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Phosphorus based epoxy terminated structural adhesive 2. Curing, adhesive strength and thermal stability

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Abstract

The curing behavior of phosphorus based epoxy terminated polymers was studied using diaminodiphenyl ether, diaminodiphenyl sulfone, benzophenone tetracarboxylic dianhydride and the commercial hardener of Ciba-Geigy's two-pack araldite, as curing agent. The adhesive strength of these adhesives was measured by various ASTM methods like lap-shear, peel, and cohesive tests on metal–metal, wood–wood and wood–metal interfaces. All these results were compared with the synthesized epoxy resins prepared from bisphenol-A and epichlorohydrin having the epoxy equivalent value of 0.519. The thermal stability of both the virgin resin and its cured form was also studied by thermogravimetric analysis. © 2001 Published by Elsevier Science Ltd.

Keywords: Epoxy resin; Curing; Adhesive strength; Thermal stability; Phosphorus containing epoxy resin

1. Introduction

The thermoplastic state of an epoxy resin is converted to the thermoset state in presence of a suitable hardener. The property of the thermoset thus obtained reflects the behavior of the adhesive and particularly its strength. Unlike other classes of materials, evaluation of adhesives requires specialized test methods. In testing, not only the adhesive material but also the bonding technique, which includes penetration of the surface, application and curing of the adhesive is evaluated. Almost without exception the available literature methods utilize specimens of standard dimensions, shape and design prepared specifically for the purpose. The resulting data are important in establishing comparative characteristics of adhesives.

In this communication, the performance of the new epoxy resins synthesized has been studied by lap-shear, peel and cohesion tests after curing the polymers with optimal curing schedules using diaminodiphenyl ether (DADPE), diaminodiphenyl sulfone (DADPS), benzophenone tetracarboxylic dianhydride (BTDA) and Ciba-Geigy's two-pack hardener as curing agent. The retention of adhesive strength after various harsh environmental treatments and role of various additives on the adhesive strength of the polymers have been reported. A comparative evaluation of these results with those of the bisphenol-A-epichlorohydrin standard resin system has been presented.

2. Experimental

2.1. Materials

The Al-sheet (supplied from HINDALCo, India) having thickness 3 mm and polyester cloth (Ke-Burgman, India) were used as such. Hydrochloric acid (s.d. Fine Chem.), sodium chloride (s.d. Fine Chem.), sodium hydroxide (s.d. Fine Chem.), toluene (BDH, India), cyclohexane (Ranbaxy, India), isooctane, *n*-butyldisulfide (s.d. Fine Chem.) and *n*-butylmercaptan (s.d. Fine Chem.) were used without purification. Precipitates silica (s.d. Fine Chem.), alumina (s.d. Fine Chem.),

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vinyltrichlorosilane (VTCS) (Fluka), diaminodiphenyl ether (DADPE) (Fluka) were used as such.

3. Testing methods

3.1. Lap-shear test

Three interfaces of adherents, viz., metal–metal (Al–Al), teak wood–metal (W–Al) and teak wood–teak wood (W–W) were used for lap-shear and other adhesive tests. The overlapping zone was $1 \times 1/2$ in.^{2} for each case. The thickness of the adhesive layer within the overlapping area was 0.03 mm. The polymers were cured using different curing agents viz. DADPS, DADPE, BTDA, and the Ciba-Geigy two-pack hardener Araldite hardener 957 under different conditions (Table 1), and their lap-shear strength was measured as per the standard procedure [1].

Before application of adhesive materials on the adherent surfaces, their surfaces were prepared. Aluminum specimens are prepared using the chromic–sulfuric acid cleaning method [2], and finally it was rubbed with 200 mesh size Cu-metal brushes to increase the surface area. Then washed with water and acetone and dried. Similarly, the wood specimens were washed with toluene and petroleum ether to remove organic oil or grease materials and dried at 100°C.

