

Epoxy–Imide Resins from N-(4- and 3-carboxyphenyl)trimellitimidates. I. Adhesive and Thermal Properties

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ABSTRACT: Epoxy–imide resins were obtained by curing Araldite GY 250 (diglycidyl ether of bisphenol-A and epichlorohydrin; difunctional) and Araldite EPN1138 (Novolac–epoxy resin; polyfunctional) with N-(4- and 3-carboxyphenyl)trimellitimidates derived from 4- and 3-aminobenzoic acids and trimellitic anhydride. The adhesive lap shear strength of epoxy–imide systems at room temperature and at 100, 125, and 150°C was determined on stainless-steel substrates. Araldite GY 250-based systems give a room-temperature adhesive lap shear strength of about 23 MPa and 49–56% of the room-temperature adhesive strength retained at 150°C. Araldite EPN1138-based systems give a room-temperature adhesive lap shear strength of 16–19 MPa and 100% retention of room-temperature adhesive strength is observed at 150°C. Glass transition temperatures of the Araldite GY 250-based systems are in the range of 132–139°C and those of the Araldite EPN1138-based systems are in the range of 158–170°C. All these systems are thermally stable up to 360°C. The char residues of Araldite GY 250- and Araldite EPN1138-based systems are in the range of 22–26% and 41–42% at 900°C, respectively. Araldite EPN1138-based systems show a higher retention of adhesive strength at 150°C and have higher thermal stability and T_g when compared to Araldite GY 250-based systems. This has been attributed to the high crosslinking possible with Araldite EPN1138-based systems arising due to the polyfunctional nature of Araldite EPN1138. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1729–1736, 2000

Key words: imide–diacids; epoxy curatives; epoxy–imide; adhesive strength, epoxy resin

INTRODUCTION

Epoxy resins have good mechanical and electrical properties, good adhesion to a variety of substrates, excellent moisture and chemical resistance, and minimum shrinkage after cure.^{1–3} They are extensively used as coatings, adhesives,

potting compounds, and matrix resins for composites. In recent years, considerable attention has been focused toward combining the versatility of epoxy resins with the high-temperature properties of imide groups.^{4–14} This was achieved by the following four approaches: (i) curing epoxy resins with imide group containing curatives,^{4–12} (ii) modifying the backbone structure of epoxy resins with imide group,¹³ (iii) curing imide group containing epoxy resins with imide group containing curatives,¹⁴ and (iv) blending epoxy resins with

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thermoplastic polyimides or with functionalized polyimides.¹⁵⁻¹⁷

In our laboratory,⁷⁻¹⁰ we have been working on the development of novel epoxy-imides by adopting the first synthetic approach described above. Various epoxy-imide resins were synthesized by curing epoxy resins with different diimide-diacids and the adhesive and thermal properties of these systems were evaluated. It was observed that the properties of epoxy-imide systems are influenced by the aromatic content, imide content, nature of the diimide-diacids, and nature of the epoxy resins.

In continuation of our efforts to synthesize novel epoxy-imide resins and to study their structure-property correlations, in the present work, we report the synthesis of novel epoxy-imide resins obtained by curing Araldite GY 250 (diglycidyl ether of bisphenol-A and epichlorohydrin; difunctional) and Araldite EPN 1138 (Novolac-epoxy resin; polyfunctional) with imide-diacids, namely, *N*-(4-carboxyphenyl)trimellitimide (IDA-I) and *N*-(3-carboxyphenyl)trimellitimide (IDA-II). The cure behavior of epoxy resins with imide-diacids and the thermal properties of epoxy-imide systems were studied. The adhesive lap shear strength of epoxy-imide systems on stainless-steel substrates was evaluated at room temperature and at 100, 125, and 150°C.

