

Heterocyclic-Based Epoxy-Terminated Structural Adhesive. II. Curing, Adhesive Strength, and Thermal Stability

Sankar Bhuniya, Sukumar Maiti

Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

Received 1 March 2001; accepted 21 November 2001

ABSTRACT: We studied the curing behavior of heterocyclic-based epoxy-terminated resins using diaminodiphenyl ether, diaminodiphenyl sulfone, benzophenone tetracarboxylic dianhydride, and the commercial hardener of Ciba-Geigy's two-pack Araldite as curing agents. The adhesive strength of the adhesives was measured by various ASTM methods such as lap-shear, peel, and cohesive tests on metal-metal, wood-wood, and wood-metal interfaces. All of these results were compared with those of an epoxy resin

prepared from bisphenol-A and epichlorohydrin resin with an epoxy equivalent value of 0.519. The thermal stability of both the virgin resin and its cured form was also studied by thermogravimetric analysis. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3520–3526, 2002

Key words: curing of polymers; differential scanning calorimetry (DSC); thermal properties

INTRODUCTION

Epoxy resin is one of the most successful industrial adhesive polymers due to its better cost-benefit aspect, versatility, and superior adhesive strength. Almost constant efforts have been made to enhance its performance by various techniques for the modification of its chemical structure^{1–3} and the use of special additives,^{4,5} curing agents,⁶ curing schedules, and so on. To increase the thermal stability of epoxy resin, a polyannular aromatic ring⁷ and a heterocyclic moiety⁸ have been incorporated.

This investigation was a part of a program for the development of a new epoxy system with better flame retardancy⁹ and thermal stability based on a heterocyclic moiety.

In this study, we examined the performance of the newly synthesized epoxy resins by lap-shear, peel, and cohesion tests after curing the polymers with optimal curing schedules using diaminodiphenyl ether, diaminodiphenyl sulfone (DADPS), benzophenone tetracarboxylic dianhydride (BTDA), and Ciba-Geigy's two-pack hardener (Araldite hardener 957) as curing agents. The retention of adhesive strength after various harsh environmental treatments and the effect of various additives on the adhesive strength of the polymers are reported. A comparative evaluation of

these results with those of the bisphenol-A-epichlorohydrin standard resin system is presented.

EXPERIMENTAL

Materials

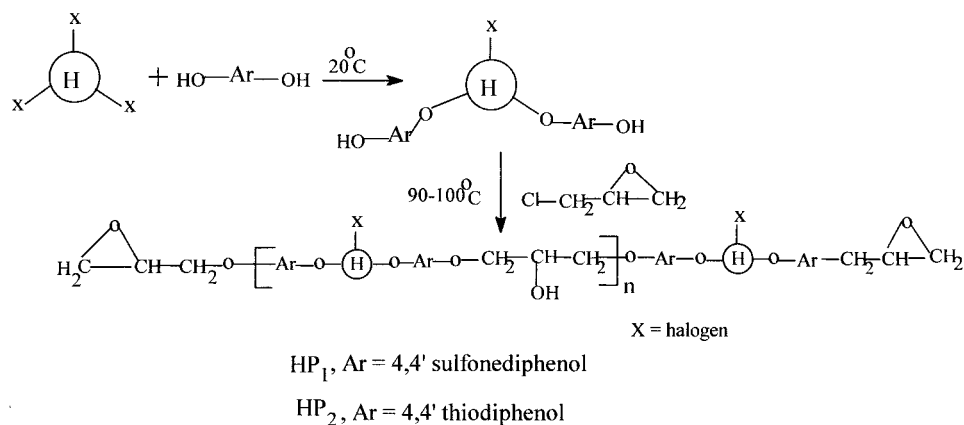
The Al sheet (supplied from Hindal Co., India), with a thickness of 3 mm, and polyester cloth (Ke-Burgman, India) were used as provided. Hydrochloric acid (s. d. Fine Chem, India), sodium chloride (s. d. Fine Chem), sodium hydroxide (s. d. Fine Chem), toluene (BDH, India), cyclohexane (Ranbaxy, India), isooctane, *n*-butyldisulfide (s. d. Fine Chem), and *n*-butylmercaptan (s. d. Fine Chem) were used without purification. Precipitated silica (s. d. Fine Chem), alumina (s. d. Fine Chem), vinyl trichlorosilane (VTCS; Fluka, Switzerland), diaminodiphenyl ether (DADPE), DADPS, and BTDA (Fluka) were used as provided. The standard bisphenol-A epoxy resin system with a 0.519-g epoxy equivalent was synthesized by the usual method.