3.2. Peel test

The peel test involves the stripping of a flexible rigid member of an assembly that has been bonded with an adhesive to another member, which may be flexible or rigid [3]. The polymer samples were tested by 180° peel test. In this test two aluminum specimens of 3 mm thickness and 1×12 in.^{2} dimensions are bonded for 6 in. length of the specimen. Two ends of the non-bonded aluminum sheets were bent sharply 90° and properly aligned to hold the specimen by the jaws of the tensile testing machine. 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 the peel rate of 50 mm/min.

Table 1
Curing temperature and curing conditions used for epoxy resin containing phosphorus

Polymer code	DADPE phr	DADPS phr	BTDA phr	Curing temperature (°C)	Curing time (h)
P-1	22.5	–	–	162	4
	–	28	–	185	4
	–	–	35	200	3
P-2	20	–	–	150	4
	–	25	–	180	4
	–	–	35	200	4
P-3	18	–	–	150	2
	–	23	–	180	2
	–	–	30	200	1.5
P-4	15	–	–	150	2
	–	20	–	180	1.5
	–	–	35	200	1

3.3. Cohesion test

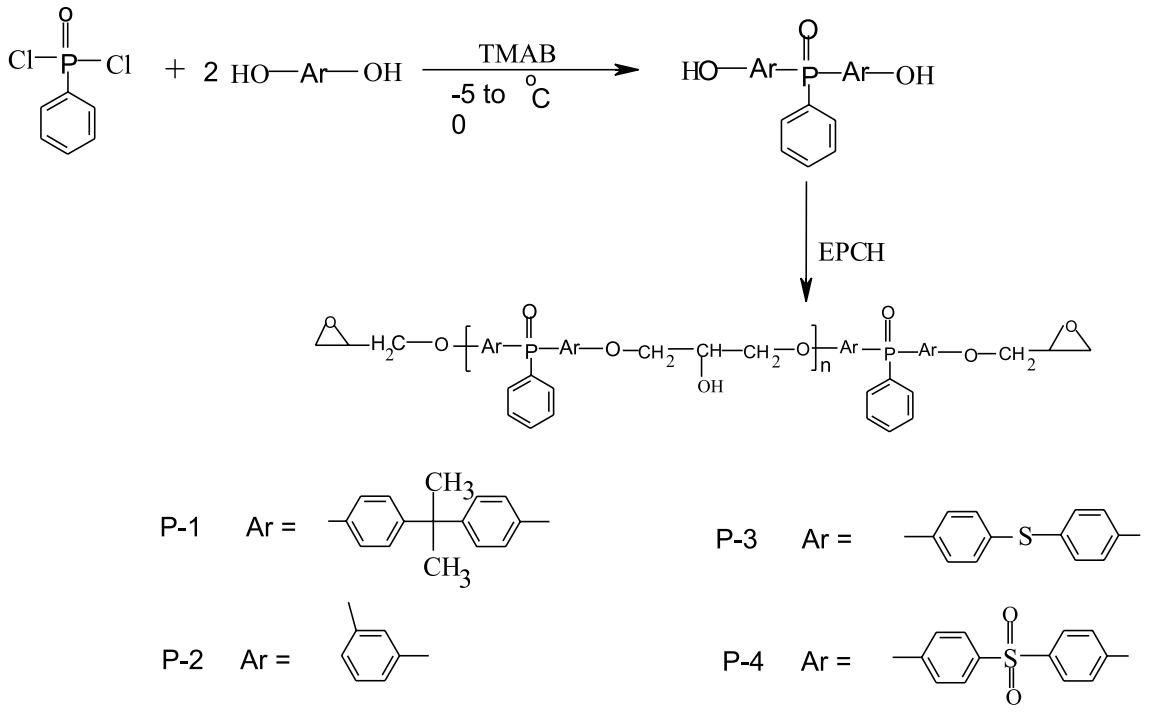
This test measures the shear force necessary to strip the polyester film from the rigid adherent surfaces, e.g. Al or wood surfaces. The test consists of one piece of polyester cloth 1×6 in.^{2} bonded to the teak wood or Al sheet substrate with a contact area of 1×2 in.^{2}. The test specimens are prepared under 100 psi and at 150°C for 4 h using the tube pack (Ciba-Geigy) hardener.