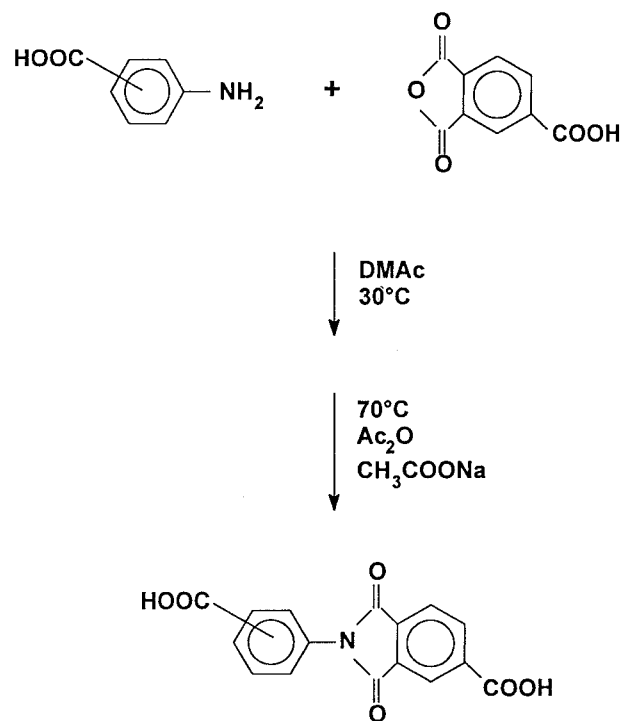
EXPERIMENTAL

Materials

Trimellitic anhydride (Aldrich, Milwaukee, WI) was purified by recrystallization from acetic anhydride. 4- and 3-Aminobenzoic acids (Aldrich) were used as received. Dimethylacetamide (DMAc) (Spectrochem, Mumbai, India) was purified by distilling over phosphorus pentoxide. Epoxy resins, Araldite GY 250 (DGEBA, epoxy value: 5.0–5.5 equiv/kg) and Araldite EPN 1138 (Novolac-epoxy, epoxy value: 5.5–5.7 equiv/kg) manufactured and supplied by M/s Hindustan Ciba-Geigy India Ltd. (Mumbai, India) were used.

Synthesis of Imide-Diacids

Imide-diacids, IDA-I and IDA-II, were synthesized through the reaction of 4- and 3-aminobenzoic acids, respectively, with trimellitic anhydride in DMAc followed by chemical imidization with acetic anhydride and anhydrous sodium acetate



Scheme 1 Synthesis of imide-diacids.

at 70°C (Scheme 1). The imide-diacids were characterized by IR, elemental analysis, and the acid value. The characteristic imide peaks were observed at 1780, 1719, 1385, and 725 cm^{-1} . The broad band around 3500 cm^{-1} is due to the —OH of the carboxylic acid groups.

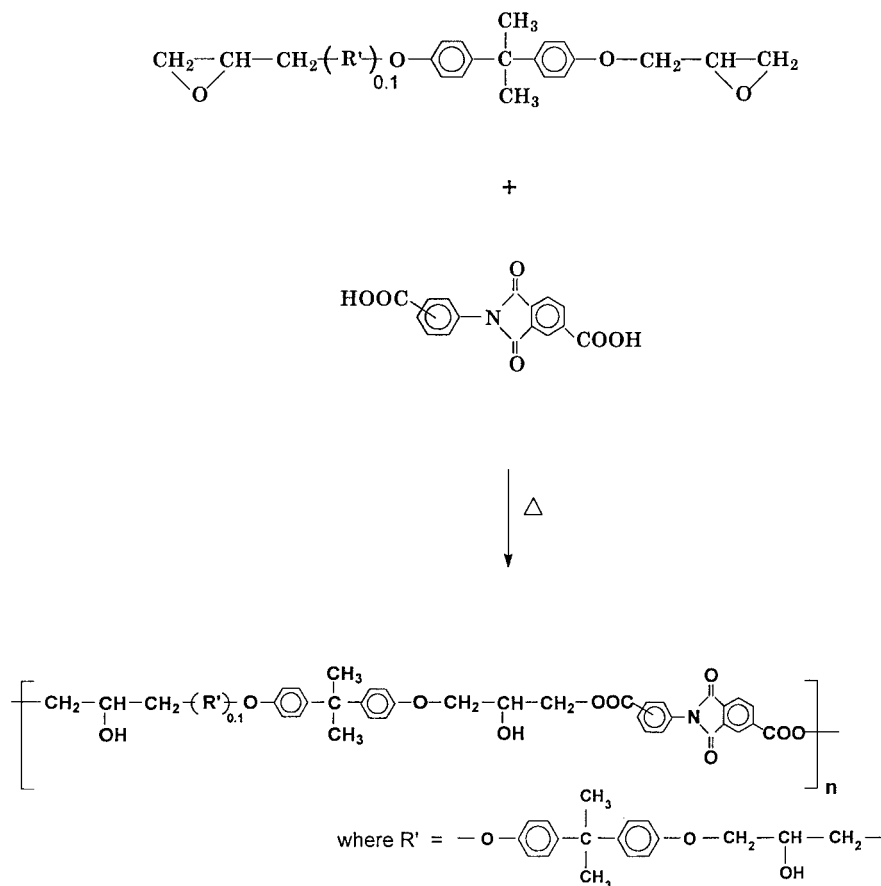
For IDA-I: ANAL Calcd: C, 61.74%; H, 2.89%; N, 4.50%. Found: C, 61.62%; H, 2.73%; N, 4.40%. Acid value Calcd: 360 mg KOH/g. Found: 355 mg KOH/g. For IDA-II: ANAL Calcd: C, 61.74%; H, 2.89%; N, 4.50%. Found: C, 61.10%; H, 2.98%; N, 4.56%. Acid value Calcd: 360 mg KOH/g. Found 350 mg KOH/g. DSC scans of IDA-I and IDA-II suggest that they do not melt up to 330°C and undergo degradation above this temperature.