Testing methods and procedures

Lap-shear test

Three interfaces of adherents, namely, metal-metal (Al-Al), teak wood-metal (W-Al), and teak wood-teak wood (W-W) interfaces, were used for lap-shear and other adhesive tests. The overlapping zone was 322.58 mm² in area (25.4 × 12.7 mm) for each case. The thickness of the adhesive layer within the overlapping area was 0.03 mm. The polymers were cured with different curing agents, namely, DADPS, DADPE, BTDA, and the Ciba-Geigy two-pack hardener under

Correspondence to: S. Maiti, Subarnarekha, J23 Bidhannagar, Midnapore 721101, W. B., India (sukumarmaiti@indiatimes.com).



Scheme 1

different conditions, and their lap-shear strength was measured as per the standard procedure.¹⁰

Before application of adhesive materials on the adherent surfaces, the surfaces were prepared. Aluminum specimens were prepared with the chromic-sulfuric acid cleaning method,¹¹ and it was also rubbed with 200-mesh Cu metal brushes to increase the surface area. The wood specimens were washed with toluene and petroleum ether to remove grease and organic oil materials and were dried at 100°C.

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.¹² The polymer samples were tested by the 180° peel test. In this test, two 25.4 × 304.8 mm, 3 mm thick aluminum specimens were bonded along 152.4 mm length of the specimens. Two ends of the unbounded aluminum sheets were bent sharply at 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 a peel rate of 50 mm/min.

Cohesion test

This test measures the shear force necessary to strip polyester cloth from the rigid adherent surfaces, for

example, Al or wood surfaces.¹³ The test consisted of one piece of polyester cloth (25.4 × 152.4 mm) bonded to the teak wood or an Al sheet substrate with a contact area of 25.4 × 50.8 mm. The test specimens were prepared under 100 psi and at 150°C for 4 h with the two-pack Ciba-Geigy hardener.

RESULTS AND DISCUSSION

The synthesis and characterization of the polymers were reported elsewhere.¹⁴ We synthesized polymers by reacting a proprietary trifunctional heterocyclic compound and 4-4'-sulfone diphenol, 4,4'-thiodiphenol, and epichlorohydrin (Scheme 1).

The adhesive performance of the HP₂ polymer (epoxy content = 0.32 equivalent) was tested by lap-shear, peel, and cohesive tests. Because the epoxy content of the HP₁ polymer was very low (0.21 equivalent), only the lap-shear test was performed on this cured polymer system.

Curing characteristics of the resins

The epoxy resins were cured with the two-pack Ciba-Geigy commercial hardener at 150°C for 4 h under 100 psi pressure. The curing schedule was followed as given in Table I with DADPS, DADPE, and BTDA as curing agents. The first formulated resin (polymers and curing agent) was recorded by differential scanning calorimetry (DSC) in an air atmosphere at a heat-

TABLE I
Curing Temperatures of the Epoxy Resin Adhesive Obtained from the DSC Study with Various Curing Agents

Epoxy resin used (parts)	DADPE (phr)	DADPS (phr)	BTDA (phr)	Curing temperature (°C)	Curing time (h)
100	25	—	—	160	3
100	—	27	—	180	4
100	—	—	40	200	2