4. Results and discussion

The synthesis and characterization of polymers were reported elsewhere [4]. Polymers were synthesized by reacting dichlorophenyl phosphine oxide and bisphenol-A, resorcinol, 4-4′-sulfone diphenol, 4,4′-thiodiphenol and epichlorohydrin. The reaction may be represented by Scheme 1.

4.1. Curing behavior

The epoxy polymers were cured with the tube pack hardener (Ciba-Geigy) at 100°C for 2 h under 100 psi pressure and at 150°C for 4 h. These polymers were also cured using DADPS, DADPE and BTDA as curing agent. Their curing conditions and curing schedules were shown in Table 1. The curing temperature of the polymer has been determined by the differential scanning calorimetry (DSC) (Fig. 1). At first formulated resin (polymers and curing agent) was recorded by the DSC in air atmosphere at a heating rate of 10°C/min (Fig. 1). The figure shows a characteristic exotherm at a particular temperature region (~150–200°C) which is disappeared in the DSC curves of the preheated formulated resin at same temperature region. The highest curing temperature (200°C) required using BTDA as the curing agent could be explained on the basis of low reactivity of the anhydride group [5]. In case of DADPS a curing exotherm peak temperature at about 175–180°C was found in the DSC thermogram. Because of low nucleophilicity of the amino group due to the electron withdrawing effect of SO_2-group, curing of epoxy occurs at a lower temperature than that using BTDA as curing agent. Similar observation was noted by earlier workers [6]. Liu et al. [7] observed that DADPS was the lowest



Scheme 1.

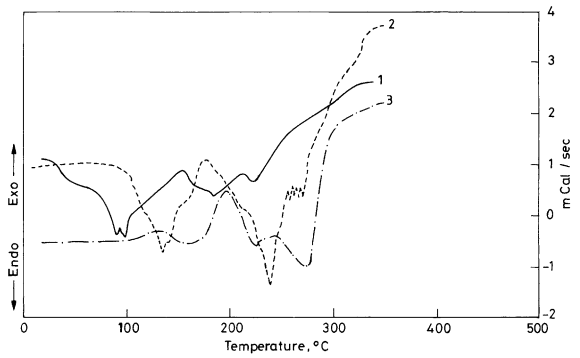


Fig. 1. DSC thermogram of polymer P-2 with (1) DADPE, (2) DADPS, (3) BTDA.

reactive curing agent among the aromatic amines. In case of DADPE, the curing temperature is the lowest (150–160°C) among these three curing agents because of the highest reactivity of the $-NH_2$ groups of this aromatic ether (DADPE) [8].

4.2. Lap-shear test

Results of lap-shear strength of the phosphorus containing polymers are compared with those of bisphenol-A-epichlorohydrin (DGEBA) epoxy resin on the Al–Al, W–W, W–Al surfaces. Adhesive strength of the polymers was measured using DADPS, DADPE, BTDA and the two pack commercial (Ciba-Geigy) hardener, under appropriate curing conditions. The results are shown in Tables 2 and 3 within the limit of standard deviation ±0.5%. The higher adhesive strength of standard resin than those of new resins on metal–metal interface may be due to better interaction of metal interfaces with highly polar groups of this resin and each case this failure at the adhesive–substrate surfaces. It is found that for metal–metal interfaces the strength of the new resins is lower and for wood–wood and wood–metal interface the strength is comparable to that of the standard DGEBA resin and for wood–metal joint adhesive failure at the metal–adhesive interfaces. This may be attributed to the lower epoxy content of the synthesized polymers. From the results of different curing systems it is found that the adhesive strength of the resins also varies with the curing agent and curing conditions. In each polymer, it is found that adhesive performance of two-pack hardener cured resins is much higher than that of BTDA, DADPS and DADPE cured system. It is also reported that particular curing system is effective for particular resin [9]. Therefore, the lower adhesive strength of new phosphorus based epoxy resins is obviously due to some other factors like, lack of an appropriate curing system or curing

