An Epoxy-Terminated Structural Adhesive. II. Curing, Adhesive Strength, and Flammability Characteristics

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ABSTRACT: Curing characteristics and the curing schedule of an epoxy-terminated polymer (ETP) were investigated using diaminodiphenyl ether (DADPE), diaminodiphenyl sulfone (DADPS), diaminodiphenyl methane (DADPM), and the hardener of a commercial epoxy, two-pack Araldite (Ciba-Geigy), as curing agents. The adhesive strength of the ETP was measured by various ASTM methods like lap-shear, cohesion, and adhesion tests on metal–metal, wood–metal, wood–wood, and metal–polymer interfaces. All these results are compared with Araldite GY250, a two-pack Araldite (Ciba-Geigy). The flame retardancy of virgin ETP, ETP–Araldite GY250 blends, and various commercial-grade fire-resistant epoxies was measured. A structure flammability correlation for the ETP–Araldite GY250 blends is also reported. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 683–691, 1997

Key words: adhesive; epoxy resin; flammability; curing

INTRODUCTION

Most engineering designs (machines, structures, etc.) require joining of parts. The designer has a variety of choices for the task including (1) mechanical connectors such as bolts, pins, screws, and rivets; (2) welding; and (3) adhesives. Use of structural adhesives has the advantages of distributing the load to transfer over larger areas, not requiring drilling of holes that can act as stress concentrators, providing the more streamlined aesthetics by eliminating bolt heads, and reducing the assembly operation.[1]

Our main aim was to develop an adhesive of high strength, better chemical durability, and high thermal stability which can satisfy the FST specifications of flammable materials. In the present communication, we report the adhesive performance and flammability behavior of an epoxy-terminated polymer (ETP) adhesive reported in part I of this series.[2]

EXPERIMENTAL

Materials

Araldite GY250, a two-pack standard Araldite epoxy, and other commercial epoxy resins such as LZ80119 N80SP (Ciba-Geigy), EIG202 FR, EIG320 FRL, EIG300 FRL (SIP Resins, Madras), diaminodiphenyl sulfone (DADPS), diaminodiphenyl ether (DADPE), and diaminodiphenyl methane (DADPM) (all from Fluka Chemicals) were used.

Testing Methods and Procedures

Lap-Shear Test

Three interfaces as adherents, e.g., metal–metal (A1–A1), wood–metal (teak wood–A1), and

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Table I Curing Schedule of the ETP Adhesive with DADPS (23 phr) and the Hardener of Two-pack Epoxy Adhesive (Ciba-Geigy)

Temperature (°C)	Curing Agent	Time (h)	Pressure Used for Curing (psi)
Three-stage curing			
100		2	25–30
150	DADPS	2	25–30
190		2	25–30
Singles-stage curing			
50	DADPS	6	25–30
70	Two-pack hardener	12	25–30

wood–wood (teak wood–teak wood), were used. The overlapping zone was 1 × $\frac{1}{2}$ in. for each case.[3] The adhesive thickness of the applied zone was 0.03 mm. The thickness of the adherent specimen was 3–4 mm. The curing schedule was followed as described in Table I (single-stage curing) using 25 phr diaminodiphenyl sulfone (DADPS) as the curing agent. The dimensions of the testing specimens are illustrated in Figure 1. Before application of the adhesive, the adherent surfaces were etched by toluene followed by rubbing with different mesh-size metal brushes, washed with running water and acetone, and dried.

Cohesion Test

Cohesion or cohesive strength was compared using a standard shear strength which determines the resistance to shear of polyester film under a constant load.[4] The test consists of one piece of polyester film 1 × 12 in. bonded to a wooden (teak wood) or metal (A1 sheet) substrate with a contact area of 1 × 8 in. The test specimens were dried in an oven at 100–110°C with DADPS as the curing agent for both ETP and Araldite resin (tube pack) for 12 h to remove all solvents and subsequently mounted vertically in the shear adhesion rack with the film extending below the wooden substrate as shown in Figure 2. A 1 kg weight was applied to the end of the film using a lightweight hook. The time required for the film to separate from the wooden substrate was measured in hours and the data presented are the average of five trials.