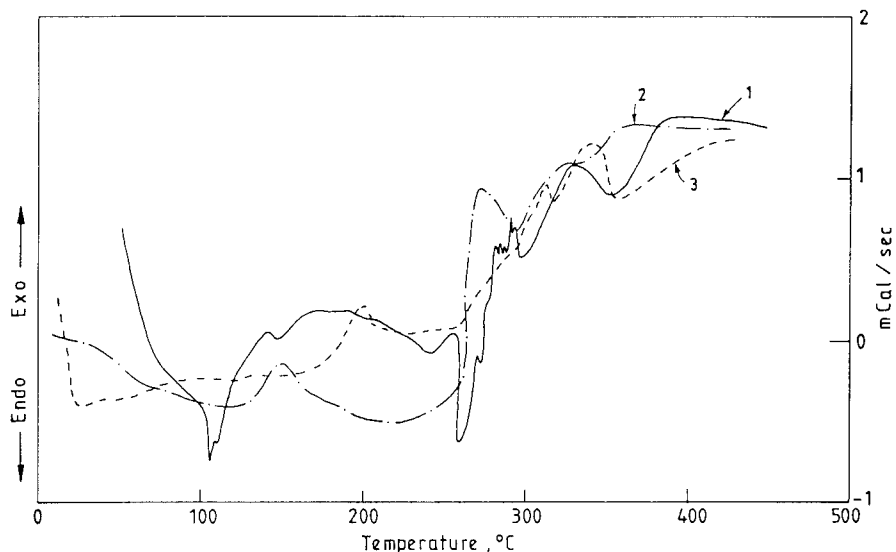


Figure 1 DSC thermogram of the HP₂ resin with (1) DADPS, (2) DADPE, and (3) BTDA.

ing rate of 10°C/min (Fig. 1). Figure 1 shows a characteristic exotherm at a particular temperature region (~150–200°C) that disappeared in the DSC curves of the preheated formulated resin in the same temperature region. Others peaks were present in both DSC scans due to unknown oxidation or reduction reactions. The curing temperature and amount of curing agent employed for the DADPS were somewhat higher than those used for DADPE because of the lower reactivity of the former and other diamines due to the electron withdrawing characteristic of these —SO₂— groups.¹³ From the DSC study, the curing temperature for DADPS was 180°C, whereas for DADPE it was 160°C (Fig. 1).

On the other hand, the curing temperature for BTDA was 200°C under the same pressure (Fig. 1). The reactivity of this anhydride is low, but in presence of a Lewis acid such as AlCl₃ (2% w/w), the rate of cure of the epoxy polymer is enhanced.¹⁵ This Lewis acid during the curing cycle coordinates with the oxygen atom of the epoxy ring to facilitate the opening of this ring.

Lap-shear test

The results of the lap-shear strength tests of the adhesive polymers were compared with those of the bisphenol-A standard epoxy resin on the Al–Al, W–W, and W–Al surfaces. The results are shown in Tables II and III within the limit of standard deviation at ±0.5%. The adhesive strength of the polymers was measured with the two-pack Ciba-Geigy commercial hardener, DADPS, DADPE, and BTDA under appropriate curing conditions. In each case, the adhesive strength of the standard epoxy resin was much higher than the new epoxy resin (HP₂; Tables II and III). This

may have been due to the lower epoxy content of newly synthesized polymers. It was reported earlier that the adhesive strength of the heterocyclic-based epoxy resin increased with increases in epoxy content.

TABLE II
Results of the Lap-Shear Test for the Standard Epoxy Resin and Epoxy Resins Cured at a High Temperature with Different Hardeners (DADPS, DADPE, and BTDA) According to the Curing Described in Table I

Resin used	Curing agent	Interfaces	Tensile strength (N/m ²) × 10 ⁻⁶
HP ₁	DADPS	W–W	10.29
		W–Al	6.95
		Al–Al	3.82
	DADPE	W–W	9.31
		Al–W	5.78
		Al–Al	3.62
	BTDA	W–W	11.85
		W–Al	8.52
		W–W	4.01
HP ₂	DADPS	W–W	13.23
		W–Al	6.95
		Al–Al	6.66
	DADPE	W–W	11.76
		Al–W	6.76
		Al–Al	6.07
	BTDA	W–W	13.91
		W–Al	7.25
		Al–Al	6.07
Standard epoxy	DADPS	W–W	16.66
		W–Al	14.01
		Al–Al	12.83
	DADPE	W–W	15.38
		W–Al	14.40
		Al–Al	11.95
	BTDA	W–W	17.14
		W–Al	15.32
		Al–Al	12.80

TABLE III
Results of the Lap-Shear Test for the Standard Epoxy Resin and Epoxy Resins Cured with Ciba-Geigy's Two-Pack Hardener

Resin used	Interfaces	Tensile strength
		(N/m ²) × 10 ⁻⁶
HP ₁	W-W	13.72
	W-Al	9.80
	Al-Al	5.68
HP ₂	W-W	17.73
	W-Al	14.79
	Al-Al	14.40
Standard epoxy	W-W	25.32
	W-Al	26.01
	Al-Al	25.57

Effect of various harsh environments on lap-shear strength

The durability of adhesive materials under various harsh environmental conditions such as boiling water, 5% salt water, 5% aqueous HCl, and various solvent mixtures was examined.¹⁶ Under these severe conditions, only the two-pack hardener cured samples were treated.