Surface Preparation of Stainless-Steel Coupons

Surface preparation of stainless-steel (AISI 304 SS cold roll) test pieces of dimensions 100 × 25 × 1.6 mm were made following the procedure described elsewhere.⁷

Curing of Epoxy Resins with Imide-Diacids and Adhesive Formulation

The epoxy resin (Araldite GY 250 or Araldite EPN 1138) and the imide-diacid (IDA-I or IDA-

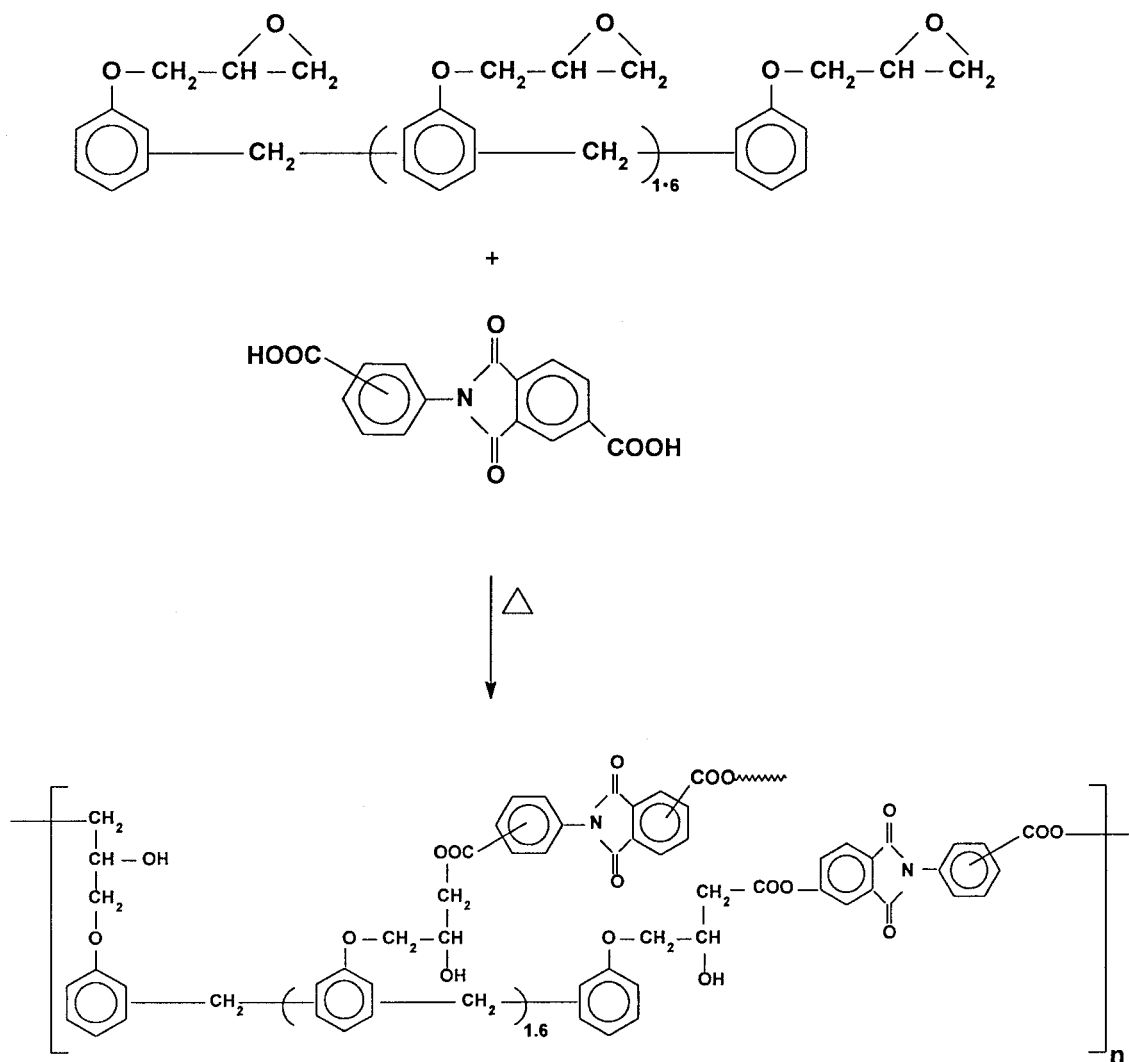


Scheme 2 Structure of epoxy-imide resins derived from Araldite GY 250 and imide-diacids.

II) in a 1:1 epoxy equivalent-to-carboxy equivalent ratio was mixed thoroughly in a pestle and mortar and the cure reaction was followed by DSC and IR spectra. From the DSC data, the initial, maximum, and final cure temperatures (T_i , T_{\max} , and T_f , respectively) were determined. The epoxy resin-imide-diacid mixture was applied on cleaned stainless-steel substrates and the steel coupons were then bonded in such a way that the bonded area was approximately 300 mm². The bonded specimens were kept in an air oven under a contact pressure and the temperature of the oven was raised to T_i and maintained at this temperature for 30 min. The temperature of the oven was further raised to T_{\max} and maintained at this temperature for 1 h and finally the oven temperature was raised to T_f and the specimens were kept at this temperature for 30 min. The oven was allowed to cool to room temperature before the specimens were removed.

Measurements

IR spectra of the samples were recorded on a Nicolet 510 P FTIR in KBr pellets or as a smear on a NaCl plate. Determination of the glass transition temperature and DSC studies were made with a Mettler DSC TA 3000 at a heating rate of 10°C/min. TGA curves were recorded with a DuPont 900 thermal analyzer