Letters

Research on cap materials for encapsulating electronic display devices

Embedding (or encapsulation) is the encasement of a part or assembly in a material, commonly a resin, with the desired external shape. The application of resins and plastics for encapsulating electronic assemblies has seen steady growth for the past 20 years, and the trend is toward further growth. The wide use of plastics in electronic encapsulation is based primarily on their excellent insulating properties.

Embedding, in general, can be considered as a design concept intended to achieve desirable functions such as mechanically stronger electronic assemblies, modular construction, protection from environmental effects and handling abuses, and mechanical support to enhance survivability throughout the life cycle. Indeed, encapsulation of electronic components and assemblies does improve environmental and structural reliability of the electronic system; it also enhances appearance. The plastic provides increased protection from adverse environmental conditions by sealing out the undesirable atmospheric conditions while supporting the internal structural integrity. Embedding of an electronic assembly also often results in cost reduction.

Embedding techniques are practiced today in a wide array of electrical and electronic applications, both military and commercial. Embedding applications include casting, potting, impregnation, encapsulation, injection moulding and transfer moulding. Casting is a process in which a plastic part is formed by pouring a liquid resin into a cavity (mould), where the material is allowed to polymerize to a solid material. In casting, the mould is removed from the cured resin whereas, in potting it remains as a permanent part of the assembly.

In a previous paper [1] promising co-polymers of diallyl phthalate (DAP) and lauryl methacrylate (80/20) that have most of the physical and performance characteristics desired in a casting resin were defined. Superior DAP/epoxy encapsulating interpenetrating polymer networks were also explored. In the potting process the cap material is as important as the encapsulation resin.

This note describes the research work that we did on polymers or their modifications and on methods to improve their receptivity to encapsulating resins.

The cap material used in moulding display caps should have the following characteristics: (a) the plastic should be tough; (b) the modulus of rigidity should be fairly high; (c) it is essential that the plastic be just slightly attacked by the potting resin, at the curing temperature. Complete or very high potting resin resistance will result in poor adhesion. Excessive attack, however, could lead to solvation and/or deformation at critical thin spots (e.g. display window and decimal points); (d) a controlled and well balanced attack on the cap material by the potting resin is desired to contribute to excellent mechanical locking of the integrated circuit frame in position in the potting resin after cure; (e) the plastic should have dimensional stability at the curing temperature while in contact with the potting resin; and (f) the plastic material should possess sufficient polarity *per se* or be capable of developing polarity on the surface by a suitable method.

More than 20 plastic materials were evaluated (see Table I). The initial evaluation of these candidate cap materials for potential utility was based on the test plan shown in Fig. 1.

Polyolefins, typified by poly-4-methylpentene-1 (TPX), polypropylene (PP) and polyethylene (PE), have good moulding characteristics and are easy to process. The polyolefins have excellent (TPX) to good (PP) to poor (PE) heat resistance. Because of their non-polar nature and chemical inertness toward polar monomeric potting resins, polyolefins generally exhibit poor adhesion to the commonly used potting resins.

Blending PP with ethylene/vinyl acetate copolymers introduced some polarity. However, a sufficient improvement in adhesion was not observed.

The polyolefins suffer from yet another disadvantage in having a flexural modulus lower than that of a polycarbonate. Filling PP with 30 to 40%

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TABLE I Materials (12% TiO_2 filled unless otherwise specified) moulded for testing and evaluation

Plastic materials
1. Polycarbonate resin (GE)
2. Poly-4-methylpentene-1, TPX, RT-20 (Mitsui)
3. Poly-4-methylpentene-1, TPX, RO-15 (Mitsui)
4. Poly-4-methylpentene-1, TPX, DX845 (Mitsui)
5. Polyethylene 6015 (Phillips)
6. Polypropylene (PP) 6523 (Hercules)
7. Polypropylene (PP) 6623 (Hercules)
8. Polypropylene (PP) 6823 (Hercules)
9. PP 6523/EVA (75/25)
10. PP 6623/EVA (75/25)
11. PP/6823/EVA (75/25)
12. Nylon resin: Zytel 151L (Du Pont)
13. Nylon resin: Zytel 158 (Du Pont)
14. Nylon resin: Zytel 801 (Du Pont)
15. Nylon resin: Vydyne 21X (Monsanto)
16. Nylon resin: Vydyne R220 (Monsanto)
17. Nylon resin: Vydyne 602M (Monsanto)
18. Arylon T, pigmented (Uniroyal)
19. Arylon T, unpigmented (Uniroyal)
20. XP-5272 (Dow)
21. Polytetramethylene terephthalate (Eastman)
22. Talc (30%) filled PP, F-65-4 (Hercules)