The percentage retention of the lap-shear strength of the polymer (HP₂) and standard epoxy resin on various surfaces such as W-W, Al-Al, and W-Al surfaces are represented in Table IV. The retention of the adhesive strength of new polymers under the boiling water treatment was poor. This result may have been due to the dissolution of the polymer in boiling water, possibly caused by the hydrolysis of the C-Cl linkage.¹⁷ Under chemical reagent treatment, the samples retained their adhesive strength to a considerable extent (≥70%), but this was always less than that of the standard resin. This was due to the lower crosslink density of the new epoxy polymer, which was probably responsible for the solvent molecule penetrating into the adhesive layer, leading to failure of the adhesive. The lower crosslink density of the new resin was due to the lower epoxy content.

TABLE V
Effect of Various Additives on the Lap-Shear Strength of the HP₂ Resin and the Standard Epoxy Resin (Hardener Cure System)

Resin system	Interfaces	Increase of critical tensile strength (%)	
		10% Al ₂ O ₃ + 10% SiO ₂	10% Al ₂ O ₃ + 10% VTCS
HP ₂	W-W	3.3	12.58
	W-Al	5.3	13.00
	Al-Al	6.8	15.00
Standard epoxy	W-W	2.4	1.00
	W-Al	2.6	9.00
	Al-Al	2.8	2.00

Resins were cured at 150°C and 100 psi pressure for 4 h.

Effect of various additives on lap-shear strength

To investigate the effect of various additives on the adhesive strength of the polymer, we mixed (1) 10% Al₂O₃ and 10% silica (precipitated type) and (2) 10% Al₂O₃ and 10% VTCS with the HP₂ polymer and the standard epoxy resin before curing. Lap-shear tests were performed under identical conditions, and the results are given in Table V. In this case of the HP₂ polymer, the enhancement of adhesive strength for Al-Al interfaces was higher than for W-Al and W-W interfaces. From these data, it was observed that VTCS was a powerful additive for the enhancement of adhesive strength in each case. Most likely, it helped form an effective bonding interaction between epoxy resins and metal or wood surfaces; that is, it acted as a good coupling agent. In this case, the Si-O bond was generated from the hydrolysis of the Si-Cl bond, which strongly interacted with the substrate surfaces. In addition, a coupling interaction arose from the reaction of the vinyl group of the silane with the adhesive polymer.¹⁸

Peel test

The peel test was performed for the HP₂ resin and the standard epoxy resin. Both the resins were cured with

TABLE IV
Percentage Retention of Adhesive Strength of the HP₂ Resin and the Standard Epoxy Resin After Various Harsh Environment Treatments

Adhesive	Interfaces	Retention of adhesive strength (%)						
		5% Salt Water treatment		5% HCl treatment		Boiling water treatment (1 h)	Chemical treatment	
		3 days	5 days	3 days	5 days		3 days	5 days
Resin HP ₂	W-W	90	60	60	31	35.90	98	82
	W-Al	84	43	53	27	19.86	87	73
	Al-Al	77	57	58	22	14.28	82	76
Standard epoxy resin	W-W	99	71	80	29.80	71.30	99.20	97.30
	W-Al	93	82	90	21.67	53.90	98.90	93.00
	Al-Al	96	86	78	21.00	54.00	99.00	96.00

TABLE VI
Results of the Peel Test of HP₂ and Standard Epoxy Resin on Al–Al Interfaces

Resin used	Peel fracture energy (kJ/m ²) ^a
HP ₂	5.56
Standard epoxy resin	9.60
HP ₂ + 10% Al ₂ O ₃ + 10% SiO ₂	6.66
Standard epoxy resin + 10% Al ₂ O ₃ + 10% SiO ₂	10.06
Standard epoxy resin + 10% Al ₂ O ₃ + 10% VTCS	10.14
HP ₂ + 10% Al ₂ O ₃ + 10% VTCS	9.87

^a Resins were cured at 150°C and 100 psi pressure for 4 h.

the two-pack Ciba-Geigy hardener at 150°C for 4 h. Results of the peel test are shown in Table VI. The peel strength in the higher temperature cure system was higher than in the lower temperature cure system. At higher curing temperatures, due to extensive crosslinking, bonding strength was higher for each system. The peel strength of the polymer–metal interface was again higher in the case of the standard epoxy resin than for the HP₂ resin. This was due to the high epoxy content of the standard epoxy resin (0.519). The peel strength also depended on the nature of additives. A mixture of 10% Al₂O₃ and 10% SiO₂ increased the peel strength to a lesser extent than did the 10% Al₂O₃ and 10% VTCS in the case of the HP₂ resin.