in conjunction with a 951 thermogravimetric analyzer at a heating rate of 10°C/min in a nitrogen atmosphere. The tensile lap shear strength of bonded stainless-steel specimens was measured using an Instron (Model No. 4202) at a crosshead speed of 10 mm/min. The tensile lap shear strength at 100, 125, and 150°C was measured after equilibrating the test specimens at the required temperature for a period of 10 min in a hot chamber attached to the Instron. To obtain a lap shear strength value at a particular temperature, five bonded coupons were tested. The lap shear strength value reported is



Scheme 3 Structure of epoxy-imide resins derived from Araldite EPN 1138 and imide-diacids.

an average of at least three measurements which fell in the range of ± 1 MPa.

RESULTS AND DISCUSSION

Curing of Epoxy Resins with Imide-Diacids

The curing of epoxy resins with imide-diacids proceeds through a carboxy-epoxy addition reaction at elevated temperatures. The structures of epoxy-imide resins thus obtained for Araldite GY 250-IDA-I/II and Araldite EPN 1138-IDA-I/II systems are given in Schemes 2 and 3, respectively. The curing of GY 250 with IDA-I/II (for epoxy equiv to carboxy equiv ratio = 1) is expected to result in the formation of a linear poly-

mer, whereas in the case of EPN 1138-IDA-I/II systems, crosslinked epoxy-imide resins are formed due to the polyfunctional nature of Araldite EPN 1138. This basic difference in the epoxy-imide resins derived from Araldite GY 250 and Araldite EPN 1138 resins is found to influence the thermal as well as the adhesive properties. For the sake of convenience, the text, Araldite GY 250-IDA-I/II and Araldite EPN 1138-IDA-I/II will be referred to as GY 250-IDA-I/II and EPN 1138-IDA-I/II, respectively.