talc brings the flexural modulus up to values roughly equivalent to that of unfilled polycarbonate. Ethylene/vinyl acetate (EVA), while introducing polarity in PP, also reduces the modulus. Filling PP/EVA with 40% talc increases the modulus, but it does not approach that of unfilled polycarbonate (see Table II).

The low modulus of polyolefins can be improved to the extent required by mineral (talc) filling. Talc filling, however, does not lend any improvement to the adhesion characteristics of polyolefins. To achieve adhesion improvements, chemical etching, flame etching, corona discharge or gas plasma bombardment are commonly employed.

Because of equipment constraints, the gas plasma approach was not tried. The corona discharge technique is most suitable on flat surfaces and large samples. Flaming did not look practical with small display caps. Chemical etching, therefore, was the method investigated.

The chemical etching method is rather simple. It involves complete immersion of the test sample (e.g. the display cap) into an etching solution for a specified time. The sample is then withdrawn, drained, washed three times with distilled water and dried. Chromic acid for 1, 2, 5, 10, 30, 60, 90 and 120 min; hydrogen peroxide, 30% for 30, 60 and 120 min; sodium hydroxide, 40% for 30, 60 and 120 min; phosphoric acid, 85% for 30, 60 and 120 min; nitric acid, 71% for 30, 60 and 120 min; methanol, 100% for 30, 60 and 120 min; diallyl phthalate (DAP) monomer for 30, 60, and 120 min;

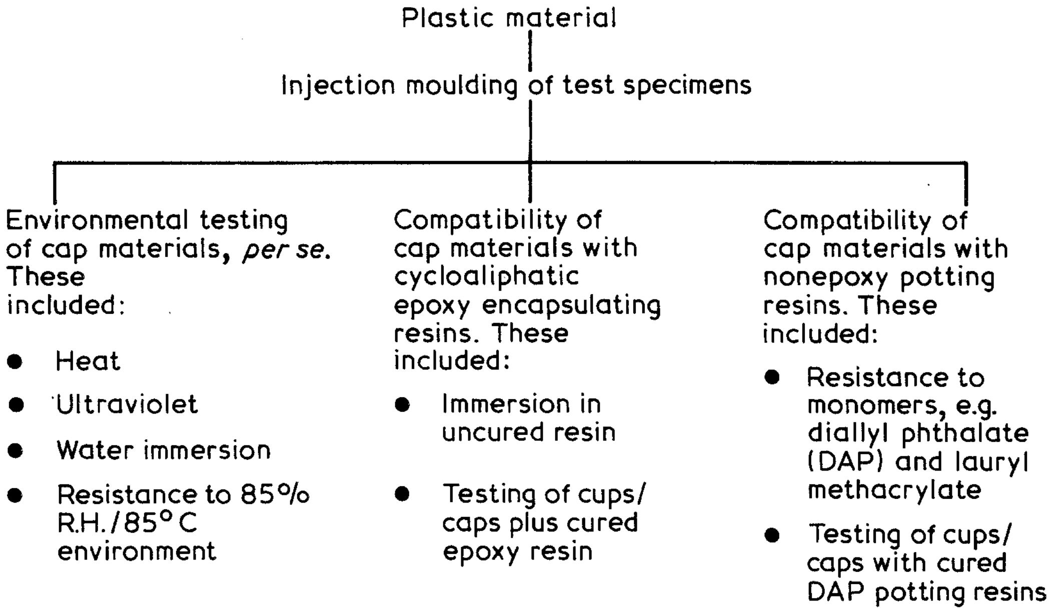


Figure 1 Test plan for evaluating cap materials.