Peel Test

The adhesion of the ETP polymer was measured by a 180° peel test.[5] The test consists of two pieces of an Al sheet of 3 mm thickness and 1 × 12 in. dimensions, bonded for 6 in. with the unbonded portions of each member being placed face to face. The test specimen was pressed under 30 psi pressure at 150°C for 6 h. Two ends of the A1 sheets were bent sharply at 90°C and properly aligned to hold the specimen by the jaws of the tensile

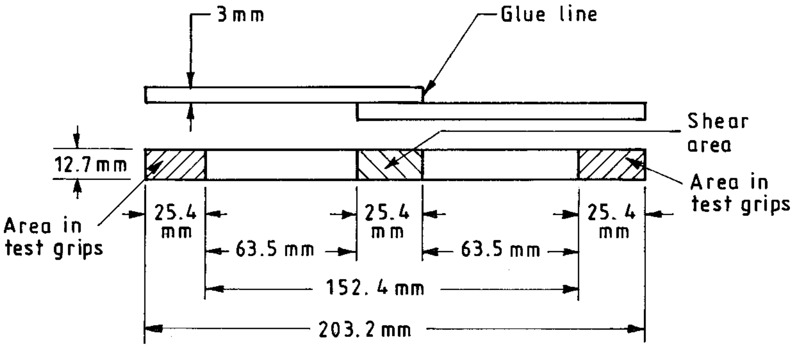

Figure 1 Schematic diagram of lap-shear test.

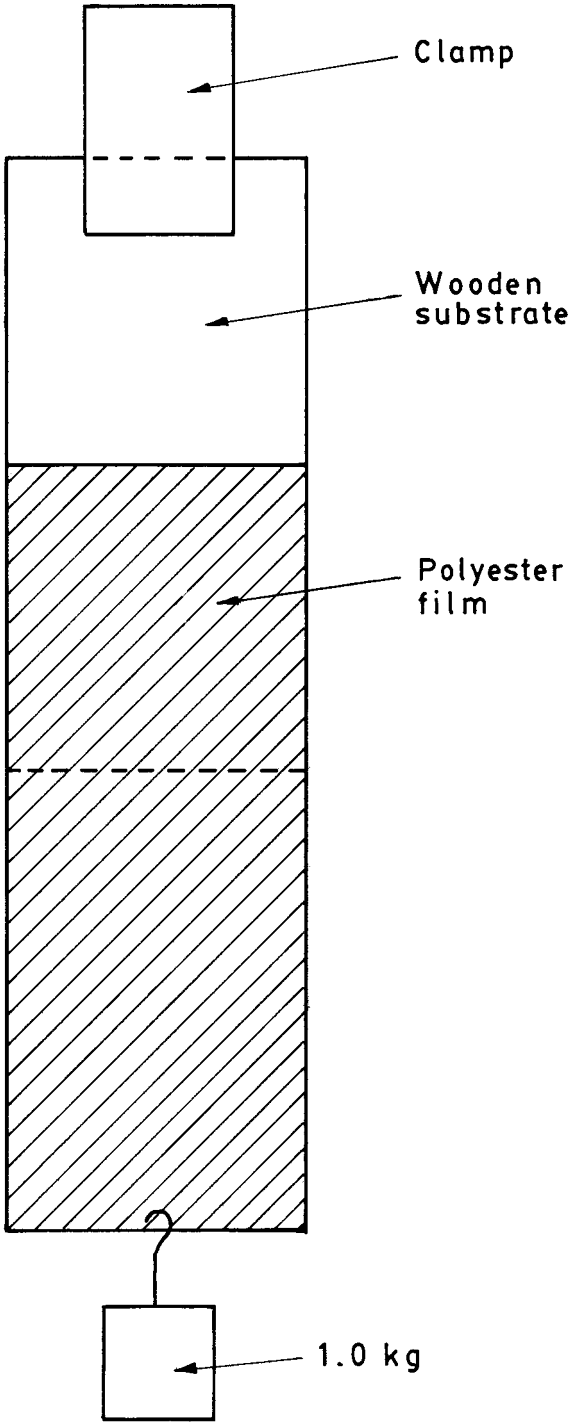

Figure 2 Schematic diagram of cohesion test.