Table 2
Results of lap-shear test of the standard epoxy resin and phosphorus based epoxy resin

Polymer code	Curing agent	Interfaces	Tensile strength $(N/m^2) \times 10^{-6}$
P-1	DADPS	W–W	1.02
		W–Al	0.92
		Al–Al	0.87
	DADPE	W–W	0.86
		W–Al	0.65
		Al–Al	0.21
	BTDA	W–W	2.11
		W–Al	1.01
		Al–Al	0.92
P-2	DADPS	W–W	3.21
		W–Al	2.01
		Al–Al	1.52
	DADPE	W–W	1.47
		W–Al	1.02
		Al–Al	0.76
	BTDA	W–W	3.01
		W–Al	2.06
		Al–Al	0.79
P-3	DADPS	W–W	0.67
		W–Al	0.43
		Al–Al	0.09
	DADPE	W–W	0.51
		W–Al	0.34
		Al–Al	0.087
	BTDA	W–W	0.78
		W–Al	0.43
		Al–Al	0.12
P-4	DADPS	W–W	0.76
		W–Al	0.47
		Al–Al	0.21
	DADPE	W–W	0.63
		W–Al	0.33
		Al–Al	0.13
	BTDA	W–W	1.03
		W–Al	0.49
		Al–Al	0.17
Standard epoxy resin	DADPS	W–W	16.6
		W–Al	14.0
		Al–Al	12.8
	DADPE	W–W	15.3
		W–Al	14.4
		Al–Al	12.8
	BTDA	W–W	17.1
		W–Al	15.3
		Al–Al	12.8

condition or absence of some coupling agents and other additives apart from the lower epoxy content of the base resin.

Table 3
Results of lap-shear test of phosphorus based polymer (cured by two-pack hardener)

Polymer code	Interfaces	Tensile strength $(N/m^2)^a \times 10^{-6}$	Tensile strength $(N/m^2)^b \times 10^{-6}$
P-1	W–W	6.31	9.01
	W–Al	2.10	4.99
	Al–Al	1.30	2.74
P-2	W–W	9.41	10.2
	W–Al	3.13	6.36
	Al–Al	1.86	2.15
P-3	W–W	4.21	7.64
	W–Al	3.62	4.16
	Al–Al	1.07	1.56
P-4	W–W	3.13	6.37
	W–Al	1.01	3.03
	Al–Al	0.08	0.90
Standard epoxy resin	W–W	20.87	25.3
	W–Al	21.68	26.0
	Al–Al	24.03	25.5

[a] Polymers were cured at 100°C under 100 psi pressure.
[b] Polymers were cured at 150°C under 100 psi pressure.

4.3. Effect of various harsh environments on lap-shear strength

The durability of adhesive materials under various harsh environmental conditions like boiling water, 5% salt water, 5% aqueous HCl and chemical mixture [10] (i.e., toluene 30%; cyclohexane 60%, isooctane 9%, *n*-butyldisulfide 0.9%; *n*-butylmercaptan 0.1%) has been tested. Under these severe conditions only the Ciba-Geigy's hardener cured samples were treated.

The retention values of the adhesive strength of polymer P-2 and standard epoxy resin on various surfaces such as wood–wood, metal–wood, metal–metal surfaces are presented in Table 4. It is clear that stability of the adhesive bond of polymer P-2 under different harsh environments is inferior to that of the standard epoxy resin. After five days of 5% HCl treatment, it is found that the percentage of adhesive strength retention in case of polymer P-2 less than 5%. This may be due to the higher acid-susceptibility of the phospho-ester linkage of the polymer which causes hydrolysis of the P–O linkage of the resin. Similar arguments were put forward by the other workers also [11].

