Modified-Amine Cured Epoxy Formulation For The Encapsulation Of Electronic Circuits

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Abstract

The chemical modification of a polyalkylene-polyamine by reaction with phenol and formaldehyde allowed the obtainment of a series of curing agents tailored for an epoxy formulation suitable for the "conformal coating" of electronic assemblies. The mechanical, physical and above all electrical properties and durability of the coatings were measured; the presence of inorganic fillers (quartz and mica) into the formulation was also experimented with satisfactory results.

Key words

Electronic circuits, Epoxy Resins, Encapsulation, Conformal Coatings, Tailored Curing Agents

1. INTRODUCTION

"Embedding" and "encapsulating" of electronic circuits are terms that are frequently used interchangeably. "Embedment" implies the complete encasement of an assembly with a very high volume of material, while "encapsulation", more correctly, is a "coating" applied on a part, a component or an assembly [1]. Indeed "conformal coating" is the term actually employed for encapsulation, because the coating [2] "conforms" to the contour of the board and its components, creating a thin (25-50 microns) layer which is both light in weight and flexible. It protects circuitry [3] from hazards such as chemicals (e.g. polluted environment, fuels, coolants, etc.), vibration, moisture, salt spray, humidity and high temperature. Such conditions can cause corrosion, mould growth, and above all leakage current, resulting in board failure of uncoated assemblies [4].

Conformal coatings allow higher power and closer track spacing for they prevent current leakage thus facilitating the demand for miniaturisation.

The problems involved in coatings are above all surface wetting, resin run off and a general lack of control in the thickness of the layer (surface uniformity) [5].

Epoxy resins are widely employed because of their high strength, low shrinkage, excellent adhesion and insulating properties (both environmental and electrical) [6]. Particularly for military and electrical applications, the epoxies are used in a broader scale, since the epoxy-coatings can supply to a high degree [6, 7]: (i) hermetic sealing against water and humidity, (ii) the placement of the components into a sealed matrix,(iii) greater mechanical strength and (iv) improved dielectric properties.

The general limitations [6, 8, 9] of a simple resin can be: (i) difficulty in repair, (ii) heat dissipation, (iii) thermal limits (i.e., maximum and minimum use temperature), (iv) increased weight and (v) shrinkage (generation of stresses at the interface).

Of course, durability is a fundamental need for all systems.

In this paper a new epoxide formulation, combining a commercial epoxy resin (DGEBA-type) with a synthetic curing agent [10], is presented. The room temperature curable coating displays improved chemical, physical, electrical, mechanical and technological characteristics, so that it is very attractive for the encapsulation of electronic assemblies. The use of mineral fillers results in a further improvement of the electrical properties of the formulation. Finally, the long term durability in water and wet environments, under thermal cycling and Ultra-Violet irradiation constitutes another great advantage of the formulation.

2. EXPERIMENTAL AND RESULTS

2.1 MATERIALS

The resin used was a commercial DGEBA-type epoxy product (Epon 828 from Shell). Its properties are (i) epoxide equivalent 182-194, (ii) viscosity 150 Pa. s at 20 °C and (iii) specific gravity 1160 Kg/m^3 at 20 °C.

The curing agent was a polyalkylene-polyaminophenylic product (PAP), obtained by chemical modification of a polyalkylenepolyamine (tetraethylenpentamine, TEPA, from Fluka) by reacting it with formaldehyde (Carlo Erba) and phenol (B.D.H.).

The characteristics and the molecular structure of the product are depicted in Table 1. The optimum curing agent synthesized was the PAP 10, obtained by condensing the TEPA, formaldehyde, phenol in the molar ratio of 1:1:1. Additionally, different curing agents with the same chemical structure were prepared and used in the experiments: PAP 2 (1:1:0.2), PAP 4 (1:1:0.4) and PAP 8 (1:1:0.8). Unmodified TEPA was employed as the "reference" curing agent.

2.2 FORMULATIONS AND CURING

The composition of the epoxy formulations were 30-35 parts of each PAP curing agent per 100 parts (w/w) of the resin. This formulation ratio was dictated by the H_2-active number of the curing agents and the epoxide equivalent of the resin. For the modified TEPA with 17 phr (parts per hundred) of resin, the curing cycle adopted was 48 hours at room temperature or, interchangeably, 3 hours at 80°C. The formulations containing unmodified TEPA, on the other hand, were always cured at 80 °C (4 hours).