testing machine. The test specimen was placed in the testing machine (Instron 4204) by clamping two ends of the peel panels as shown in Figure 3. The 180° peel adhesion was measured in terms of the force necessary to strip off the metal substrate at a 180° angle from the metal substrate at peel rates of 25 and 50 mm/min. The data reported are the average of four trials.

Flame-retardancy Test

The modified oxygen indices of the ETP adhesive and its blends with Araldite GY250 prepared by liquid-phase mixing of the above two resins in the desired proportions, dried at 150°C overnight and powdered, were measured in a Stanton Redcroft FTA Flammability Unit according to the specification ASTM D 2863-77. A mixture of nitrogen and oxygen is allowed to pass around the sample in a carefully controlled rate to determine the LOI value by the following formula:

$$\mathrm{LOI} = \frac{[\mathrm{O_2}]}{[\mathrm{N_2}] + [\mathrm{O_2}]} \times 100$$

where $[\mathrm{N_2}]$ = volume concentration of nitrogen and $[\mathrm{O_2}]$ = volume concentration of oxygen.

The LOI method used for self-supporting samples was modified[6] for powder or viscous samples and the values are denoted by (OI)m. The measurements were carried out as follows: About 1 g of the polymer sample was placed in a glass cup (diameter 20 mm, height 10 mm) fitted to the specimen holder. An external flame of 20 mm length was maintained in contact for 10 s with the polymer. The (OI)m value was taken as the minimum percentage of oxygen in an oxygen–nitrogen atmosphere surrounding the sample to maintain its combustion. The (OI)m of each sample was taken as the average of five replicates with an average experimental error of ±1.0%.

RESULTS AND DISCUSSION

Physical Characteristics of the ETP Adhesive

The physical properties and solubility characteristics of the ETP adhesive were reported elsewhere.[2]

Curing Characteristics of the Adhesive ETP

The ETP polymer was cured with the tube-packed commercial hardener (Ciba-Geigy) at 70°C for 12 h under 30 psi pressure. A curing schedule was followed as given in Table I using DADPS as the

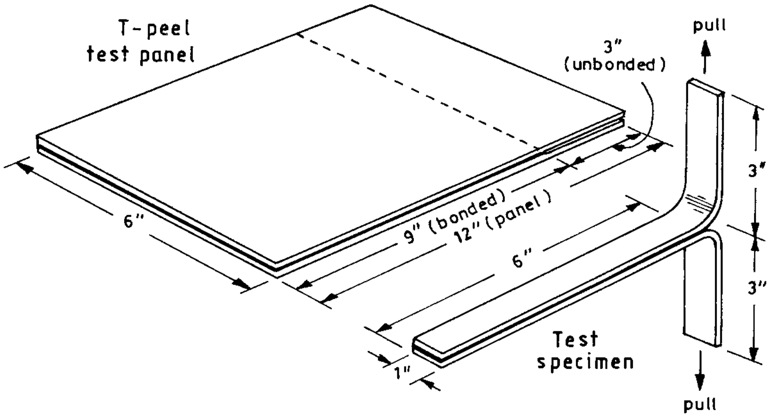

Figure 3 Schematic diagram of 180° peel test.

curing agent. From the differential scanning calorimetry study (Figs. 4 and 5), the curing temperatures of the ETP resin were determined (Table II). The highest curing temperature (195°C) was for DADPS, which can be explained on the basis of its lowest basicity of the amino groups because of higher conjugation with the phenyl ring and the —SO_2 group. When DADPM is used, the curing temperature is lower (183°C), which is due to the somewhat higher basicity of DADPM than that of DADPS. In the case of DADPE, the curing temperature is the lowest (175°C) among these three amines because of the highest reactivity of —NH_2 groups. The curing temperature, 190–192°C, is obtained when three amines are used in a particular proportion (Table II). The curing temperature is wide because of mixed reactivity of the aromatic amines. The ETP adhesive was also cured by DADPS and a two-pack commercial Araldite hardener in a single-stage schedule at 150 and 70°C, respectively (Table I).