4.4. Effect of various additives on lap-shear strength

To investigate the effect of various additives on the lap-shear adhesive strength of the polymer, a mixture of 10.0% Al_2O_3 and 10.0% silica (precipitated type) together and 10% Al_2O_3 and 10% vinyltrichlorosilane were

Table 4
Standard percentage retention of adhesive strength of polymers, P-2, and standard resin after various harsh environment

Polymer code	Interfaces	Retention of adhesive strength (%)						
		Boiling water treatment (1h)	5% HCl treatment		5% Salt water treatment		Chemical treatment	
			3 days	5 days	3 days	5 days	3 days	5 days
P-2	W–W	23.0	38.0	5.0	42.0	13.0	60.0	32.0
	W–Al	20.6	22.0	2.0	37.0	7.0	51.0	21.0
	Al–Al	9.7	21.0	Nil	29.0	5.0	48.0	18.0
Standard resin	W–W	71.3	80.0	62.0	90.0	78.0	99.2	97.3
	W–Al	53.9	90.0	73.0	84.7	73.5	98.9	93.0
	Al–Al	54.0	87.3	65.0	77.6	77.0	99.0	96.0

Ciba-Geigy's two-pack hardener cures polymers at 150°C under 100 psi pressure for 4 h.

Table 5
Effect of various additives on lap-shear strength of polymer P-2 and standard resin

Polymer code	Inter-faces	Percentage increase of critical lap-shear strength	
		With 10% ($Al_2O_3 + SiO_2$)	With 10% (Al_2O_3 + VTCS)
P-2	W–W	3.80	7.5
	W–Al	3.00	12.3
	Al–Al	31.8	38.1
Standard epoxy resin	W–W	2.40	1.0
	W–Al	2.60	9.0
	Al–Al	2.80	2.0

Polymers were cured by two-pack hardener at 150°C under 100 psi pressure for 4 h.

mixed with polymer P-2 and the standard epoxy resin before curing. Lap-shear test was performed under identical conditions. The results were shown in Table 5.

In case of polymer P-2 the enhancement of adhesive strength for metal–metal interfaces is higher than wood–wood and wood–metal interfaces. Even percentage of enhancement of adhesive strength is higher than that of the standard resin. It is observed that vinyltrichlorosilane is a powerful additive for enhancement of adhesive strength in each case by forming an effective bonding between epoxy polymers and metal or wood surfaces i.e., it acts as a good coupling agent [12]. In the case, Si–O bond is generated from the hydrolysis of Si–Cl bond of vinyltrichlorosilane which strongly interacts with the metal substrate surfaces forming Si–O bond. On the silane/adhesive interface, a coupling interaction arises from the polymerization of the vinyl group of vinyltrichlorosilane under curing conditions, and the polymer thus formed interacts with the base resin. Thus using vinyltrichlorosilane as an additive the bonding between the adherents is enhanced more than in other cases.

4.5. Peel test

The peel test was performed for polymer P-2 and the standard epoxy resin. Both the resins were cured using the tube pack hardener (Ciba-Geigy) at 150°C and 100°C for 4 h respectively. Results of the peel test are shown in Table 6. The peel strength of the polymer–metal interfaces is again higher in case of the standard epoxy resin than polymer P-2. This is due to the high epoxy content of standard epoxy resin (0.519). The peel strength also depends on the nature of additives. A mixture of 10% Al_2O_3 and 10% SiO_2 increases the peel strength from 4.5% to 17% whereas a mixture of 10% Al_2O_3 and 10% vinyltrichlorosilane increases from 7% to

Table 6
Results of peel test of the phosphorus containing polymer P-2 and standard epoxy resin on Al–Al interface

Adhesive formulation	Peel fracture energy $(N/m^2)^a \times 10^{-6}$	Peel fracture energy $(N/m^2)^b \times 10^{-6}$
P-2	1.96	2.80
P-2 + 10% ($Al_2O_3 + SiO_2$)	2.01	3.13
P-2 + 10% (Al_2O_3 + VTCS)	2.03	3.15
Standard resin	7.13	9.60
Standard resin + 10% ($Al_2O_3 + SiO_2$)	9.81	10.0
Standard resin + 10% (Al_2O_3 + VTCS)	10.0	10.1

[a] Polymers were cured by two-pack hardener at 100°C under 100 psi pressure for 4 h.
[b] Polymers were cured by two-pack hardener at 150°C under 100 psi pressure for 4 h.

