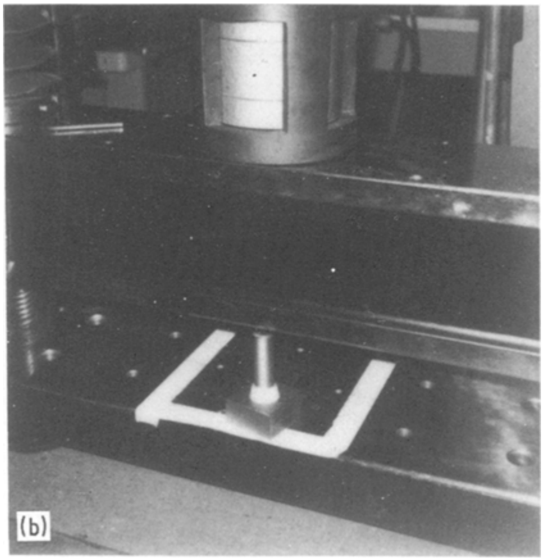


Figure 1 Potting resin/plastic material adhesion testing: (a) shows the accessory and (b) shows the actual testing on an Instron machine.

0.1 wt % De-foamer 110S, and 0.1 wt % hypophosphorous acid. The curing was done at 125° C; three detaping times (2, 3, and 4 h) were investigated. In each case, the freed units were cured to completion at 125° C for a total of 12 h. Syrups of viscosities 0.86 and 1.15 Pa sec produced parts that, at least visually, appeared to be the best, free of any surface defects. The lowest viscosity syrup (0.43 Pa sec) gave parts with slight surface striations. Detaping with each syrup and at every de-taping time was complete and without loss of any potted resin to the tape. For production, a de-taping time of 3 h would be the most practical.

2.3.3.7. Thermal shock and adhesion testing. For quick temperature adaptability testing the 0 to 100° C thermal shock test was used. Two beakers were prepared containing water at 0° C and 100° C respectively. The identical units were bundled into individual sacks which were immersed in the water at 0° C for 5 minutes. The sacks were then withdrawn from the water and immediately transferred to water at 100° C. After being immersed for 5 minutes they were withdrawn. This completed one cycle of the thermal shocking. Ten consecutive cycles completed the test. The test specimens were visually and microscopically examined. They were then dye-stained.

The superiority of DAP/LMA over other allylic resins was seen in the thermal shock tests. In DAP/EHMA/HPMA and DAP/diallyl adipate/triallyl citrate about 30% resin cracking was seen after thermal shocking. DAP/LMA (80 wt %/20 wt %) did not show any cracking after thermal shocking if properly cured (cured at 125° C/12 h with 0.3 wt % DiCup alone, and in combination with 0.3 wt % benzoyl peroxide). When low (0.03 wt % of both DiCup and Bz_2O_2) and high (1.0 wt % of both DiCup and Bz_2O_2) levels of catalysts were used for DAP/LMA curing, about 20% resin cracking occurred.

On curing, DAP/LMA syrup shrinks slightly. This shrinkage, in conjunction with the inertness of the syrup toward the cap material can lead to a separation at the resin–plastic interface in the encapsulated units. Microscopic examination was routinely used to check for separation. A dye-staining test, using a non-aqueous red dye, was used in spot-checking microcracks and pores.

Adhesion of the potting resin to the cap material and adhesion retention after the thermal shocking test are both essential. An Instron adhesion test, using an improvized accessory, was found useful. The method is now described. The bottom of the potted 5 cm^3 cup was removed by machining. The cup was then inverted, placed on a die, and pushed from the bottom by the Instron's cross-head via the plunger. Fig. 1a shows the accessories used and Fig. 1b shows the actual testing. The plunger precisely matches the smaller diameter of the potted material. From the surface area and the force used to push out the potting resin, the degree of adhesion, expressed as strength in psi, was determined.

Adhesion was followed as a function of per cent DiCup catalyst added in a DAP/LMA (80 wt %/20 wt %) resin cured at 125° C/12 h. This test shows (Table III) that 0.3 wt % DiCup is the optimum catalyst level.

TABLE III Effect of catalyst level on the degree of adhesion of DAP/LMA to a nylon 612 cup

Catalyst		Adhesion, expressed as strength (psi)
Bz_2O_2 (wt %)	Dicup (wt %)	
0.06	0.06	163
0.12	0.12	163
0.18	0.18	183
0.24	0.24	1550
0.30	0.30	3630
	0.18	2410
	0.24	3410
	0.30	6510
	0.45	4930
	0.60	5310

2.3.3.8. The DAP/LMA encapsulation process. The standard DAP/LMA encapsulation procedure performed in this work was undertaken through the steps given below, in the sequence listed.