The pot-life of the PAP formulations was about 40 min at room temperature.

The heat of the curing reaction was also measured by a Perkin- Elmer Pyris 1 DSC equipped with a sub-ambient accessory - Intercooling 2P. The heat evolved ranged from 350 J/g (PAP 2 and PAP 4) up to 430 J/g (PAP 8 and PAP 10)

2.3 MECHANICAL STRENGTH

Tensile (ASTM D 3039) and flexural (ASTM D 790) strength, Young's modulus (ASTM D 638), KV2-Charpy impact strength (ASTM D 256) and shore D hardness (ASTM D 2240) of the cured formulations were measured (Table 2).

2.4 ADHESION

Adhesion testing of the coatings to the plastic material sections of the commercial grade circuit boards were carried out by doing tear tests using an adhesion tester, aluminium dollies and per ASTM D 1002. The measurement of the bend test (Fig.1) was performed using a copper sheet (0.5×10^{-3} m thick) coated with the formulations (Table 3).

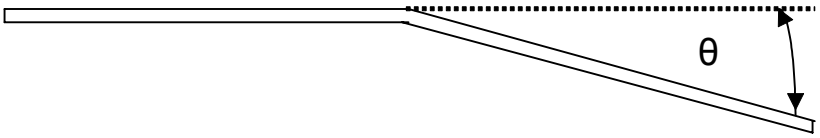


Figure 1. Bend test of a coated copper sheet (0.5×10^{-3} m thick) on a mandrel (Ø = 3×10^{-3} m), up to the angle θ of fracture of the coating.

Table 1. Characteristics and molecular structure of the PAP curing agents [10].

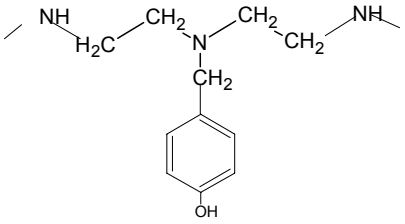
	PAP 4	PAP 6	PAP 8	PAP 10
Molecular Weight (cryoscopic)	300	360	380	420
Active Hydrogen Atoms/molecule	7	6	5	5
Specific Gravity at 20°C, Kg/m^3 (pycnometric)	1010	1015	1030	1040
Steady Shear Viscosity, 20°C, Pa . sec	3.9	4.2	4.65	39.9
Molecular Structure:  Poly-alkylene-poly-amino-phenylic				

Table 2. Mechanical strength of some cured (48 hours at room temperature or 3 hours at 80 °C) formulations epoxy-PAP (massive specimens), in comparison to the epoxy-TEPA formulation (curing: 4 hours at 80°C).

	Curing agent			
	TEPA (as reference)	PAP 4	PAP 8	PAP 10
Impact Strength, (KV 2 Charpy) kJ/ m^2	3.04 ± 1.07	2.19 ± 0.67	2.5 ± 1.2	2.7 ± 1.1
Tensile strength MPa	25.0 ± 2.1	27.1 ± 0.9	28.8 ± 1.2	29.5 ± 1.5
Flexural strength MPa	40.1 ± 0.5	-	39.0 ± 0.58	61.8 ± 0.77
Hardness Shore D	78 ±0.5	80 ± 0.6	80 ± 0.4	81 ± 0.2
Young's Modulus GPa	3.9 ± 0.8	3.2 ± 0.5	3.2 ± 0.7	3.0 ± 0.6

Table 3. Adhesion of the epoxy-PAP formulations.

	Curing agent			
	TEPA	PAP 4	PAP 8	PAP 10
Tear test (ASTM D 1002) Adhesion to a plastic commercial stand kPa (Film: 1×10^{-3} m thick)	100	200	220	310
Bend test on a coated copper sheet: angle of fracture of the film (Mandrel Ø 3×10^{-3} m) (Film: 1×10^{-4} m thick)	50°	43°	55°	130°

2.5 Water Absorption

This was determined by full water-immersion at room temperature for one month using large specimens of the cured formulation (0.01×0.01×0.05 m). The TEPA cured formulation absorbed water up to 13.05 % (w/w), the PAP 4: 20.1 %, PAP 8: 8.2 %, and PAP10: 7.7 %.

2.6 Physical And Technological Properties

(i) Coefficient of linear thermal expansion, α, (between 20 °C and 110 °C) =1.66×10^{-4}/ °C.
(ii) Flame resistance, U.L. 94 Test: Class 94 V-1.

