Epoxy–Imide Resins from 2,2-Bis[4-(4-trimellitimidophenoxy)phenyl]propane: Adhesive and Thermal Properties

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ABSTRACT: Epoxy–imide resins were obtained by curing the epoxy resin Araldite® GY 250 (DGEBA; difunctional) and Araldite® EPN 1138 (Novolac epoxy; polyfunctional) with the diimide–diacid, 2,2-bis[4-(4-trimellitimidophenoxy)phenyl]propane. The adhesive lap shear strength of epoxy–imide resins at room temperature and at 100 and 150°C was determined on a stainless-steel substrate. The effect of solvent on the adhesive strength of epoxy–imide resins was studied, and tetrahydrofuran was found to give the best results for improving the wetting behavior of epoxy resins. It is observed that with the increase in imide content the adhesive strength at room temperature as well as at elevated temperature increases when tetrahydrofuran is used as a solvent in the adhesive formulation. The room temperature adhesive strength for GY 250-based systems is in the range of 20.8–23.5 MPa and 45–58% of this strength is retained at 150°C. For EPN 1138-based systems, the room temperature adhesive strength is in the range of 14.3–20.3 MPa, and in fact, an increase in adhesive strength by 1–26% is observed at 150°C. All these systems are stable up to 370°C, and char residues of GY 250- and EPN 1138-based systems at 800°C are in the range of 27–31 and 33–41%, respectively, in nitrogen atmosphere. The overall thermal stability and retention of room temperature adhesive strength at elevated temperature are higher for EPN 1138-based systems when compared to those of GY 250-based systems, and this observation has been attributed to the higher crosslinking possible for EPN-based systems when compared to GY 250-based systems. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1737–1746, 2003

Key words: dimide–diacid; epoxy curatives; epoxy–imide resins; adhesive strength; adhesives; crosslinking

INTRODUCTION

Epoxy–imide resins have gained attention of researchers as they combine the versatility and ease of processability of epoxy resins and high temperature properties of imide groups.[1–12] Epoxy–imide resins are used as matrix resin in composites, organic insulators, potting and encapsulating compounds, and adhesives.[2–4] In our laboratory, we have been synthesizing epoxy–imide resins by curing epoxy resins with different types of diimide–diacids.[6–10] We have observed that the adhesive and thermal properties of epoxy–imide resins synthesized from diimide–diacids are greatly influenced by the nature of the aromatic diamines used for the synthesis of diimide–diacids.

In the present article, we report the adhesive and thermal properties of epoxy–imide resins based on the diimide–diacid, 2,2-bis[4-(4-trimellitimidophenoxy)- phenyl]propane (DIDA-V), the structure of which is shown below:
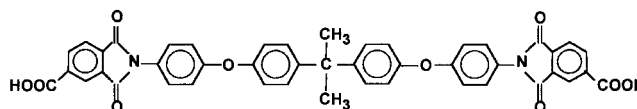
Epoxy–imide resins were obtained through the reaction of epoxy resins, Araldite® GY 250 (DGEBA; difunctional) and Araldite® EPN 1138 (Novolac epoxy; polyfunctional) with DIDA-V. Cure behavior of the epoxy resins with DIDA-V was studied by differential scanning calorimetry (DSC). Adhesive lap shear strength of the cured epoxy–imide resins at room temperature and at 100 and 150°C was obtained for different carboxyl equivalent to epoxy equivalent (equiv) ratios. The effect of solvent used for the adhesive formulation on the adhesive lap shear strength was investigated. Thermal properties of the cured epoxy–imide resins were also studied.
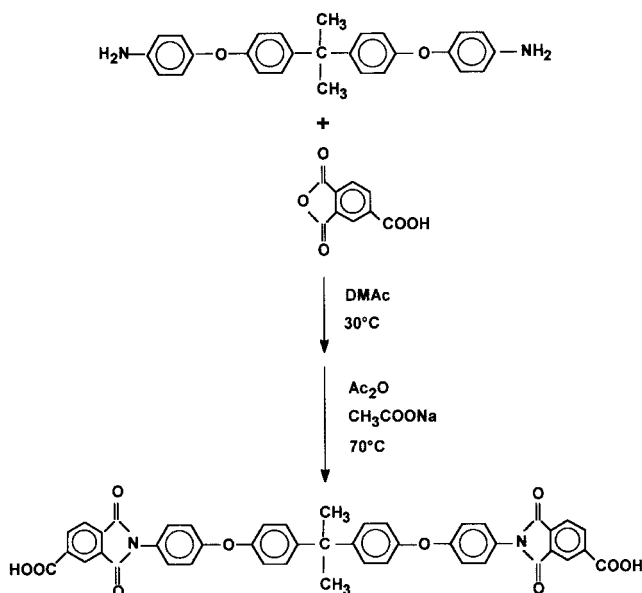
EXPERIMENTAL

Materials

Trimellitic anhydride (Aldrich, Milwaukee, WI) was purified by recrystallization from acetic anhydride.