(a) Mix DAP/LMA (80 wt %/20 wt %) syrup, 1.13 Pa sec (100.0 g), benzyoyl peroxide (0.3 g), DiCup (0.3 g), hypophosphorous acid, 50% strength (0.1 g), and Mazu Defoamer 110S (0.1 g) in a 4 fl oz glass jar. Cap jar tightly.

(b) Put the jar on a laboratory roller, at low speed, for 1 hour, or until complete solution is achieved.

(c) Allow the resin solution to stand undisturbed overnight for a normal selfde-bubbling. Alternatively, de-gas the resin solution in a vacuum oven at room temperature for 5 minutes.

(d) Attach two rows of Tape 92 (3M Company), adhesive side up, on the curing rack.

(e) Place empty display caps (12 wt % TiO_2 filled nylon 612) 1 inch apart on the exposed surface of tape.

(f) Condition the assembly for 10 minutes at 125° C; then cool to room temperature.

(g) Fill the display cap cavities with the resin solution prepared in Step 1, using medicine dropper.

(h) Place the rack in a vacuum oven; evacuate to 25 mm Hg or better vacuum. Let segment-filling and de-gassing continue for 5 minutes. Break vacuum slowly and remove the rack from the oven.

(i) Insert LED-containing frames onto each cap and make sure that they are well-fitting.

(j) Envelop the completed assembly with aluminum foil, then place in a 125° C pre-heated oven.

(k) After 3 h, remove the assembly from the oven. Immediately open the aluminum foil and detach the Tape 92 strip from the rack. Allow to cool for 30 sec, then quickly de-tape all the units.

(l) Following de-taping, place all the freed units in the 125° C oven, allow to cure for an additional 9 h.

(m) Remove the fully-cured units from the oven; allow them to cool to room temperature.

2.3.3.9. Potting variations. Twenty variations of the standard potting method using DAP/LMA (80 wt %/20 wt %) were studied in an effort to eliminate or decrease the extent of separation at the resin–plastic interface in the encapsulated units. In each variant set, ten units (10 mm Nylon 612 display caps) were prepared and tested. Table IV describes the 20 sets and their methods of preparation, and summarizes the result of the testing.

Incorporation of 20–30 wt% ground powdered DAP/LMA helped to decrease separation at the resin–plastic interface. The most dramatic improvement was obtained by incorporating 33 wt% aromatic epoxy in the 80 wt %/20 wt % DAP/LMA syrup and doubling the amount of DiCup to 0.6 wt %. Non-reactive liquid fillers, e.g. tricresyl phosphate, were found to be detrimental to the properties (e.g., adhesion) and also slowed down the rate of curing of DAP/LMA syrup.

2.3.4. Development of DAP/EHMA/HPMA resins

Before LMA became the preferred plasticizing monomer for the DAP potting resin, the bulk of the resin development work was done on EHMA. EHMA alone or in combination with HPMA was used to plasticize DAP mixtures. EHMA at 20 wt % and 10 wt % were initially developed. These were followed by the development of DAP/EHMA/HPMA (80 wt %/15 wt %/5 wt %) and (80 wt %/10 wt %/10 wt %).

Of all the resins in this category, DAP/EHMA/HPMA (80 wt %/15 wt %/5 wt %) was the most studied with respect to the syrup preparation method, catalyst type and concentration, dye selection, de-bubbler and stabilizer concentration, polymerization method and cycle, and thermal shock resistance. DAP/EHMA/HPMA (85 wt %/15 wt %/5 wt %) can be cured with 0.3 wt % Bz_2O_2 and 0.3 wt % DiCup in the fast nitrogen cycle and the 125° C/12 h air cycle. Colourless castings were obtained with inclusion of 0.1 wt % HPA. Defoamer 110S at 0.1% was required for de-gassing. DAP/EHMA/HPMA produced clear castings. Hence, an external diffuser (e.g., blanc fixe or powdered