(iii) Mean thickness of the film obtainable by means of a bristle brush = $0.13 \pm 0.01 \times 10^{-3}$ m.
(iv) Time for removing the cured film immersed in methylene chloride, CH_2Cl_2, at room temperature = 4 hours.

2.7 DURABILITY

The durability (hardness, impact strength, tensile strength and adhesion) of both the massive specimens and of the films was tested, by evaluating the properties after water immersion, wet environment exposure, repeated thermal cycling and Ultra Violet irradiation as shown in Tables 4 and 5.

Table 4. Durability of the full cured (room temperature) different formulations: full immersion in water (20°C) up to the saturation (1 month) followed by thermal cycling (1hour at 20 °C + 1 hour at 80°C).

	Curing agent	Starting "dry" value	After water saturation	After 10 thermal cycles
Coatings Shore D hardness	TEPA	78	74	73
	PAP 4	80	76	76
	PAP 8	80	79	79
	PAP 10	81	80	81
0.01×0.01×0.05 m Specimens KV 2 Charpy Impact Strength kJ/m^2	TEPA	3.04	2.90	2.70
	PAP 4	2.19	2.10	2.15
	PAP 8	2.49	2.40	2.31
	PAP 10	2.68	2.68	2.73

Table 5. Durability of the epoxy-PAP 10 coatings exposed to the U.V. irradiation, to 100 % R.H. environment, to thermal cycling (1hour at -18 °C + 1 hour at + 80 °C).

Exposure	Mechanical property of the film	Starting value	Final value
U.V. irradiation (18 hours, 8×10^{-3} W/10^{-4} m^2)	Shore D hardness	81	80
	Tensile strength on film 1×10^{-3} m thick, MPa	24.3	28.7
30 days of exposure to R.H. 100 % at 20°C	Adhesion, kPa (tear test) on stand for circuits	310	305
Thermal cycling: 10 cycles	Shore D hardness	81	80

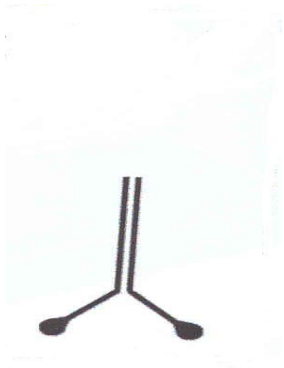


Figure 2. Standard circuit for the measurement of the "through" current (120 seconds).

Table 6. Electrical properties: standard circuits coated with different formulations. Curing at room temperature (*) (mean values, 10 specimens) (the results on the formulations cured at 80 °C were practically the same)

Curing agent	Electrical resistance, Mohm	Through current (120 sec), pA
TEPA (reference)	1.9×10^5	5200
PAP 8	3.7×10^5	2710
PAP 10	7.87×10^5	1270

(*) Except the TEPA-containing formulation (3 hours at 80°C)

2.8 ELECTRICAL MEASUREMENTS

The "standard circuit" as shown in Fig. 2 as per MIL.I. 46058. C.H. and Mil.STD.810 D-1986 and also ASTM D 257 and ASTM D 150 was carefully coated with the formulation to be tested (10 specimens for each formulation) by means of a bristle-brush.

After full curing (five specimens at room temperature, five at 80 °C) the thickness of the films was measured. The electrical resistance of the coating was then calculated by measuring (at 23 °C and 40 % R.H.) the "through" current traversing the insulation material that is between the tracks when an electric potential of 1000.0 Volts, D.C. was applied for 120 seconds. The measurements were carried out using a digital teraohmeter-picoammeter. The current was recorded at 2, 10, 60, 120 seconds though Table 6 shows the current values after 120 seconds.

TEPA was used as the reference material and was cured at 80 °C for 3 hours. The other formulations were cured at room temperature. It should be noted that the values for the other formulations cured at 80 °C were approximately the same as those cured at room temperature.

Table 6 indicates that the most promising formulation was the epoxy-PAP 10, with an insulation resistance of 7.87×10^5 M ohm.

2.9 FILLERS

An increase in the electrical insulation resistance of the epoxy-PAP 10 formulation was obtained by using different powdered fillers, such as, powdered quartz and mica. The percentage (w/w) of the fillers used was 10, 20 and 30%.

The powdered materials were previously sieved to ensure that the granulometric fraction was below 200 microns.