Lap-shear Test

The results of the lap shear strength of the ETP adhesive were compared with those of Araldite GY250 (Ciba-Geigy), the Araldite tube-pack adhesive (Ciba-Geigy), and the Araldite GY250/ETP blends as described in Table III. Adhesive strength was also measured using the hardener of the tube-pack adhesive following the curing

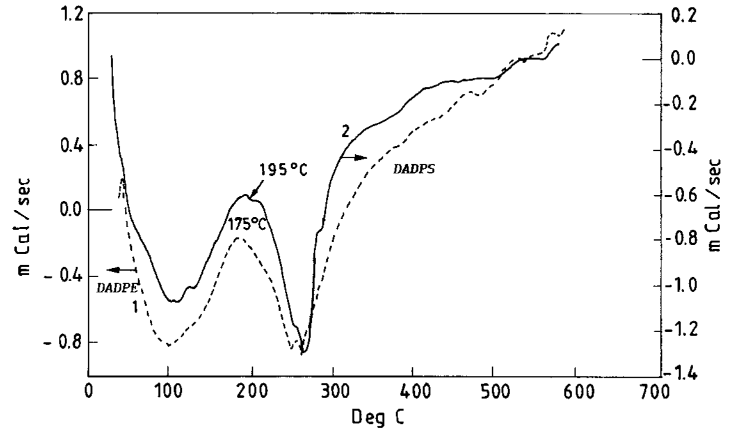

Figure 4 DSC thermograms of ETP with DADPE and DADPS.

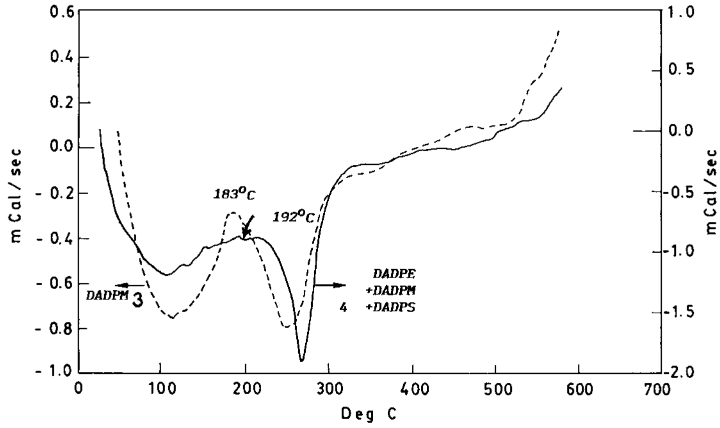

Figure 5 DSC thermograms of ETP with DADPM and a suitable combination of DADPE, DADPS, and DADPM.

schedule of 70°C at 30 psi pressure overnight for both Araldite and the ETP adhesive (Table III). The higher adhesive strength of Araldite than that of ETP on metal–metal interfaces may be due to better interaction of metal interfaces with some coupling agent present in the Araldite. It is found that for metal–metal interfaces the strength of the ETP polymer is lower, and for wood–wood and wood–metal interfaces, the strength is comparable to the specified Araldites. This may be attributed to the lower epoxy content, i.e., 0.17, of the ETP than that of Araldite (0.519).

To test the adhesive strength at a heat-aging condition, both the ETP and Araldite GY250 (Ciba-Geigy) were cured at 150°C under 25–30 psi for 6 h using 25 phr DADPS as the curing agent. After bringing the cured specimen to room temperature, the samples were tested for tensile strength. Similar samples were aged at 200°C for 1 h and their tensile strengths were measured. The results are shown in Table IV. It was found that both the ETP and Araldite show better strength when they are cured at higher temperature, and after heat aging, their strength remains more or less constant.