The cure reaction of epoxy resins, Araldite GY 250 and Araldite EPN 1138 with IDA-I and IDA-II, was followed by IR and DSC. The IR spectra of the GY 250-IDA-I mixture and the corresponding epoxy-imide resins are given in Figure 1, and in a

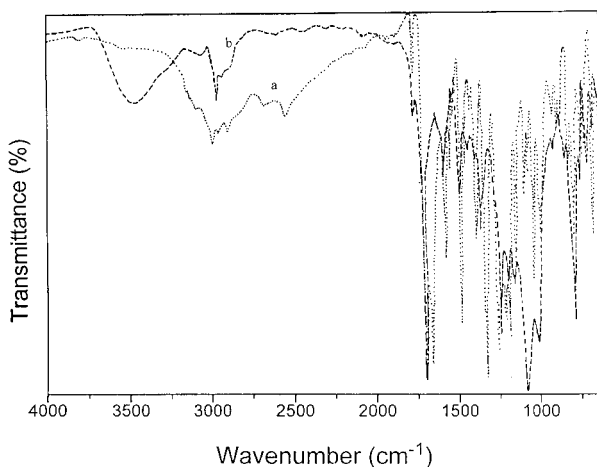


Figure 1 IR spectra of (a) mixture of Araldite GY 250 and IDA-I and (b) the corresponding cured sample.

similar way, the IR spectra of the EPN 1138-IDA-I system are given in Figure 2. The peak observed at 910 cm^{-1} corresponding to the epoxy group in the IR spectra of the uncured resins disappeared in the IR spectra of the cured resins. This indicates that the cure reaction is complete. The IR spectra of the cured resins show absorptions at 1780 , 1719 , 1385 , and 725 cm^{-1} arising due to the imide group. The broad band around 3500 cm^{-1} is due to the $-\text{OH}$ group obtained as a result of an esterification reaction of the epoxy and the $-\text{COOH}$ group. The characteristic ester peak has probably merged with the imide absorption at 1719 cm^{-1} .

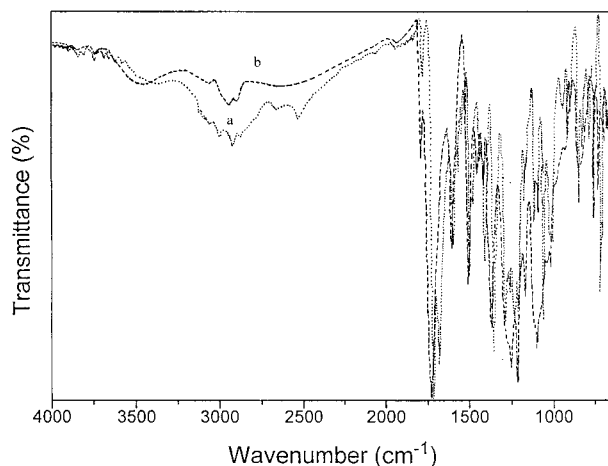


Figure 2 IR spectra of (a) mixture of Araldite EPN 1138 and IDA-I and (b) the corresponding cured sample.

Table I Curing of Epoxy Resins with Imide-Diacids: DSC Studies

System	T_i (°C)	T_{\max} (°C)	T_f (°C)
GY 250 + IDA-I	150	200	230
GY 250 + IDA-II	170	230	250
EPN 1138 + IDA-I	170	230	270
EPN 1138 + IDA-II	200	250	270

The DSC data for the cure reaction are summarized in Table I. It is observed that for both Araldite GY 250- and Araldite EPN 1138-based systems, T_i and T_{\max} are lower by $20\text{--}30^\circ\text{C}$ for IDA-I when compared to those of IDA-II. This observation may be attributed to the higher reactivity of IDA-I. The carboxylic acid in the *N*-4-carboxyphenyl group of IDA-I is expected to be more acidic than that present in the *N*-3-carboxyphenyl group of IDA-II due to the $-I$ effect of the trimellitimido group in the former. It is noticed that T_i , T_{\max} , and T_f are higher for EPN 1138-based systems when compared to those for GY 250-based systems. Interestingly, in our earlier investigation⁷ on curing of Araldite GY 250 and Araldite EPN 1138 with diimide-diacids, we observed that T_i is lower for EPN 1138-based systems. This suggests that the temperature range for curing depends on the nature of the imide-acids and the epoxy resins and it is difficult to arrive at a generalized conclusion on the trends of T_i , T_{\max} , and T_f .