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Scheme 1 Synthesis of DIDA-V.

4-Chloronitrobenzene (CDH Ltd., Mumbai, India), bisphenol A, and nickel–aluminum alloy (S. D. Chemicals, Mumbai, India) were used as received. Dimethylacetamide (Spectrochem, Mumbai, India) was purified by distilling over phosphorous pentoxide. Tetrahydrofuran (THF) (Qualigens, Mumbai, India) was refluxed over calcium hydride and distilled before use. Diglyme (Spectrochem, Mumbai, India) and hydrazine hydrate (S. D. Fine Chemicals, Mumbai, India) were used as received. Epoxy resins, Araldite® GY 250 (DGEBA; epoxy value: 5.0–5.5 equiv/kg; difunctional) and Araldite® EPN 1138 (Novolac epoxy: epoxy value: 5.5–5.7 equiv/kg; polyfunctional) manufactured and supplied by M/s. Hindustan Ciba-Geigy India Ltd., Mumbai, India, were used. Silane-treated E-glass fiber (Unnathi Corporation, Ahmedabad, India) having a density of 2580 kg/m^3 and linear density[13] of 4473 Denier, was used as received.

Synthesis of DIDA-V

Disodium salt of bisphenol A, prepared through the reaction of bisphenol A with sodium hydroxide solution, was reacted with 4-chloronitrobenzene to obtain 2,2-bis[4-(4-nitrophenoxy)phenyl]propane. This dinitro compound was subsequently reduced to the corresponding diamino compound by using Raney nickel catalyst and hydrazine hydrate in ethanol medium.[14] DIDA-V was synthesized (Scheme 1) by reacting the above diamine with trimellitic anhydride in 1:2 mole ratio in dimethylacetamide followed by chemical imidization adopting the procedure described elsewher.[7] DIDA-V was obtained as a yellow powder in 90% yield. It was characterized by acid value, elemental analysis, and infrared (IR) spectral studies. Acid value

calcd.: 148 mg KOH/g; found: 141 mg KOH/g. Anal. calcd. C, 71.2%; H, 3.95%; N, 3.69%; found: C, 70.9%; H, 3.68%; N, 3.71%. The characteristic imide peaks were observed at 1780, 1722, 1385, and 727 cm^{-1} in the IR spectrum. The broad band observed around 3500 cm^{-1} is due to —OH stretching of —COOH group; mp > 290°C.

Surface preparation of stainless-steel coupons

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

Adhesive preparation and curing of epoxy resins with DIDA-V

Epoxy resin (Araldite® GY 250 or Araldite® EPN 1138) and DIDA-V, in the required epoxy equiv to carboxyl equiv ratio, were 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 the final cure temperatures (T_{ic}, T_{maxc}, and T_{fc}, respectively) were determined. The epoxy resin–DIDA-V 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 3 cm^2. The bonded coupons were kept in an air oven and a contact pressure of 3.3 kg/cm^2 was applied using a lever press for facilitating the formation of a uniform thin adhesive layer between the stainless-steel coupons. Then the temperature of the oven was raised to T_{ic} over a period of 30 min and maintained at this temperature for 30 min. The temperature of the oven was further raised to T_{maxc} over a period of 15 min and maintained at this temperature for 1 h. Finally, the oven temperature was raised to T_{fc} over a period of 15 min and the coupons were kept at this temperature for 30 min. The oven was allowed to cool to room temperature before the coupons were removed.

In selected cases, solvents such as dimethylacetamide (DMAc), diglyme, and THF were used in the adhesive formulation to improve the wetting of the substrate by epoxy resin–DIDA-V mixture. To 5 g of the epoxy resin–DIDA-V mixture, 3 mL of DMAc, diglyme, or THF was added, thoroughly mixed in a pestle and mortar; the mixture was applied on cleaned stainless-steel coupons. The coupons applied with the epoxy resin–DIDA-V–DMAc and epoxy resin–DIDA-V–diglyme mixture were kept in an air oven at 120°C for 15 min, whereas the coupons applied with epoxy resin–DIDA-V–THF mixture were dried at 100°C for 5 min before bonding to remove some of the solvent from the epoxy–imide blend. The bonded coupons were cured following the procedure described earlier.