Effect of Various Harsh Environments on Lap-shear Strength

To test the adhesive durability under various harsh environmental conditions like boiling wa-

Table II Curing Temperatures of the ETP Adhesive Obtained from the DSC Study with Various Aromatic Diamines

ETP Resin Used (Parts)	DADPE[a] (phr)	DADPS[b] (phr)	DADPM[c] (phr)	Curing Temperature (°C)
100	22	—	—	175
100	—	23	—	195
100	—	—	22	183
100	12.5	6.25	6.25	190–192

[a] Diaminodiphenyl ether.
[b] Diaminodiphenyl sulfone.
[c] Diaminodiphenyl methane.

Table III Results of Lap-shear Test for Araldite and the ETP Adhesive Cured at Low Temperature (70°C, Single-stage Curing) with Tube Hardener and High Temperature (Three-stage Curing) According to the Curing as Described in Table I

Types of Resin Used	Interfaces[a]	Tensile Strength of Low-temperature Cured Resin $(N/m^2) \times 10^{-6}$	Tensile Strength of High-temperature Cured Resin $(N/m^2) \times 10^{-6}$
Araldite GY 250	M–M	9.20	13.50
Araldite (two-packed)	M–M	9.50	13.86
Araldite GY250/ETP (70:30, w/w)	M–M	6.60	7.85
ETP	M–M	2.20	3.02
Araldite GY 250	W–M	1.75	2.17
Araldite (two packed)	W–M	1.84	2.38
Araldite GY250/ETP (70:30, w/w)	W–M	1.85	1.85
ETP	W–M	1.74	1.73
Araldite GY 250	W–W	5.13	5.34
Araldite (two-packed)	W–W	5.60	5.45
Araldite GY250/ETP (70:30; w/w)	W–W	3.93	4.50
ETP	W–W	2.49	2.53

[a] M, aluminum metal; W, teak wood.

ter, 5% HCl, and 2% saline water, the cured specimens are treated under these severe conditions. The percentage retentions of tensile strength of wood–wood, wood–metal, and metal–metal surfaces are presented in Table V. The retention of the adhesive strength of ETP under boiling water treatment is not good, possibly due to dissolution or swelling of the polymer in boiling water as ETP contains active chlorine. Under salt water and 5.0% aqueous HCl treatment, the ETP sample retains its adhesive strength to a considerable extent (≥70%).

Effect of Various Additives on Lap-shear Strength

To investigate the effect of various additives on the adhesive strength of the ETP polymer, 1.0% Al_2O_3 and 1.0% silica (precipitated type) were separately mixed with ETP and Araldite GY250 (Ciba-Geigy) before curing. Lap-shear tests were

Table IV Results of Lap-shear Test for Araldite and the ETP Adhesive Samples Cured at 150°C for 6 h and Also for Heat-treated Samples at 200°C for 1 h

Type of Resin Used	Interfaces	Tensile Strength Cured at 150°C $(N/M^2) \times 10^{-6}$	Tensile Strength After Heat Treatment at 200°C $(N/M^2) \times 10^{-6}$
Araldite	M–M	6.70	6.72
ETP	M–M	2.25	2.16
Araldite	W–M	5.72	5.50
ETP	W–M	1.74	1.72
Araldite	W–W	5.70	5.07
ETP	W–W	2.50	2.93

M, metal; W, wood.

Table V Percentage Retention of Adhesive Strength of the ETP Adhesive and Araldite GY250 After Boiling Water Treatment for 30 Min, 5.0% HCl for 1 h, and Salt Water for 6 h

		% Retention of Adhesive Strength		
Adhesive	Interfaces	Boiling Water Treatment	Salt-water Treatment (2% Salt)	5.0% HCl Treatment
Araldite	M–M	98	95	98
ETP	M–M	51	81	72
Araldite	W–M	93	96	94
ETP	W–M	76	88	75
Araldite	W–W	95	95	95
ETP	W–W	52	95	95

All tests were performed under wet conditions. M, metal; W, wood.

performed under identical conditions and results are shown in Table VI. The percentage increment of adhesive strength is 0–12% on various interfaces. The effect of metal oxide additives such as Al_2O_3 and SiO_2 on the adhesive strength of ETP was found to be pronounced on metal–metal and wood–metal interfaces. This may be explained on the basis of coupling interactions of metal oxides with the metal interface and the coordination of the polar groups of the wood surface.