Thermal Properties

Thermal stability of different epoxy-imide resins was studied by thermogravimetric analysis. The TGA curves of GY 250/EPN 1138-IDA-I/II systems are given in Figure 3. It is observed that all these systems are stable up to 360°C , above which they undergo rapid degradation. A similar observation was made for the GY 250/EPN 1138-diimide-diacid system. The char residues of the GY 250-IDA systems at 900°C fall in the range of $22\text{--}26\%$, whereas for EPN 1138-IDA systems, char residues are in the range of $41\text{--}42\%$. The higher char residue of EPN 1138-based systems when compared to GY 250-based systems is attributed to the higher crosslinking possible for the former system due to the polyfunctional nature of Araldite EPN 1138.

The glass transition temperature of the epoxy-imide systems was determined by DSC and the

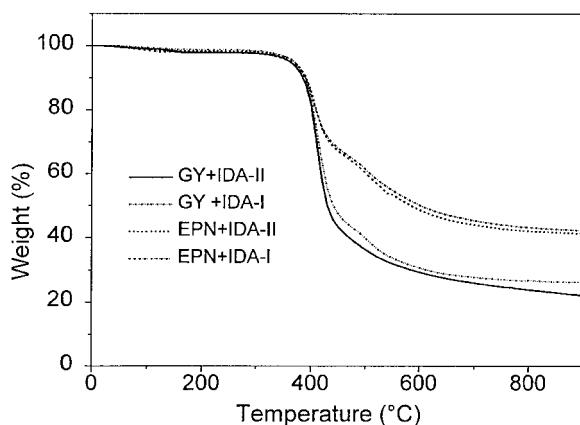


Figure 3 TGA curves of epoxy-imide resins.

values are compared in Table II. The glass transition temperatures of Araldite EPN 1138-based systems are higher than those of Araldite GY 250-based systems. A similar trend was observed with epoxy-imide resins derived from Araldite GY 250/Araldite EPN 1138 and diimide-diacids.⁷ The polyfunctional nature of Araldite EPN 1138 contributed to high crosslinking, which is responsible for the increase in T_g .

Adhesive Properties

Room-temperature Adhesive Strength

Adhesive lap shear strength values obtained at room temperature for the epoxy-imide resins are compared in Table III. It is observed that Araldite GY 250-based systems give a considerably higher adhesive strength when compared to that of Araldite EPN 1138-based systems. A similar observation was made during our investigation⁷ on epoxy-imide resins derived from bis(carboxyphthalimide)s. The lower adhesive strength of Araldite EPN 1138-based systems is probably caused by increase in the crosslinking and correspondingly brittle character arising due to the

Table II Glass Transition Temperature of Different Epoxy-Imide Systems

System	Glass Transition Temperature (°C)
GY 250 + IDA-I	139
GY 250 + IDA-II	132
EPN 1138 + IDA-I	170
EPN 1138 + IDA-II	158

Table III Adhesive Lap Shear Strength of Epoxy-Imides at Room Temperature

System	Adhesive Lap Shear Strength (MPa) at Room Temperature
GY 250 + IDA-I	23.1
GY 250 + IDA-II	22.5
EPN 1138 + IDA-I	15.8
EPN 1138 + IDA-II	19.0

polyfunctional nature of Araldite EPN 1138 resin. Although the adhesive strength values of GY 250-IDA-I and GY 250-IDA-II (22.5 and 23.1 MPa, respectively) are almost the same, the adhesive strength value of the EPN 1138-IDA-II system is higher by 3 MPa when compared to that of the EPN 1138-IDA-I system.