Preparation of unidirectional composites

Unidirectional (UD) composites were made using E-glass fiber as the reinforcement and epoxy-imide resin as the matrix resin. In a typical example, the resin was prepared through the prereaction of 7.56 g of DIDA-V and 3.81 g of Araldite® GY 250 (1:1 carboxyl equiv to epoxy equiv ratio) in 40 mL of ethylmethylketone (MEK)/DMAc (8:1 by volume) solvent mixture. Eight grams of glass fiber tows were wound on four stainless-steel metallic brackets each having length of 20 cm. The fiber tows were dipped in the resin solution and allowed to stand in air for 30 min. The above resin-impregnation procedure was repeated thrice. The resin-impregnated fiber tows were allowed to stand overnight in nitrogen atmosphere at room temperature and then dried under vacuum at 40°C for 8 h and then for 8 h at 70°C to remove the solvent from the prepreg. The resin impregnated glass fiber tows were removed from the brackets and weighed. The resin content was found to be 52% by weight. The prepreg strands were then stacked together and compressed in a mold of dimension $18 \times 0.6 \times 0.3$ cm under a pressure of 16.4 MPa in a hydraulic press of capacity 30 tons. It was then cured in three stages following the cure schedule used for making adhesives with an exception as explained below. The temperature of the mold was raised to T_{ic} over a period of 1 h at a slower heating rate in order to minimize the bleeding of resin, and when the bleeding of resin was reduced, a pressure of 33 MPa was applied and cured. The molded composite was cut using a diamond wheel cutter into specimens of required dimensions for measurement of interlaminar shear strength (ILSS). In a similar way, UD composites were made using prereacted resin of GY 250–DIDA-V for 0.5:1 carboxyl equiv to epoxy equiv ratio and EPN 1138–DIDA-V for 1:1 carboxyl equiv to epoxy equiv ratio.

Determination of fiber content of UD composite

The fiber content of the composite was determined by digesting the composite in DMAc/hydrazine hydrate mixture (1:1 by volume). Hydrazine hydrate causes cleavage of imide linkages resulting in the degradation of epoxy–imide matrix while the glass fiber remains unaffected. The amount of 1.5 g of the composite piece (made out of either GY 250–DIDA-V or EPN 1138–IDA-V) was soaked for 48 h in 20 mL of the DMAc/hydrazine hydrate mixture. After 48 h, the solution was decanted out, and 20 mL of DMAc/hydrazine hydrate was added and again soaked for two more days. Resin was completely removed from the composite based on GY 250 whereas some amount of resin was left behind in the composite based on EPN 1138 due higher crosslinking. In order to remove the remaining amount of resin from the EPN 1138-based composite, it was digested with the DMAc/hydrazine hydrate mixture at 70°C for two days. This procedure was repeated for one more time to remove the resin completely from the fiber. Finally, the fiber was washed thoroughly with distilled water and dried in an air oven at 100°C to constant weight. The fiber content of the composite is expressed in weight %.

Measurements

IR spectra of the samples were recorded on a Perkin–Elmer Spectrum GXA Fourier transform infrared (FTIR) spectrometer. The samples before curing were run as a smear on CsI plate. The IR spectra of the cured samples were recorded using universal attenuated total reflectance (ATR) with diamond crystal. DSC studies were made with a Mettler DSC TA 3000 at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) curves were recorded with a DuPont 900 thermal analyzer in conjunction with 951 thermogravimetric analyzer at a heating rate of 10°C/min in nitrogen atmosphere.

Viscosity of Araldite® GY 250 and Araldite® EPN 1138 was measured using a Brookfield Viscometer (model: HBTD). Viscosity at 30°C of Araldite® GY 250 was measured using spindle 4 at 50 rpm and that of Araldite® EPN 1138 was measured using spindle 7 at 2.5 rpm. Rheological studies of epoxy resin–DIDA-V mixture for carboxyl equiv to epoxy equiv ratios 0.5, 0.75, and 1 were carried out with a StressTech Reologica Rheometer using 20 mm parallel plate assembly in oscillation mode at a frequency of 3 Hz and a controlled stress of 100 Pa. The gap between the plates was maintained at 0.5 mm. The epoxy resin–DIDA-V mixture was loaded on to the plates at 200°C and instantaneously cooled to 140°C. The complex viscosity (η^*) was monitored at different temperatures at a heating rate of 10°C/min.

Tensile lap shear strength of bonded stainless-steel coupons was measured using a universal testing machine (Instron model no. 4549) at a crosshead speed of 10 mm/min. The tensile lap shear strength at 100 and 150°C was measured after equilibrating the test coupons at the required temperature for a period of 10 min in a hot chamber attached to the Instron. To obtain the lap shear strength value at a particular temperature, five bonded coupons were tested. The lap shear strength value reported is an average of at least three measurements, which fell in the range of ±1 MPa. Adhesive lap shear measurements were repeated when the above criterion was not met.