TABLE VII
Results of the Cohesive Test of the Resins Cured by the Two-Pack Hardener

Resin used	Interface	Cohesive failure energy (N/m ²) × 10 ⁻⁶
HP ₂	Polyester–metal	4.75
	Polyester–wood	6.73
Standard epoxy resin	Polyester–metal	8.70
	Polyester–wood	9.32

Resins were cured at 150°C and 100 psi pressure for 4 h.

The percentage enhancement of peel strength by various additives was higher in the case of HP₂ than for the standard epoxy resin.

Cohesive test

The results of this test are given in Table VII. The cohesion of both the standard resin and new epoxy resin HP₂ was better on the wood substrate than on the metal substrate. This may be attributed to the higher cohesive interaction of the polymers with wood (teak wood). The cohesive strength of polyester cloth for the new epoxies was lower than that of the standard resin for both the cases (e.g., metal and wood). However, mixing 10% Al₂O₃ + 10% SiO₂ and 10%

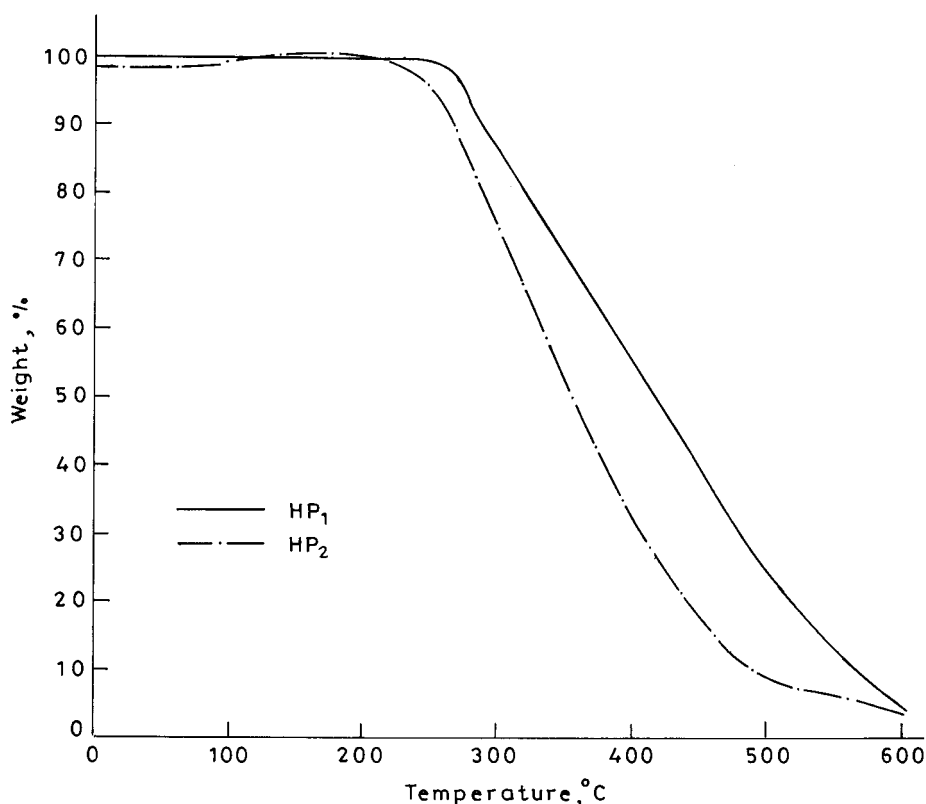


Figure 2 TGA curve of the HP₁ and HP₂ resins.