In our earlier study⁷ on bis(carboxyphthalimide)s (BCPIs), derived from aromatic diamines, as curatives for Araldite GY 250 and Araldite EPN 1138, we observed that the maximum adhesive lap shear strength of 18.3–19.3 and 13–16 MPa was realized for the GY 250-BCPI and EPN 1138-BCPI systems, respectively. It is interesting to note that the adhesive lap shear strength of both the GY 250-IDA and EPN 1138-IDA systems is higher than that of the GY 250-BCPI and EPN 1138-BCPI systems. The reason for the above observation can be understood by considering the way in which the curing proceeds in BCPI- and IDA-based systems. In the case of the GY 250-BCPI and EPN 1138-BCPI systems, the carboxy equivalent to the epoxy equivalent ratio to obtain the maximum lap shear strength fell in the ranges of 0.25–0.75 and 0.37–0.40, respectively. Although the carboxy equivalent to the epoxy equivalent ratio is less than 1 in the above systems, there was no unreacted epoxy groups and this was attributed to the reaction of dangling hydroxyl groups (produced through an epoxy-carboxy addition reaction) present in the growing polymer chain with epoxy groups. Attempts to increase the imide content of BCPI-based epoxy-imides with a view to improving the high-temperature properties met with limited success as it was difficult to increase the loading of BCPIs whose molecular weights are relatively higher than those of the conventional acid curatives. Unlike BCPIs, IDA-I and IDA-II are low molecular weight compounds and, hence, it has been possible to achieve a carboxy equivalent-to-epoxy equivalent ratio as high as 1:1. For this composi-

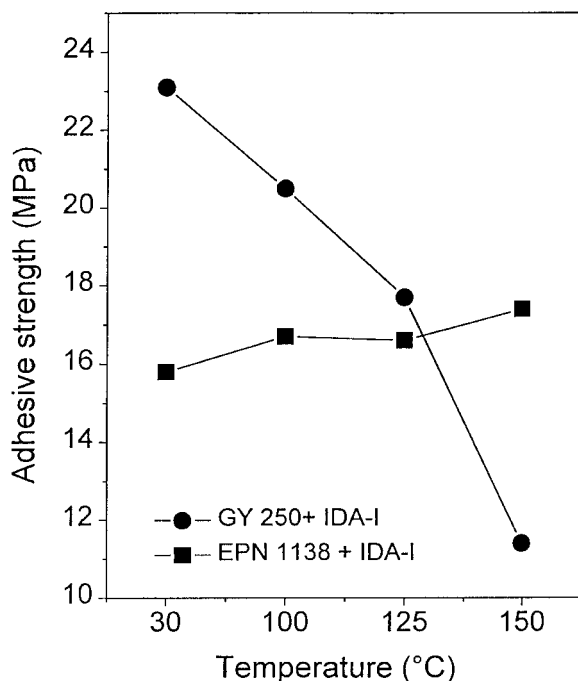


Figure 4 Effect of temperature on adhesive strength of epoxy-imide resins based on IDA-I.

tion, it is expected that the carboxy-epoxy addition reaction is the predominant one, resulting in the formation of a high molecular weight polymer, although the reaction of dangling—OH groups with the epoxy groups cannot be completely ruled out. Probably, the above factors contribute to a higher room-temperature adhesive strength obtained with IDA-based epoxy-imides when compared to BCPI-based epoxy-imides.

Effect of Temperature on Adhesive Strength

The adhesive strength of the GY 250-IDA and EPN 1138-IDA systems at room temperature, and at 100, 125, and 150°C is compared in Figures 4 and 5, respectively, and the percentage retention of the adhesive strength at different temperatures with respect to the room-temperature adhesive strength is presented in Table IV. It is observed that Araldite GY 250-IDA systems retain reasonably good adhesive strength (16–18 MPa; 72–77% retention) at 125°C. At 150°C, these systems retain about 49–56% of the room-temperature adhesive strength. GY 250-IDA systems are thermoplastic in nature and have glass transition temperatures in the range of 132–139°C. Hence, with increase in temperature to 150°C, there is considerable reduction in the adhesive strength for the above systems.