ILSS of UD composites was measured using UTM (Instron model no. 4202). A test specimen of dimension $30 \times 6 \times 3$ mm was end rested in the Instron on two supports with a span to thickness ratio of 5 and center loaded at a crosshead speed of 1.3 mm/min and the breaking load (P) in N was determined.
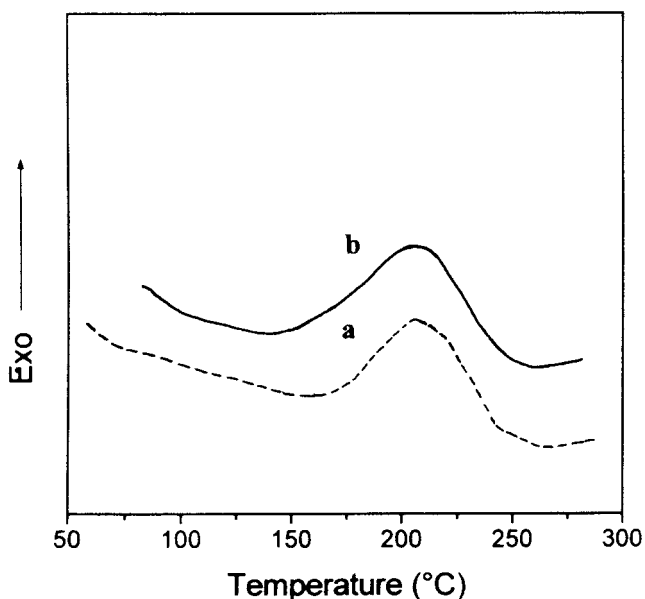
Figure 1 DSC curves of epoxy–imide resins: (a) GY 250–DIDA-V and (b) EPN 1138–DIDA-V

ILSS was calculated using the equation,

$$ILSS\ (MPa) = \frac{(0.75\ P \times 10^{-6})}{bd}$$

where b and d are width and thickness of the specimen respectively in meters. Five specimens were tested in each case and ILSS reported is an average value of these five measurements.

RESULTS AND DISCUSSION

Curing of epoxy resin with DIDA-V

Curing of epoxy resins GY 250 and EPN 1138 with DIDA-V was studied using DSC for the composition 1:1 (carboxyl equiv to epoxy equiv ratio), and the DSC curves are shown in Figure 1. It is noticed that both the systems undergo curing in the range of 150–250°C. The initial temperature for curing is lower for the EPN 1138–DIDA-V system than that of the GY 250–DIDA-V system. This is probably due to the polyfunctional nature of EPN 1138. A similar observation was made with epoxy–imide resins prepared from diimide–diacids such as sulfuryl-bis[N-(4-phenylene)-4′-(carboxy)phthalimide], sulfuryl-bis[N-(3-phenylene)-4′-(carboxy)phthalimide], methylene-bis-[N-(4-phenylene)-4′-(carboxy)phthalimide], and oxy-bis[N-(4-phenylene)-4′-carboxyl-phthalimide].[7]
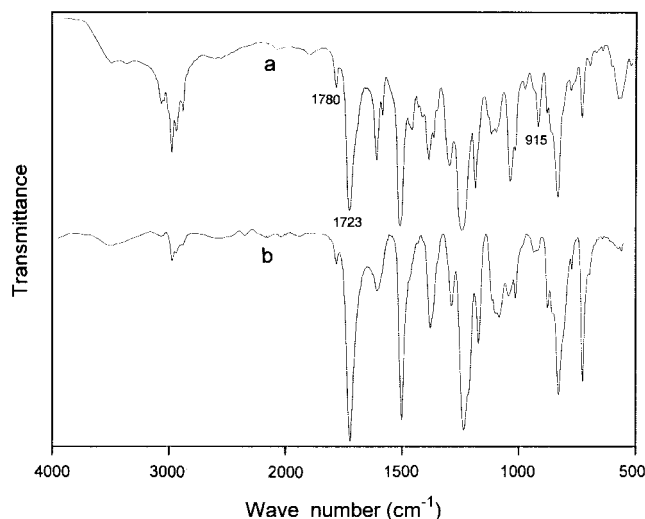
The IR spectra of the GY 250–DIDA-V system, before and after cure, are shown in Figure 2. The IR spectra of the cured epoxy–imide resins show absorptions at 1780, 1723, 1383, and 727 cm^{-1} arising due to imide peaks and at 3500 cm^{-1} due to —OH group

obtained as a result of esterification of epoxy group and —COOH group. The characteristic ester peak has probably merged with the imide absorption at 1723 cm^{-1}. In the IR spectra of the cured resin, the peak at 915 cm^{-1} corresponding to epoxy group is totally absent, indicating the completion of carboxyl–epoxy addition reaction. A similar observation is made with the EPN 1138-based system. The structures of epoxy–imide resins obtained from Araldite® GY 250 and Araldite® EPN 1138 (for carboxyl equiv to epoxy equiv ratio, 1:1) are shown in Schemes 2 and 3, respectively. The epoxy–imide obtained from GY 250–DIDA-V is expected to be a linear polymer whereas the epoxy–imide formed from EPN 1138–DIDA-V is a crosslinked polymer resulting from the polyfunctional nature of EPN 1138.