Effect of Epoxy Content on Lap-shear Strength

Lap-shear strength of the ETP adhesive of different epoxy contents was measured using the tube-pack adhesive hardener (Ciba-Geigy) cured at 80°C for 12 h under 30 psi pressure. The results are presented in Table VII. There is an appreciable increment of the adhesive strength with increase of the epoxy content of the ETP. This observation can be explained by the fact that the number of pendant hydroxy groups in the cured polymer increases with increase in the epoxy content of the polymer. These polar hydroxy groups are responsible for better anchorage to the adherent surfaces and, hence, higher strength.

Cohesion Test

The results of the above test are shown in Table VIII. It was found that the cohesion of both Araldite and ETP resin is better on the wood substrate than on the metal substrate. This may be attributed to better cohesive interaction of the polymers with wood (teak wood) through OH groups. The cohesive strength of polyester film for the ETP adhesive is lower than that of Araldite in both the cases (e.g., metal and wood). But mixing of 1% Al_2O_3 with resins before curing improves the cohesive strength to a significant extent which may be

Table VI Effect of Various Additives on Lap-shear Strength of ETP and Araldite Polymer

		Percentage Increase of Critical Tensile Strength	
Type of Resin	Interfaces	With 1% Al_2O_3	With 1% SiO_2
Araldite	Metal–metal	2.85	4.20
ETP	Metal–metal	8.62	10.34
Araldite	Wood–metal	2.50	11.15
ETP	Wood–metal	10.34	11.55
Araldite	Wood–wood	1.16	1.20
ETP	Wood–wood	0.36	2.10

Curing was done at 150°C for 6 h using DADPS as the curing agent.

Table VII Effect of Epoxy Content of Lap-shear Strength of the ETP Adhesive

	Tensile Strength N/m^2 × 10^{-6}		
Epoxy Content	M–M	W–M	W–W
0.13	2.00	1.70	2.20
0.14	2.00	1.74	2.28
0.16	2.08	1.85	2.34
0.17	2.25	1.84	2.49
0.27	2.83	2.58	3.05

Table VIII Results of Cohesion Test of the ETP Adhesive and Araldite on Various Interfaces

Polymer Used	Interface	Cohesive Failure (h)
ETP	Polyester–metal	124
ETP	Polyester–wood	130
Araldite	Polyester–metal	192
Araldite	Polyester–wood	210
ETP + 1% Al_2O_3	Polyester–metal	131
Araldite + 1% Al_2O_3	Polyester–metal	216

due to a better coupling interaction of Al_2O_3 with the resin. This type of reinforcing activity of Al_2O_3 fillers has been reported earlier[7] also.

Peel Test

Results of the peel test are shown in Table IX. The peel strength on polymer–metal and polymer–wood interfaces is higher in the case of Araldite than that of ETP. This may be due to the lower epoxy content of the ETP resin. The peel strength is enhanced by 2–8% on metal–metal surfaces for both the ETP and Araldite resins when Al_2O_3 and SiO_2 were separately added to the resin systems. This may be due to better interaction of the metal oxide with the metal adherent.

Flame Retardancy of the ETP–Araldite Blends

The (OI)m values obtained for ETP, Araldite GY250, the tube-pack Araldite adhesive, LZ 8011 N80 SP (Ciba-Geigy), EIG 300 FRL, EIG 320 FRL, EIG 202 FR (SIP Resins, Madras), and the ETP–Araldite GY250 blends are shown in Table X. It is observed that the (OI)m values of various commercial flame-retardant-grade epoxies range from 27.5 to 42.0. Araldite GY250 (Ciba-Geigy) is not self-extinguishing because the (OI)m value is 26.5. The ETP adhesive, on the other hand, is self-extinguishing and shows higher flame resistance as the (OI)m is 38.0. Incorporation of 5% ETP into Araldite GY250 resin makes it self-extinguishing.