37% for polymer P-2. Again the percentage enhancement of peel strength by various additives is higher in case of P-2 than the standard epoxy resin. This indicates that there is further scope for improvement of the adhesive performance of these synthesized resins.

4.6. Cohesive test

The results of the above test are given in Table 7. It has been found that cohesion of both the standard resin and new epoxy resin (P-2) is better on the wood substrate than on the metal substrate. This may be attributed to higher cohesive interaction of the polymers with wood (teak wood). The cohesive strength of polyester cloth for the new epoxies is lower than that of the standard resin for both the cases (e.g., metal and wood). But mixing of (10% $Al_2O_3 + 10\%$ SiO_2) and (10% $Al_2O_3 + 10\%$ vinyltrichlorosilane) with resins before curing improves cohesive strength to a significant extent.

4.7. Thermal behavior of virgin and cured resins

The thermal stability of these polymers was determined by TGA (Fig. 2). The phosphorus based epoxies are thermally very stable, and their thermal decomposition is single step. Earlier Varma and Gupta [6] and Liu et al. [7] reported that DGEBA and phosphorus based resins were degraded by almost single stage decomposition. These observations were similar to those reported by earlier workers [6,7]. Phosphorus based P-1 epoxy resin starts to degrade as low as at 180°C due to presence of the bisphenol-A moiety.

However, other phosphorus based resins are stable even above 230°C. In this series the highest thermal stability is found for polymer P-4, i.e., 275°C, possibly due to the presence of highly thermostable –SO_2– moiety in the polymer chain [13]. All these phosphorus based epoxy resins leave char residues more than 30% at 600°C. In case of polymer P-2 the char residue is maximum (Fig. 2). This is attributed to the highest phosphorus content of the polymer. It is reported that presence of phosphorus helps from the phospho-ester network structure in the polymer matrix [14]. Thermal stability of the cured epoxy resin P-2 was also studied by TGA analysis. In general the thermal stability in each thermosetting stage of the epoxy resins is much higher than that of the uncured state of the corresponding resin. To compare the thermal properties of the cured resins, these cured polymers are grouped into three

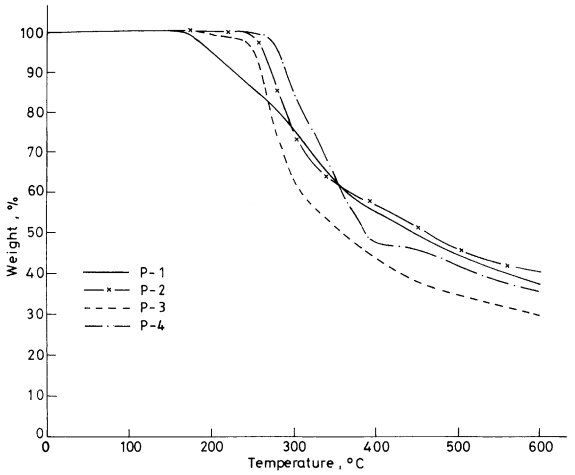


Fig. 2. TGA thermogram of phosphorus containing polymers.