In the IR spectra of epoxy–imides synthesized by using carboxyl equiv to epoxy equiv ratio 0.5, the absorption peak at 915 cm^{-1} corresponding to epoxy group is absent. As the epoxy group is present in excess of carboxyl group, the peak corresponding to unreacted epoxy group should be present in the IR spectra of the cured epoxy–imide resins if the curing proceeds only through carboxyl–epoxy addition reaction. The absence of the peak at 915 cm^{-1} suggests that in addition to carboxyl–epoxy reaction, additional cure reaction involving the dangling —OH group present in the growing polymer chain and epoxy group probably takes place.[7,11]

Adhesive properties

During our investigation on epoxy–imide resins obtained by curing epoxy resins with imide–diacids[9] and diimide–diacids,[10] we have observed that the adhesive lap shear strength at room temperature and at

**Figure 2** FTIR spectra of GY 250–DIDA-V system (a) before cure and (b) after cure.
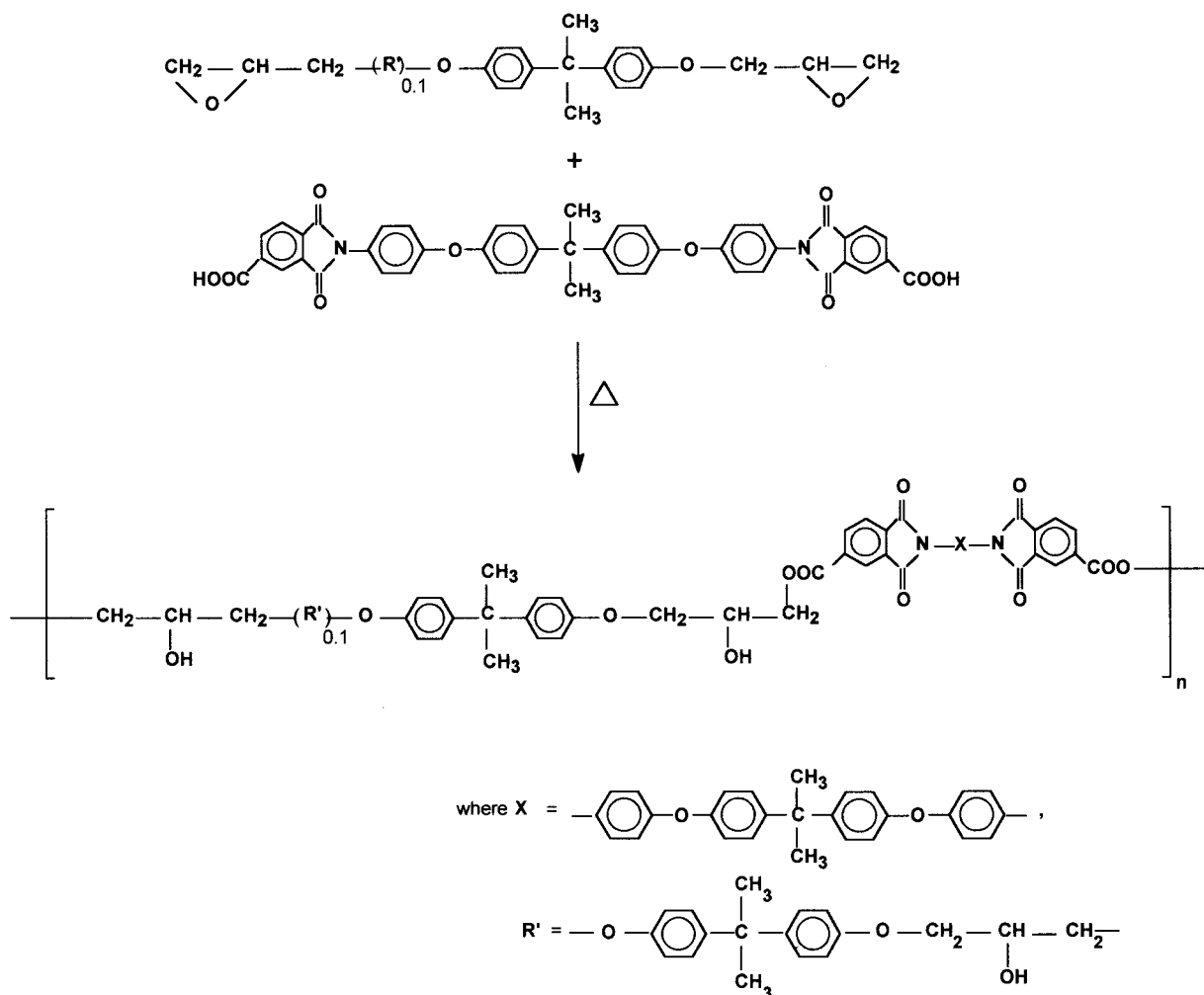
Scheme 2 Synthesis of epoxy–imide resin from Araldite® GY 250 and DIDA-V.