TABLE II Flexural properties of unmodified and EVA-modified polyolefins

Material	Filler	Filler (%)	Condition	Flexural strength (psi)	Flexural modulus ($\times 10^5$ psi)
Polycarbonate	–	–	Lit.*	–	3.2
Polypropylene 6523	–	–	AM†	7280	1.77
Polypropylene 6523	talc	30	AM	8750	3.53
Polypropylene 6523	talc	40	AM	8640	4.33
Polypropylene 6523	–	–	AN†	7940	1.87
Polypropylene 6523	talc	30	AN	8860	3.40
Polypropylene 6523	talc	40	AN	8900	3.96
Polypropylene 6523	TiO_2	10	AM	7630	2.36
Polypropylene 6523	TiO_2	30	AM	8260	3.09
Polypropylene 6523	TiO_2	50	AM	8080	4.17
F-65-4‡	talc	40	AM	8480	6.12
PP/EVA (75/25)§	–	–	AM	5410	1.64
PP/EVA (75/25)	talc	30	AM	5970	2.12
PP/EVA (75/25)	talc	40	AM	5950	2.38
PP/EVA (75/25)	–	–	AN	6030	1.79
PP/EVA (75/25)	talc	30	AN	6500	2.38
PP/EVA (75/25)	talc	40	AN	6500	2.78
TPX, RT-20	–	–	Lit.	4300	1.14
TPX, DX 845	–	–	Lit.	6150	2.14

*Literature value.

†AM = as moulded. AN = annealed samples.

‡Hercules compound.

§PP 6523 used with Ultrathene UE-648 (an ethylene vinyl acetate resin of USI).

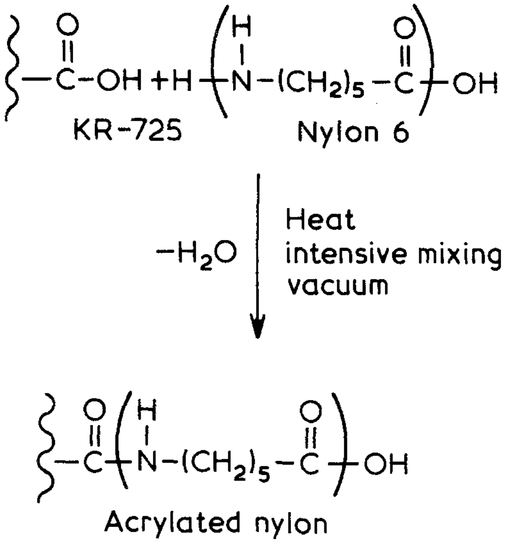
and DAP monomer at 125° C for 30, 60 and 120 min were investigated with the various polyolefins.

Chromic acid etching was the most effective. The extent of etching was empirically found to be nearly independent of the etching time in chromic acid. Other etching solutions were less effective or only slightly effective. Chromic acid etching of modified or unmodified polyolefins greatly improved their receptivity to painting. A significant improvement in adhesion to the potting resin was also achieved by chromic acid etching.

Nylons process well insofar as pigment compounding and injection moulding are concerned. They have fairly good heat and solvent resistance. Nylon 66 and Nylon 69 do pick up some water which could act as a plasticizer for the resin, degrade the resin during moulding (unless carefully dried) and/or detract from electrical performance and ageing resistance in high temperature/humidity environments. Nylon 612 (e.g. Du Pont's Zytel 151L), because of its relatively small water pickup, is more suitable as a display cap material than are other nylons.

Paints stick very well to nylons. The polar groups in nylons also contribute to adhesion with polar epoxy potting compounds. Zytel 151L, without any fillers, has good rigidity properties (flexural strength = 10 700 psi and flexural modulus = 2.5×10^5 psi). Incorporation of 10% TiO_2 further improves strength to 12 000 psi and modulus to 3.0×10^5 psi. The flexural properties could be increased still more by raising the TiO_2 content to 30%. Zytel 158 is an unlubricated higher molecular weight version of 151L. Importantly, either Zytel 151L or 158 can be used with aliphatic and aromatic epoxies, diallyl phthalate resins and combinations of aromatic epoxies and diallyl phthalates, although 158 is slightly more difficult to mould.