TABLE IV Methods of unit preparation and summarized test results

Set number	Brief Description of Preparation				De-tape (h)	Total cure time at 125° C (h)	Test results			
	Syrup wt/wt	Catalyst on Syrup		Modification (if present)			Before thermal shock		After thermal shock	
		Bz_2O_2 (%)	Dicup (%)				Remarks*	Rating*	Remarks*	Rating*
1	80/20	0.3	0.3	–	3	12	C	7	D	9
2	80/20	0.3	0.3	–	12	12	C	7	D	9
3	80/20	0.03	0.03	–	3	12	B	3	C	6
4	80/20	0.03	0.03	–	12	12	B	3	C	5
5	80/20	0.3	0.3	10 wt % tricresyl phosphate	3	12	C	5	D	9
6	80/20	0.3	0.3	10 wt % tricresyl phosphate	12	12	B	3	D	8
7	80/20	0.3	0.3	3 wt % maleic anhydride	3	12	A	2	B	6
8	80/20	0.3	0.3	3 wt % maleic anhydride	12	12	A	1	B	3
9	72/28	0.3	0.3	–	12	12	B	3	D	8
10	80/20	0.3	0.3	–	4	12	C	7	D	9
11	80/20	0.3	0.3	After de-taping immerse in 80 wt %/20 wt % monomer	4	12	A	1	C	5
12	80/20	0.3	0.3	Cap half-filled, de-tape after 3 h then complete filling	3	12	A	2	B	4
13	80/20	0.3	0.3	Cap half-filled; cure for 3 h then complete filling	12	12	A	3	C	6
14	80/20	0.3	0.3	After 3 h de-tape; over-varnish window with 80 wt %/20 wt % syrup	3	12	A	2	B	6
15	80/20 (Monomer)	0.3	0.3	–	6	16	A	1	B	4
16	80/20 (Monomer)	0.3	0.3	–	16	16	A	1	B	4
17	80/20	–	0.1	–	12	12	B	3	C	4
18	80/20	–	0.2	–	12	12	B	2	C	4
19	80/20	–	0.3	–	12	12	A	1	A	2
20	80/20	–	0.4	–	12	12	A	1	B	3

*Remarks and ratings are based, before thermal shock on 6 units and, after thermal shock, on 4 units in every set.

Remarks: A = No dye penetration; B = Window red but no dye penetration; C = Dye slightly penetrated; D = Dye penetrated from window side to the other side.

Rating: 1 = absolutely no dye penetration; 10 = complete dye penetration.

glass) must be included in the formula. The shortcomings of DAP/EHMA/HPMA (80 wt %/15 wt %/5 wt %) are:

(a) EHMA is slightly volatile;

(b) The resin does not lend itself to an early de-taping;

(c) HPMA did not improve adhesion to the cap to the anticipated extent;

(d) DAP/EHMA/HPMA syrup was slightly yellow even if polymerized under nitrogen (this colouration was due to the HPMA);

(e) DAP/EHMA/HPMA resin is more sensitive to cracking during polymerization than DAP/LMA however, the catalyst level and curing cycle required to produce crack-free units was not difficult to optimize;

(f) The most serious draw-back of DAP/EHMA/HPMA is that some cracking invariably occurred after thermal shocking (~ 30 units out of 100 tested cracked after thermal shocking).

2.3.5. Other allylic resins

After studying non-allylic flexibilizing monomers for DAP (e.g., MMA, BMA, EHMA, LMA, and SMA) allylic monomers were investigated. Two other monomers of commercial origin closely resemble DAP: diallyl adipate (DAA), which polymerizes slowly with DAP, and triallyl citrate (TAC), a hydroxyl-containing tri-functional monomer which polymerizes at a rate about ten-fold faster than DAP or DAA. It was hoped the hydroxl group in TAC would help improve resin adhesion to the metal frame.

Initially, a DAP/DAA (80 wt %/20 wt %) potting resin was developed in the form of a syrup. DAP/DAA monomer mixture was converted to the syrup by the bottle method. DAA flexibilized the DAP, and the low vapour pressure of DAA assured minimum vapour loss in the open polymerization method. DAP/TAC (80 wt %/20 wt %) syrup was made by subjecting the monomer mixture to 80° C, in the presence of 0.2 wt % benzoyl peroxide, under conditions of continuous stirring and with a nitrogen blanket, in a 32 fl oz glass jar. It took about 5½ h to prepare this syrup. The syrup was cured by 0.3 wt % Bz_2O_2 and 0.3 wt % DiCup; 0.1 wt % hypophosphorous acid (HPA) and 0.1 wt % de-foamer 110S were used as functional additives. De-taping was possible after a 3 h initial cure at 125° C. Curing of the freed units was continued for an additional 9 h at 125° C. Crack-free units were obtained only with small display caps. Invariably, cracking occurred when large display units were encapsulated. TAC has a very low vapour pressure, and this assured negligible monomer loss during curing in the open.