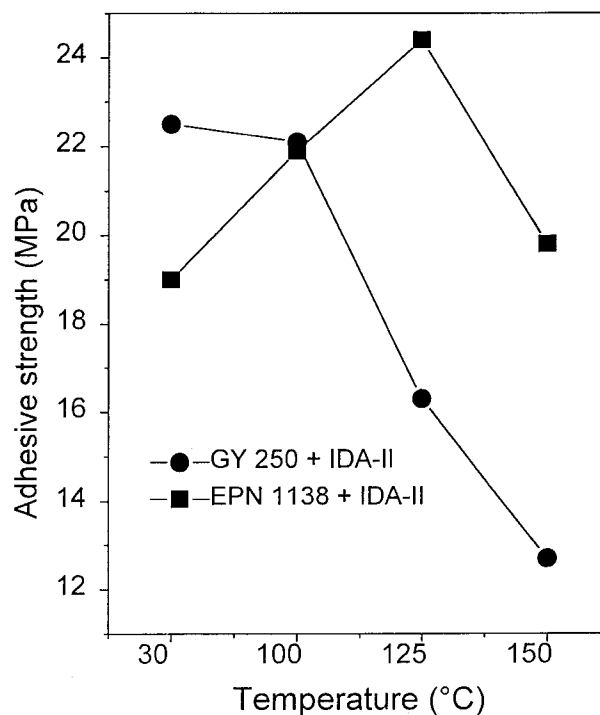


Figure 5 Effect of temperature on adhesive strength of epoxy-imide resins based on IDA-II.

Unlike in the case of GY 250-IDA systems, the adhesive-strength values of EPN 1138-IDA systems at 100, 125, and 150°C are higher than those of the corresponding room-temperature adhesive-strength values. The combined effect of the polyfunctional nature of Araldite EPN 1138 and the rigidity of imide curatives probably reduces the molecular mobility needed to properly position two reactive end groups for reaction. This restricted mobility imparts stresses in the epoxy-imide systems at room temperature and makes the EPN 1138-

Table IV Percentage Retention of Different Epoxy-Imide Systems at Elevated Temperatures with Respect to Their Room-temperature Adhesive Strength

System	% Retention of Room Temperature Adhesive Strength at		
	100°C	125°C	150°C
GY 250 + IDA-I	89	77	49
GY 250 + IDA-II	98	72	56
EPN 1138 + IDA-I	106	102	108
EPN 1138 + IDA-II	115	128	104

based system brittle. With increase in the temperature, the mobility increases, which, in turn, reduces the brittleness of the system. Thus, in the case of the EPN 1138-based system, lap shear strength increases with increase in temperature.

At 150°C, the EPN 1138-IDA-I and EPN 1138-IDA-II systems retain 108 and 104% of the room-temperature adhesive strength, respectively. It is remarkable that the retention of the adhesive strength at 150°C is almost double in the case of EPN 1138-IDA systems when compared to that of GY 250-IDA systems and this has been attributed to the presence of crosslinked rigid structures in the former systems.

Comparison of the percentage retention of the adhesive strength at 150°C for GY 250-IDA systems with that of GY 250-BCPI systems investigated by us earlier⁷ suggests that the latter systems have better adhesive strength retention than that of the former systems. The better performance of GY 250-BCPI-based systems at elevated temperature may be attributed to their high aromatic and imide content when compared to that of GY 250-IDA systems. For EPN 1138-IDA systems, the percentage retention of the adhesive strength at 150°C is comparable to that of the EPN 1138-BCPI systems, although the aromatic and imide content of the former is less than that of the latter. As the epoxy-imide derived from Araldite EPN 1138 are highly crosslinked systems when compared to Araldite GY 250-based systems, the effect of the aromatic and imide content is less pronounced on the adhesive strength of the former systems.

CONCLUSIONS

Epoxy-imide resins were obtained by curing Araldite GY 250 and Araldite EPN 1138 with imide-diacids, IDA-I and IDA-II, and the adhesive and thermal properties of these resins were evaluated. Araldite GY 250-based systems give an adhesive lap shear strength of about 23 MPa on stainless-steel substrates at room temperature and retain about 49–56% of this strength at 150°C. On the other hand, Araldite EPN 1138-based systems give a 16–19 MPa adhesive strength at room temperature and show a marginal increase in adhesive strength at 150°C.

TGA studies of the epoxy-imide resins suggest that they are stable up to 360°C and undergo rapid degradation above this temperature. Araldite EPN 1138-based systems have better overall thermal stability and high T_g when compared to Araldite GY 250-based systems. The bet-

ter performance of Araldite EPN 1138-based systems is attributed to the high crosslinking possible with the former systems arising from the polyfunctional nature of Araldite EPN 1138.

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