An acrylic or rubber modification of nylon resin could improve adhesion because the potting resin will slightly attack the acrylic or rubber component of the modified nylon. Szamborski [2] has recently reported *in situ* acrylic modification of Nylon 6 with the aid of a carboxylated Acrylic Modifier KR-725 (Rohm and Haas). The pendant carboxylic groups of the acrylic polymer were reacted with the amine end-groups of the nylon in an extruder according to the following reaction.



The work of Szamborski [2] was adapted to modify Zytel 151L. Both Zytel 151L and KR-725 were dried in a vacuum oven at 80° C for 48 h. Using a 3/4 inch extruder fitted with a vacuum vent, 180 g dried Zytel 151L and 20 g dried KR-725 were reacted and extruded under a mechanical pump vacuum at 40 rpm. The temperature of the barrel was maintained at 240° C and that of strand die at 280° C. The strands were chopped for injection moulding.

TABLE III Adhesion of cycloaliphatic epoxy to various plastic cups

Plastic cup made of	Adhesion, expressed as strength (psi)
Polycarbonate	2600
Nylon 612	3730
PTMT	3710
Polypropylene 6523	< 50
Arylon T	2900
XP-5272	2140

Since a rubber modified Nylon 66 is commercially available from Du Pont, we did not attempt the rubber modification in our laboratory. Zytel ST-801 super tough nylon resin is a rubber modified Nylon 66. ST-801 combines a high notched Izod impact strength with the well recognized strength, heat resistance and high tensile impacts of nylon.

Uniroyal markets an acrylic alloyed polyaryl ether under the trade name Arylon T. Arylon T has excellent heat, light and moisture resistance and it processes well.

The flexural properties of Arylon T (strength = 13 000 psi, modulus = 3.7×10^5 psi) compare well to those of polycarbonate. Arylon T can be

TABLE IV Adhesion of potting resins to modified nylon cap materials

Cap material	Potting resin	Adhesion (psi)	Examination of plastic/potting resin interface after adhesion test
Acrylated nylon	Aromatic epoxy	1210	Very slight attack seen
ST-801	Aromatic epoxy	2620	Slight attack seen
Acrylated nylon	Cycloaliphatic epoxy	519	No attack seen
ST-801	Cycloaliphatic epoxy	1100	No attack seen
Acrylated nylon	DAP/LMA	982	Very slight attack seen
ST-801	DAP/LMA	4820	Attack seen

TABLE V Effect of 1000 h at 85% r.h./85° C on adhesion plotted in various plastic cups

Plastic cup made of	Adhesion, expressed as strength in psi after 1000 h at 85% r.h./85° C for cups cured at		
	125° C/16 h	160° C/16 h	125° C/12 h + 160° C/4 h
Polycarbonate	180	< 20	83
Arylon T	3100	3020	1160
Nylon 612	1130	1330	751
Polypropylene 6523	47	38	82
TPX, RT-20	< 20	20	33

TABLE VI Reactions of potting resins with various cap materials

Cap material	Adhesion	Plastic–resin Interface separation	Other remarks
Cycloaliphatic epoxy cured at 125° C/16 h			
Polycarbonate	good	no	–
Nylon 612	good	no	–
XP 5272	good	no	Deforms display window
PP 6523	poor	yes	–
Arylon T	good	no	–
Aromatic epoxy cured at 125° C/12 h			
Polycarbonate	good	no	Slight solvent etch
Nylon 612	good	no	–
XP 5272	good	no	Slight solvent etch
PP 6523	poor	yes	–
Arylon T	good	no	Very slight solvent etch
Styrenated polyester, room temperature cured for 24 h + 100° C/2 h			
Polycarbonate	slight stress crack	no	Poor form stability and poor water resistance of polyester
Nylon 612	poor	yes	Poor form stability and poor water resistance of polyester
XP 5272	good	no	Poor form stability and poor water resistance of polyester
PP 6523	poor	yes	Poor form stability and poor water resistance of polyester
Arylon T	good	no	Poor form stability and poor water resistance of polyester
Polymeg-based polyurethane room temperature cured for 24 h			
Polycarbonate	slight stress crack	no	Difficult to encapsulate
Nylon 612	good	no	Difficult to encapsulate
XP 5272	good	no	Difficult to encapsulate
PP 6523	poor	yes	Difficult to encapsulate
Arylon T	good	no	Difficult to encapsulate
DAP/LMA (80/20) syrup cured with 0.3% Dicup at 125° C/12 h			
Polycarbonate	stress crack	no	–
Nylon 612	good	very slight	–
XP 5272	good	very slight	Deforms display window; slight yellowing
PP 6523	poor	yes	–
Arylon T	good	no	Deforms display window due to DAP's excessive attack on Arylon T
DAP/LMA (syrup to powder 80/20) IPN cured with 0.3% Dicup at 125° C/12 h			
Nylon 612	good	no	–
DAP/LMA/aromatic epoxy IPN cured with 0.3% Dicup			
Nylon 612	good	no	Depending on IPN composition, adhesion equals or exceeds polycarbonate/aliphatic epoxy