After coating and curing, the standard circuits were retested using the same test conditions as were used previously. The electrical results are shown in Tables 7 and 8 and the mechanical results are shown in Table 9.

Table 7. Electrical properties. Standard circuits coated with the epoxy-PAP 10 formulations, different fillers

Filler		Electrical resistance	Through current
Nature	% w/w	Mohm	(120 sec.) pA
Quartz	10	1.26×10^8	8.0
	20	0.65×10^8	17.0
	30	0.66×10^8	17.0
Mica	10	$> 10\times10^8$	0.0 (not measurable)
	20	0.39×10^8	25.5
	30	0.29×10^8	34.0

Table 8. Electrical properties of the coatings (epoxy-PAP 10 curing agent + mica 10 % w/w) after water immersion and after thermal cycling

Curing agent	After 7 days of water immersion (20°C)		After thermal cycling between -18 °C (1 hour) and +80 °C (1 hour)			
			5 cycles		10 cycles	
TEPA	Electric resistance Mohm	Through current pA	Mohm	pA	Mohm	pA
PAP 10	3.6×10^5	2790	6.0×10^5	1650	7.75×10^5	1260
	1.6×10^6	621	2.6×10^6	384	3.30×10^6	328

Table 9. Mechanical properties of the epoxy-PAP 10 formulations containing different fillers

Filler		Impact Strength KV 2 Charpy kJ/m^2	Tensile strength MPa	Flexural strength MPa	Bend test (coatings) θ, degrees
Nature	% w/w				
Quartz	10	1.9	29.9	63.6	56
	20	2.1	30.5	-	74
	30	2.2	24.6	70.0	49
Mica	10	1.9	27.3	68.4	65
	20	2.1	32.0	-	57
	30	3.3	27.0	69.6	58

3. DISCUSSION

The characteristics that an epoxy formulation must have in order to be used as the base-material for conformally coating electronic assemblies are determined by many factors the, chief among them being its chemical structure and the "tailoring" of the curing agent that is employed.

The

"tailoring" of curing products or of a mix of curing products can be easily obtained, starting with the most widely employed and cheap chemical products, such as the aliphatic polyamines [7-11], alone or as a mix [12], or by using various chemical modifications [13]. Moreover, the presence of some inorganic fillers in the formulations can

also improve the electrical properties of the films. Since the fillers are cheaper than the epoxy resins, they can help reduce the overall cost of the whole formulation.

The "tailoring" of the series of polalkylenepolyaminophenylic (PAP) products shown in Table 1 was done on the basis of their molecular structure and related properties. The relatively high molecular weight of the PAP curing agents give raise to the flexibilization of the cured resin, thus decreasing the Young's modulus (Table 2) to a value that is appropriate for a mechanically durable coating, that is, able to bear the strains the assembly must undergo and has reduced its linear thermal expansion coefficient to a low value. The value of the tensile, impact, flexural strength and hardness of the product are shown in Table 2 and are adequate for the stated scope of this application.

The chemical modification of the original polyalkylenepolyamine (TEPA) with phenol (linked to the main chain of the product by using the formaldehyde as a condensing agent [10]), decreases the number of "active" Hydrogen atoms in the PAP curing agents (Table 1) so that their percentage in the formulation containing the Epon 828 resin must be raised up to 30 %; this is not a drawback, since the PAP-products are cheaper than the resin.

The introduced phenolic group imparts various positive properties to the formulation. (i) Its hydrophobic nature hinders the absorption of water when the coated assembly is exposed to wet environments (the water saturation takes place at 7.7 % w/w, whereas a TEPA-cured formulation absorbs water up to 13.0 % w/w). (ii) Hardness and impact strength (Table 4), and the adhesion of the film (Table 5) stand practically unchanged after prolonged exposure to water. And (iii) the phenolic group accelerates the curing reaction: the full curing can be done either at room temperature for 48 hours or at 80 °C for 3 hours, while that for the unmodified TEPA must be at 80 °C for 4 hours.

However, the heat of the curing reaction of the PAP-curing agents is higher than that of the TEPA. The PAP formulations have a relatively shortened Pot-life of 40 minutes compared to that of 1.5 hours for TEPA. However, this assures that there is enough time for completing coatings, additionally, the formulation up to gel-time remains fairly fluid enabling the ability to obtain thin and homogeneous films (a spraying device could allow the obtainment of thinner films).