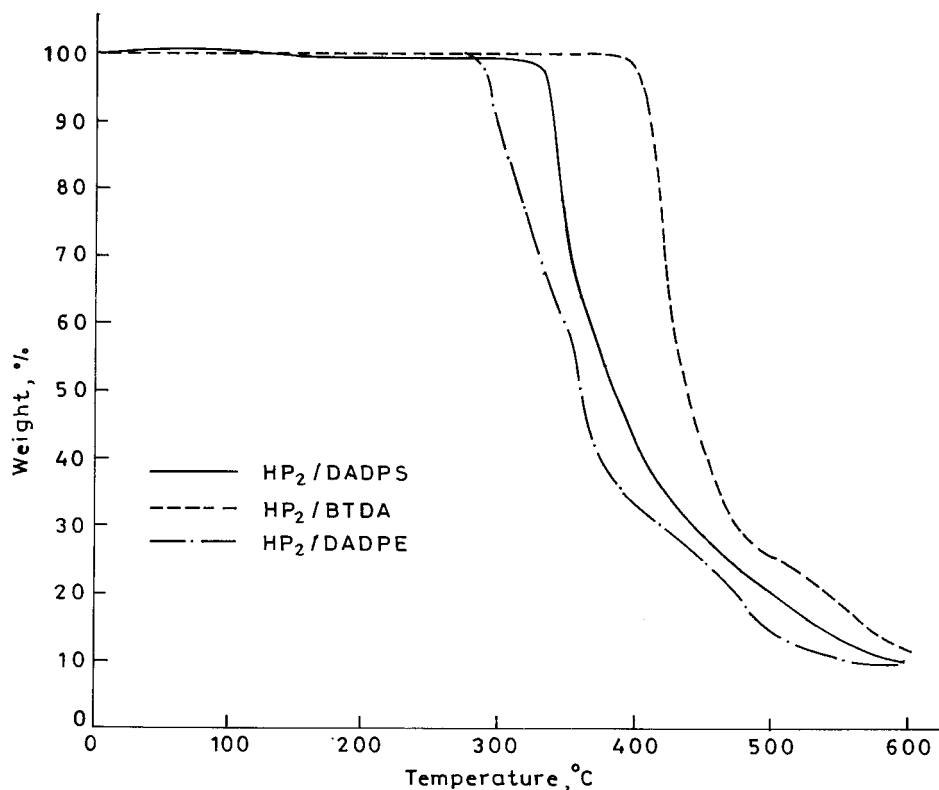


Figure 3 TGA thermogram of HP₂ cured with DADPS, DADPE, and BTDA.

Al₂O₃ + 10% VTCS with the resins before curing improved the cohesive strength to a significant extent.

Thermal stability

The thermal stability of the cured resin and uncured resins was studied by thermogravimetric analysis (TGA; Figs. 2 and 3). From the TGA curve, it is evident that the uncured resin (HP₂) started to degrade at 245°C, leaving a char residue of 3% at 600°C, whereas the standard resin started to degrade from about 200°C.¹⁹ The thermal stability of the BTDA cured resin, which started to degrade at 388.8°C, was much higher than that of the others due to extensive crosslinking and higher thermal stability of the ester linkage.¹⁹ Similarly, due to the presence of thermo-stable —SO₂— groups in the DADPS cured resin, the thermal stability of the DADPS cured resin was higher than that of the DADPE cured resin. From this investigation, it is clear that thermal stability of the resin systems vary with the curing agents.

CONCLUSIONS

The epoxy resins were cured with DADPS, DADPE, BTDA, and Ciba-Geigy's two-pack hardener. In each case, cured resins had lower adhesive strengths compared with the bisphenol-A epichlorohydrin standard epoxy resin on Al–Al, W–W, and W–Al interfaces.

This may have been due to the lower epoxy contents of these polymers compared with those of the standard epoxy resins (5% epoxy equivalent). The retention of adhesive strength in harsh environments was inferior for our adhesive as compared with the standard epoxy resin. The effect of various additives (e.g., Al₂O₃, SiO₂, and VTCS) on the adhesive strength was studied, where VTCS acted as a good coupling agent.

The thermal stability of various cured resin systems was also studied, and the BTDA cured resin (HP₂) had a higher thermal stability compared to the other curing resin systems, and there was further possibility to increase the thermal stability of the cured resin systems, depending on curing agents.

S. Bhuniya thanks Council of Scientific & Industrial Research, New Delhi, for the award of a fellowship.

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