painted and it has excellent adhesion to potting resins. The main drawback of Arylon T is its insufficient resistance to diallyl phthlate and alkyl methacrylates.

XP-5272 is a Dow experimental rubber-modified styrene maleic anhydride terpolymer with a 62 psi heat distortion temperature of 230° C. It is fairly low in cost and processes well. It has a flexural strength of 7700 psi and a modulus of 2.5×10^5 psi. XP-5272 can be painted but has insufficient resistance to diallyl phthalate and epoxy resins. The rubber portion of XP-5272 is susceptible to oxidation and yellowing. XP-5272 was of most interest in combination with low temperature curing polyesters and polyurethane potting resins.

Tenite PTMT-650 (polytetramethylene terephthalate) is medium in cost and has exceptional heat resistance. It processes well and has good flexural properties and good solvent resistance.

The cap materials were encapsulated by the following potting resins: anhydride-cured cycloaliphatic epoxy; anhydride-cured aromatic epoxy; styrenated polyester; polymeg-based polyurethane; diallyl phthalate (DAP)/lauryl methacrylate (LMA), 80/20; and DAP/epoxy interpenetrating polymer networks (IPN).

Injection-moulded cups ($5\,cm^3$) of various cap materials were potted with anhydride-cured cycloaliphatic epoxy and cured at 125° C for 12h. Adhesion was then determined by a method described in previous paper [1] (see Table III).

Cycloaliphatic epoxy did not adhere well to Polypropylene 6523 but showed excellent adhesion to Nylon 612, Arylon T and PTMT. It also showed good adhesion to polycarbonate.

The adhesion of epoxy and DAP potting resins to modified nylons are shown in Table IV. Rubber modified nylon gave superior results with the DAP potting resin. Acrylic modification did not improve the adhesion.

The results of adhesion tests on potted cycloaliphatic epoxy, after 1 000h in an 85° C/85% r.h. environment are shown in Table V.

To be useful, the cap material and the potting resin must be combined to make a functional assembly. Factors such as compatability of cap material with potting resin and freedom from cracks and separation between cap structure and the potting resin must be considered. The reactions of potting resins with various cap materials are summarized in Table VI.

Compatible systems are those in which there is little or only slight attack of the potting resin on the cap during curing. This promotes adhesion of the potting resin to the cap. If the solvent attack is too great it will cause deformation of the cap.

For cycloaliphatic and aromatic epoxy potting resins, Nylon 612 and Arylon T are better cap materials than polycarbonate. Their superiority stems from their good adhesion to epoxy potting resins and their ability to retain adhesion after 1 000h in an 85° C/85% r.h. environment.

The adhesion of the DAP/LMA resin to Nylon 612 and modified Nylon ST-801 is good. DAP/aromatic epoxy IPN also has good adhesion to Nylon 612 and produced promising encapsulated parts. The IPN described, in combination with a Nylon 612 cap, represents a potentially superior and advanced system compared with the polycarbonate–cycloaliphatic epoxy system.

References

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Dielectric properties of some oxynitride glasses

Currently there is considerable interest in the preparation and properties of oxynitride glasses [1] in which, because some of the oxygen has been replaced by nitrogen, new families of glass systems may be envisaged which may have advantageous physical properties. Initial measurement of the dielectric properties of some calcium–aluminium–silicon and magnesium–aluminium–silicon glasses recently prepared by Jack *et al.* [2] at the Uni-

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