Because of cracking of the DAP/TAC (80 wt %/20 wt %) units, a DAP/DAA/TAC (80 wt %/10 wt %) resin was also prepared. Syrup was made in the same way as with DAP/TAC (80 wt %/20 wt %). De-taping was possible after 3 h/125° C. Continuing with the freed units, the final curing was completed in 9 h at 125° C to give crack-free, colourless units in both large and small displays.

DAP/DAA/TAC (80 wt %/10 wt %/10 wt %) resin failed during the thermal shock testing (~ 50% failures). Subsequently, DAP compositions with up to 40 wt % DAA and up to 40 wt % TAC were made, but none of these resins passed the thermal shock test. It is possible that these resins could be thermal shock-proofed by development of a different curing cycle but it is more likely that the functionality of the system needs to be reduced, starting with the DAP, to lower the degree of cross-linking and thereby improve toughness and resistance to cracking.

3. DAP/epoxy encapsulating interpenetrating polymer networks (IPN)

3.1. Description of IPN

IPN are mixtures of two or more distinct polymeric phases that cannot be separated by conventional physical resolution techniques. They offer another method of modifying the architectural design of a polymer, like graft and block copolymerization. By varying the network composition it is possible to effect the resulting properties. Optimum properties (maxima or minima) can be obtained with such a binary or ternary IPN.

Most IPN, on the molecular scale, are heterogeneous, with phase domains rich in one or more of the polymer components. Many IPN, on a colloidal scale, however, appear to be compatible (i.e. homogeneous) blends of the component networks. Thus, IPN are a unique class of molecular topology that represents different ways of embedding molecules in three-dimensional space. Because permanent entanglements will restrict the motion of segments, they would be expected to closely mimic covalently-bound chemical cross-links. In this work, advantage was taken of these mimicking cross-links to develop a superior encapsulating resin. The following proper-

TABLE V IPN encapsulating resins and results of their performance in LED devices

Set number	Title and brief description of the method	Before thermal shock		After thermal shock	
		Remarks	Rating	Remarks	Rating
1	80/20 syrup with 20% powder: 20% of powdered DAP/LMA $< 88\,\mu$m incorporated in DAP/LMA syrup. Then 0.3 wt% DiCup, 0.1 wt% De-foamer 110S and 0.1 wt% HPA added. Cure at 125° C for 12 h.	A	1	A	2
2	80/20 syrup with 30% powder: Same procedures as 1 except 30% powder used instead of 20%.	A	1	A	2
3	80/20 syrup with 100 phr aromatic epoxy (bisphenol A diglycidyl ether and hexahydrophthalic acid): With 80/20 syrup 100 phr epoxy/anhydride in 1 : 1 ratio, 0.6 phr DiCup, 0.1 phr HPA, 0.2 phr De-foamer 110S was used. Cure at 125° C for 12 h.	A	1	A	1
4	80/20 syrup with 50 phr aromatic epoxy: same as 3 except 50 instead of 100 parts epoxy used.	B	1	A	1
5	80/20 syrup with 10 phr aromatic epoxy: same as 3 except 10 instead of 100 parts epoxy used.	A	1	B	3
6	80/20 syrup with 20 phr aromatic epoxy: same as 3 except 20 instead of 100 parts epoxy used.	A	1	A	2
7	80/20 syrup with 30 phr aromatic epoxy: same as 3 except 30 instead of 100 parts epoxy used.	A	1	A	1
8	80/20 syrup with 40 phr aromatic epoxy: same as 3 except 40 instead of 100 parts epoxy used.	A	1	A	1
9	Syrup/powder/epoxy (60/15/25): 0.1% HPA, 0.1% De-foamer 110S and 0.3% DiCup based on total formula used as additives. Cure at 125° C for 12 h.	A	1	A	1
10	Syrup/powder/epoxy (52.5/22.5/25): 0.1% HPA, 0.1% Defoamer 110S and 0.3% DiCup based on total formula used as additives. Cur at 125° C for 12 h.	A	1	A	1
11	Syrup/powder/epoxy (52/13/35): 0.1% HPA, 0.1% De-foamer 110S and 0.3% DiCup based on total formula used as additives. Cure at 125° C for 12 h.	A	1	A	1
12	Syrup/powder/epoxy (45/20/35): 0.1% HPA, 0.1% De-foamer 110S and 0.3% DiCup based on total formula used as additives. Cure at 125° C for 12 h.	A	1	A	1

Rating legend: Rating is based, before thermal shock on 6 units and, after thermal shock, on 4 units in every set.
Rating scale: 1 = absolutely no dye penetration; 10 = complete dye penetration.
Remarks: A = No dye penetration; B = Very slight dye penetration.

ties of IPN have been measured and reported in the literature: viscoelastic strength, dynamic strength [9, 10], static strength [9, 11–13], modulus, hardness, electrical resistance, surface tension, surface wetting, surface contact angle, barrier permeability, barrier diffusion, barrier sorption, chemical structure [9, 13, 14], bulk modulus [10, 15], thermal properties [16–18].