Table 7
Results of cohesive test of polymer and the standard epoxy resin

Adhesive system	Interfaces	Cohesive failure energy (N/m^2) $\times 10^{-6}$
P-2	Polyester–Wood	3.10
	Polyester–Metal	2.82
P-2 + 10% ($Al_2O_3 + SiO_2$)	Polyester–Wood	3.21
	Polyester–Metal	2.85
P-2 + 10% (Al_2O_3 + VTCS)	Polyester–Wood	3.30
	Polyester–Metal	3.20
Standard epoxy resin	Polyester–Wood	9.32
	Polyester–Metal	8.70
Standard epoxy resin + 10% ($Al_2O_3 + SiO_2$)	Polyester–Wood	10.0
	Polyester–Metal	8.93
Standard epoxy resin + 10% (Al_2O_3 + VTCS)	Polyester–Wood	10.30
	Polyester–Metal	8.92

Polymers were cured by two-pack hardener at 150°C under 100 psi pressure for 4 h.
VTCS – Vinyltrichlorosilane.

Table 8
Thermal behavior of the cured epoxy polymer (P-2)

Polymer system	Initial decomposition temperature (°C)	Percentage of weight loss at 400°C	Percentage char residue at 600°C
P-2/DADPE	282.60	55	32
P-2/DADPS	289.00	45	30
P-2/BTDA	346.98	40	10

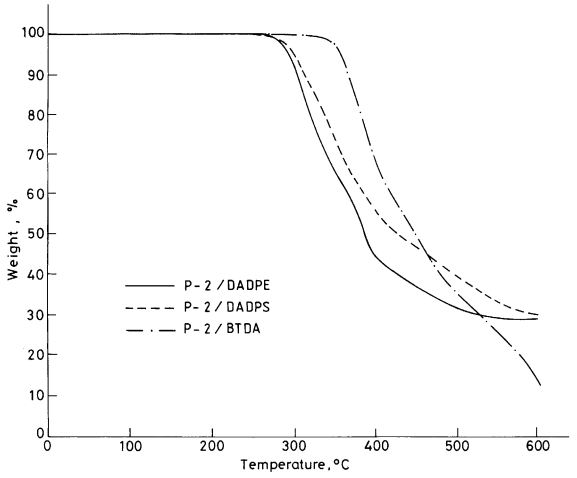


Fig. 3. DSC thermogram of polymer P-2 with different curing agents.

classes according to the curing agents used, viz., (i) P-2/DADPE (ii) P-2/DADPS (iii) P-2/BTDA. To determine the thermal property of the cured polymer, initial decomposition temperature and temperature of some characteristics weight losses are listed in Table 8 and shown in Fig. 3. It is found that the BTDA cured epoxy resin have shown the highest thermal stability compared with all the other resin systems. During the curing cycle, the anhydride group and hydroxyl group of the resin to form ester crosslinks. These ester networks is more thermostable than other types of linkage [5].

Therefore, the BTDA cured resins are thermally more stable than other cured resin systems. Since the thermal stability of $–SO_2–$ linkage is higher than that of –O– linkage, it is obvious that the resins cured with DADPS exhibit higher thermal stability than those cured with DADPE [5]. The amine-cured phosphorus based epoxy resin (P-2) after heating at 600°C leaves a char residue ~30%. This is perhaps due to formation of the P–N network structure of the polymer [14].

5. Conclusion

The epoxy resins were cured using DADPS, DADPE, BTDA and two-pack Ciba-Geigy's hardener. In each case cured resins have lower adhesive strength compared to the bisphenol-A epichlorohydrin standard epoxy resin on metal–metal, wood–wood, wood–metal interfaces. That may be due to the lower epoxy content of these polymers compared to the standard epoxy resins (0.519 epoxy equivalent). The retention of adhesive strength varies harsh environment of our adhesive inferior compared to the standard epoxy resin. The effect of various additives e.g., Al_2O_3, SiO_2 and vinyltrichlorosilane on the adhesive strength was studied where vinyltrichlorosilane acts as a good coupling agent.

The thermal stability of various cured polymer system is also studied where BTDA cured resin (P-2) has higher thermal stability compared to the other curing resin system including the standard epoxy resin.

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