elevated temperatures is influenced by the ratio of imide–diacid/diimide–diacid to epoxy resin. Thus, it would be of interest to study the effect of variation of the ratio of DIDA-V to epoxy resin, or in other words carboxyl equiv to epoxy equiv ratio, on the adhesive properties of GY 250/EPN 1138–DIDA-V systems.

The room temperature adhesive lap shear strength of the GY 250–DIDA-V system for the carboxyl equiv to epoxy equiv ratios 0.25, 0.5, 0.75, and 1.0 is compared in Figure 3. It is observed that the adhesive strength increases from 8 to 20 MPa when the carboxyl equiv to epoxy equiv ratio is increased from 0.25 to 0.5, and decreases thereafter with the increase in imide content. As DIDA-V is a high molecular weight compound, a large amount of this compound is required to obtain carboxyl equiv to epoxy equiv ratios of 0.75 and 1.0, which reduces the flow of the GY 250–DIDA-V mixture. In order to understand the effect of carboxyl equiv to epoxy equiv ratio on the flow characteristics, the complex viscosity (η^*) of GY 250–DIDA-V mixtures having carboxyl equiv to epoxy equiv ratios 0.5, 0.75, and 1.0 was measured in the temper-

ature range 145–245°C, which is close to the temperature range used for curing the GY 250–DIDA-V system, and the results are shown in Figure 4. In the temperature range prior to gelation (<220°C), η^* follows the trend η^* (1.0) > η^* (0.75) > η^* (0.5). For instance, η^* values are 0.36, 18.7, and 210 at 202°C Pa s for GY 250–DIDA-V mixtures having carboxyl equiv to epoxy equiv ratios 0.5, 0.75, and 1.0 respectively. An increase in η^* with the increase in imide content, or in other words, an increase in carboxyl equiv to carboxyl equiv, would result in a poor flow of the GY 250–DIDA-V system during cure. For this reason, GY 250–DIDA-V mixtures prepared using carboxyl equiv to epoxy equiv ratios 0.75 and 1 have poor wetting characteristics when compared to the GY 250–DIDA-V mixture prepared using carboxyl equiv to epoxy equiv ratio of 0.5. Increasing the carboxyl equiv to epoxy equiv ratio could also increase the inhomogeneity of the mixtures affecting the molecular weight buildup, which in turn affects the adhesive properties.