The adhesion of the conformal coating film to the copper and also to the plastic sections of the circuit board is an extremely important property. The PAP curing agent based formulations behave better than the unmodified TEPA (Table 3 - tear and bend tests); the PAP 10 is the most superior one even after prolonged exposure to 100 % R.H. (tear test, Table 5).

The durability of the film under U.V. irradiation and thermal cycling (Table 5) and under the combined action of water and thermal excursions (Table 4) is fairly satisfactory.

The electrical insulation resistance of the PAP-cured epoxy films (Table 6) meet the requirements of the standards; additionally, it is greatly enhanced by the experimented fillers. The best results were obtained by adding 10% of powdered mica, but even 10 % of quartz, which is cheaper, is very suitable (Table 7). Water saturation and subsequent thermal cycling of the coating based on a formulation containing PAP 10 curing agent and 10 % of mica slightly affects the electrical properties of the film, however, this is to a minor extent in comparison to the TEPA-cured formulation (Table 8). Finally, it must be noted that the films containing the fillers (Table 9) have good mechanical properties and superior adhesion values.

Other properties of the epoxy-PAP 10 formulation, such as the flame resistance (class 94 V-1) and the easy removal of the film in case of repair (methylene chloride at room temperature) are clear pluses.

4. CONCLUSIONS

The mechanical, chemical, physical and electrical characteristics that the "tailored" PAP-curing agents impart to the experimented epoxy resin are very satisfactory for the use of such formulations as the base-material for the conformal coating of electronic assemblies.

The use of 10 % (w/w) of mica or 10-20 % (w/w) of quartz as powdered fillers can be advantageous from both the electrical and economical point of view. The durability of the coatings is also satisfactory.

REFERENCES

[1] Harper Charles, "Electronic Packaging With Resins", McGraw-Hill Publishers, New York, Chapters 3 and 4, pp 31-93, 1961

[2] Suppa Manfred, "Conformal Coatings For Component Protection", Circuits Assembly, Vol. 6, pp26-30, June 2002

[3] Licari John and Huges Len, "Handbook of Polymer Coatings Electronics", Nyes Publishers, Perk Ridge, New York, Chapters 1, pp 1-48, 1990

[4] Tautscher Charles, "Contamination Effects on Electronic Products", M. Dekker Publishers, New York, Chapters 2, pp 75-88, 1992

[5] Cummings Robert and Nitin Parekh, "Conformal Coatings an Overview", NASA Parts and Packaging Program, Goddard Space Flight Center, Greenbelt, Maryland, July 1996

[6] Lee H. and Neville K., "Handbook of Epoxy Resins", McGraw-Hill Publishers, New York, Chapters 3 and 4, pp 31-93, 1997

[7] Sanjay Patei, Baraiya Rajesh, Jitenda Patel, "Epoxy Resins. Polyamide Coating System", International Journal of Polymeric Materials, vol. 41, No. 1-2, pp 1-5, March, 1998

[8] Jain Preeti and Choudari Veena, "Effect of Structure on Thermal Behaviour of Epoxy Resins", European Polymer Journal, vol. 39, No. 1, pp 181-187, January, 2003

[9] R.W. Chan, Bever M.B., "Encyclopedia of Material Science and Engineering", Pergamon Press, Oxford, U.K., vol.2, Chapter "Epoxy Resins", pp 1571-1573, 1990

[10] Maura Giancarlo and Rinaldi Gilberto, "Durable Glass Epoxy-Composites Cured at Low Temperature-Effects of Thermal Cycling, UV Irradiation and Wet Environment", Polymer International, vol. 31, pp 339-345, 1993

[11] Sabra Albert, Pascault Jean, Seytre George, "Epoxy Thermosetting System Based on Cycloaliphatic Diamines", Journal of Applied Polymer Science, vol. 33, No. 5, pp 5146-5160, May, 1986

[12] Khurana Parveen and Choudari Veena, "Curing and Thermal Behaviour of DGEBA in Presence of a Mixture of Amines", Journal of Applied Polymer Science, vol. 90, No. 7, pp 1739-1747, June, 2003

[13] Bannerjee M. and Mukherjee G., "Studies on the Conductivity Properties of a Family of Cyanoethylated Amine Cured Epoxy Resins", Journal of Applied Polymer Science, vol. 88, No. 7, pp 1627-1631, July, 2003