Structure Flammability Relationship of Araldite–ETP Blends

The (OI)m values of the ETP–Araldite blends show a linear relationship (obtained by regression analysis) with the ETP content of the blends (Fig. 6), which may be written as (OI)m = 0.20PO + 26.99 [(OI)m ≤ 38.0], where PO = percentage of ETP and (OI)m = modified oxygen indices.

CONCLUSION

The ETP adhesive exhibits a lower adhesive strength than does commercial epoxy, Araldite

Table IX Results of Peel Test of the ETP and Araldite on Metal–Metal Surfaces

	Elongation Rate (25 mm/min)	Elongation Rate (50 mm/min)
Polymer Used	Peel Fracture Energy (kJ/m^2)	Peel Fracture Energy (kJ/m^2)
Araldite	13.95	14.97
ETP	8.23	8.58
Araldite + 1% Al_2O_3	15.80	16.10
ETP + 1% Al_2O_3	8.17	8.67
Araldite + 1% SiO_2	14.90	15.00
ETP + 1% SiO_2	8.29	8.80

All tests were performed at room temperature.

Table X Modified Oxygen Indices of ETP Adhesive, Araldite GY250, Various Commercial FR-grade Epoxies, and ETP Blends with Araldite GY 250.

(OI)m Values of Base Resin		(OI)m Values of Blend Resin	
Name of the Resin	(OI)m Value	Blend Composition Araldite GY250:ETP	(OI)m Value
ETP	38.0	95:05	28.0
Araldite GY 250	26.5	90:10	30.0
LZ 8011 N80 SP	27.5	85:15	30.2
EIG 300 FRL	33.8	80:20	30.6
EIG 320 FRL	42.5	75:25	31.0
EIG 202 FR	37.5	70:30	33.4

GY250, and the two-pack Araldite adhesive system (Ciba-Geigy) on metal–metal (Al–Al) and wood–wood (teak wood–teak wood) interfaces. However, the adhesive strength of these two systems is comparable on wood–metal interfaces. The lower adhesive strength of ETP may be attributed to its lower epoxy content (0.17) than that of the commercial epoxy (0.519). Besides, the selection and appropriate dose of the curing agents used for ETP may not be proper. The retention of adhesive strength under a mild acid and salt-water condition is over 70%. The effect of metal oxide additives, e.g., Al_2O_3 and SiO_2, on the adhesive strength was studied. The fire-retardant behavior of ETP is superior to that of Araldite GY250, the modified oxygen index [(OI)m] values being 38 for ETP and 26.5 for Araldite. Thus, ETP is self-extinguishing. The (OI)m values of various flame-retardant-grade epoxies vary from 27.5 to 42.0, which are either highly halogenated or compounded with various conventional flame-retardant additives. An empirical equation was established for the ETP–Araldite GY250 blends for practical application.

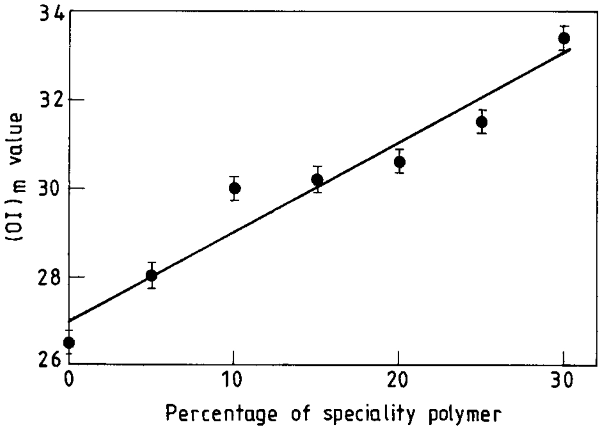

Figure 6 $(OI)_m$ value vs. ETP content in ETP–Araldite GY250 blends.

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