In order to understand the effect of variation of epoxy resin on the adhesive lap shear strength, the
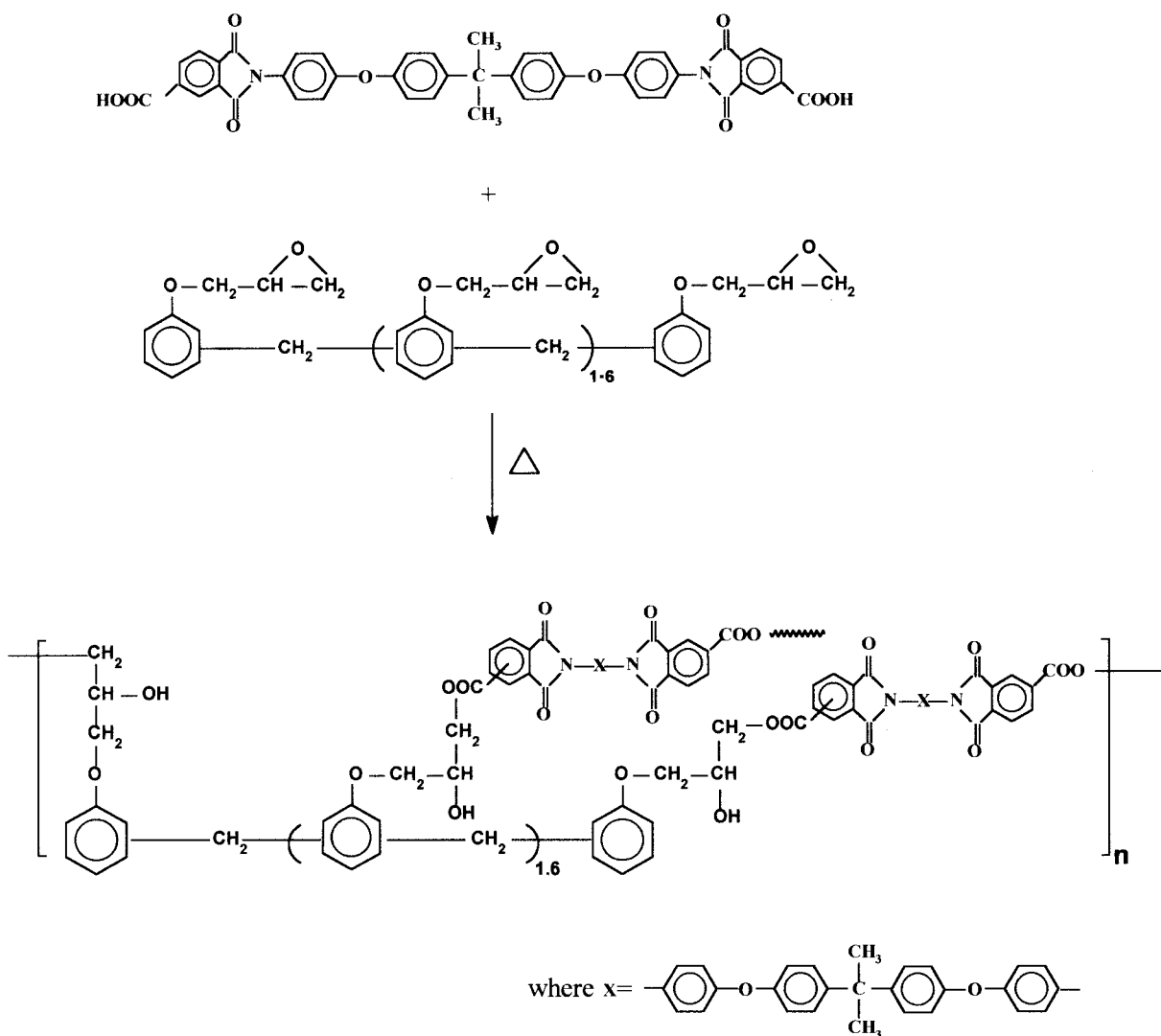
Scheme 3   Synthesis of epoxy–imide resin from Araldite® EPN 1138 and DIDA-V.

adhesive strength values at room temperature and at 100 and 150°C of EPN 1138–DIDA-V system for the carboxyl equiv to epoxy equiv ratios of 0.5 and 1.0 are
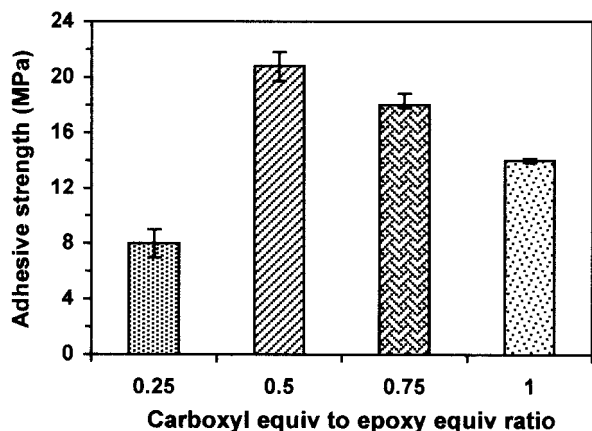
Figure 3   Effect of imide content on the room temperature adhesive strength of GY 250–DIDA-V system.

compared with the corresponding ones made from GY 250 in Figure 5. It can be noticed that the room temperature adhesive strength of the EPN 1138–DIDA-V system is considerably lower than that of the GY 250–DIDA-V system. A similar observation was made with epoxy–imide resins obtained from imide–diacids[9] and other diimide–diacids.[10] The lower adhesive strength of the EPN 1138-based system is attributed to the higher crosslinking and correspondingly brittle character arising due to the polyfunctional nature of the EPN 1138 resin. It is interesting to note that for the carboxyl equiv to epoxy equiv ratio of 0.5, the GY 250–DIDA-V system retains only 86 and 45% of its room temperature adhesive strength at 100 and 150°C respectively, whereas in the case of the EPN 1138–DIDA-V system, for the same composition, an increase in adhesive strength by ~48 and ~26% is observed at 100 and 150°C respectively. The above observation is attributed to the higher crosslinking possible with the latter system when compared to the former system.
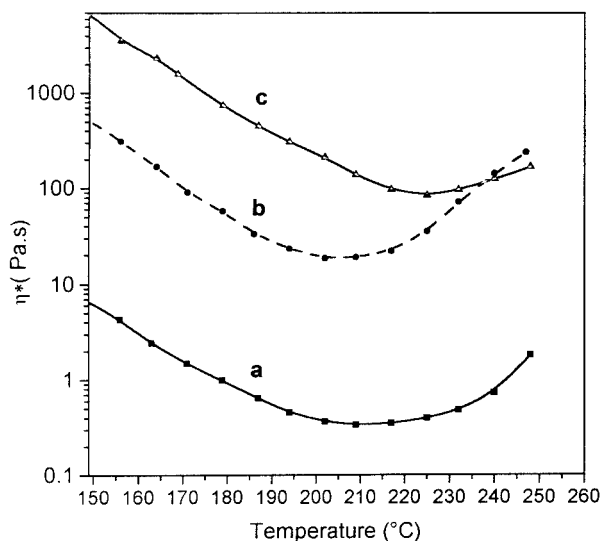
Figure 4 Complex viscosity (η^*) vs temperature for the GY 250–DIDA-V system for different carboxyl equiv to epoxy equiv ratios: (a) 0.5, (b) 0.75, and (c) 1.0.