3.2. Development of IPN encapsulating resins

Two types of IPN were developed.

Type I: In this type, DAP/LMA (80 wt%/ 20 wt%) syrup is first converted into a solid, fully-cured polymer using 0.3 wt% DiCup at 125° C for 12 h. The solid polymer is then chopped, powdered, and sieved to produce a powder of particle size less than 88 μm. This powder, in combination with the DAP/LMA syrup, forms the basis of the IPN. Examples are Set 1 and 2 in Table V. Use of solid DAP powder reduced both the tendency to crack in the thermal shock test and the tendency to separate at the plastic–resin interface.

Type II: The rate of DAP/LMA syrup polymerization by a free radical polymer is about the same as the rate of an epoxy reacting with an anhydride. When both mixtures were mixed and allowed to cure, an IPN was formed. Examples

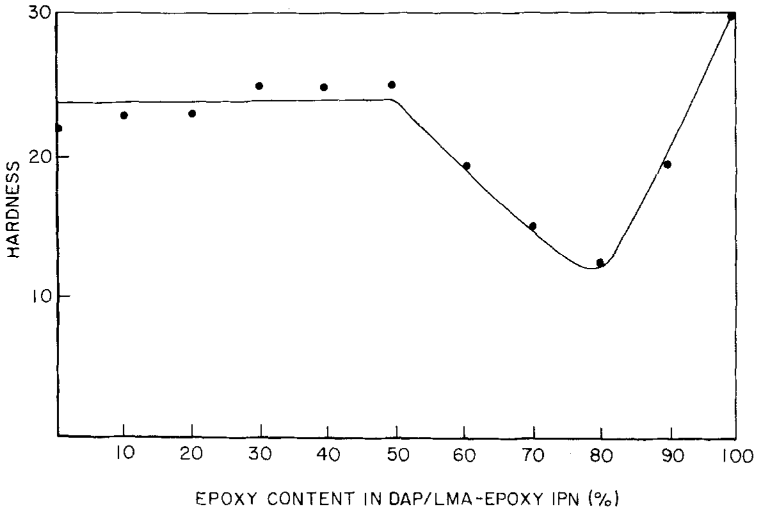


Figure 2 Hardness plotted against DAP/LMA-epoxy IPN composition.

are Sets 3 to 12 in Table V. Reduction in cracking due to thermal shock improved potting adhesion to the display cap, and elimination of separation at the plastic–resin interface was achieved by using an aromatic epoxy resin with the DAP/LMA potting resin.

The DAP/LMA system has been described in an earlier section. Aliphatic dicyclohexane ester diepoxide and methyl substituted dicyclohexane ester diepoxide cured with hexahydrophthalic anhydride were found to be unsuitable in the preparation of IPN. Bisphenol A diglycidyl ether with hexahydrophthalic acid was used in the present work.

Methods of encapsulation and performance-testing were the same as those described earlier. Results of the IPN encapsulating resins are given in Table V. An example of property control is shown in Fig. 2.

4. Applicability of the new resins in an automated casting process

The resin systems that have been developed are amenable to rapid polymerization in a closed mould. Casting of these resins can be speeded up where the polymerization cycle time is of the order of minutes. Rapid casting could also be automated with suitably developed mixing and dispensing equipment. These resins would also find utility in a modified reaction injection-molding process.

5. Conclusions

Flexibilized diallyl phthalate encapsulating resins have been developed that have superior properties to the currently used epoxy materials. In addition, DAP/epoxy encapsulating interpenetrating polymer networks were successfully explored. These encapsulation resins will find application in the electronics industry in potting the small LED modules used in "display" devices for watches, calculators, etc. Our encapsulating resins have the correct combination of many performance properties required in resins for this application including: a high refractive index, receptivity to light-diffusing fillers, adhesion to a Nylon 612 (or polyaryl ether) display cap, absence of cracking during polymerization or in later unit thermocycling tests and a technically and economically feasible production cycle. With limited further research, to reduce the level of crosslinking, it is believed that a truly superior casting resin for LED display applications could be developed from one or more of the promising DAP co-polymer/terpolymer compositions found in this study. It is also believed that these resins will lend themselves to an automated production encapsulation process of LED and other electronic assemblies.

Since these materials represent a relatively new technology of potential importance, investigators are encouraged to study the systems to further extend the field of useful applications.

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