When the carboxyl equiv to epoxy equiv ratio is increased from 0.5 to 1.0, for both the GY 250- and EPN 1138-based systems the adhesive strength decreases, and the decrease is found to be more for the EPN 1138-based systems when compared to that of the GY 250-based systems. This observation may be explained by considering the viscosity of EPN 1138 and GY 250 resins. EPN 1138 has a viscosity of 1702 Pa s at 30°C whereas GY 250 has viscosity of 4 Pa s at 30°C. From Figure 4 it is evident that increasing the carboxyl equiv to epoxy equiv ratio increases the complex viscosity of the GY 250–DIDA-V system. As the viscosity of EPN 1138 is much higher than that of GY 250, the increase in complex viscosity of the EPN 1138–DIDA-V system is expected to be higher than that of the GY 250–DIDA-V system when the carboxyl equiv to epoxy equiv ratio is increased from 0.5 to 0.75 or 1.0. Thus, increasing the carboxyl equiv to epoxy equiv ratio would affect the wetting characteristics to a greater extent in the case of the EPN 1138–DIDA-V system than in the case of the GY 250–DIDA-V system. In addition, the inhomogeneity in the cured resin arising due to the increase in the carboxyl equiv to epoxy equiv ratio is expected to be more for the EPN 1138–DIDA-V system than for the GY 250–DIDA-V system.
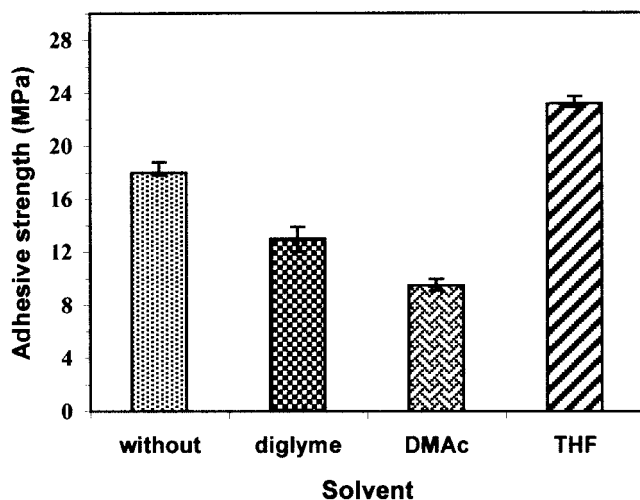
Effect of solvent on the adhesive strength of epoxy-imide resins

In the epoxy adhesive formulations, it is desirable to avoid the use of solvents in order to prevent void formation. However, addition of solvents to adhesive formulations, particularly to systems where high molecular weight solid curatives are employed, is often useful to improve the homogeneity of the system and also to improve the wetting characteristics.[15] As discussed earlier, the study on the effect of carboxyl equiv to epoxy equiv ratio on the room temperature adhesive strength for the GY 250–DIDA-V system suggests that the adhesive strength decreases when the ratio is 0.75 and above. Hence, the carboxyl equiv to epoxy equiv ratio of 0.75 was chosen for studying the effect of addition of solvents to adhesive formulation on the adhesive strength. Solvents such as DMAc, diglyme, and THF were used for this study. Room temperature adhesive strength values obtained after the addition of different solvents are compared in Figure 6. It is observed that the adhesive strength decreases by 45 and 28%, respectively, when DMAc and diglyme are used, and increases by 29% when THF is used. The results obtained can be explained by considering the following aspects: (1) As DMAc and diglyme are high boiling solvents when compared to THF, trace quantity of these solvents is probably retained in the cured resin (in the glue line). (2) While attempting to remove DMAc and diglyme from the adhesive formulation at 120°C, partial curing of epoxy resin would have taken place, affecting the effective bonding of the substrate. (3) Since DMAc and diglyme are more polar when compared to THF, wetting of the
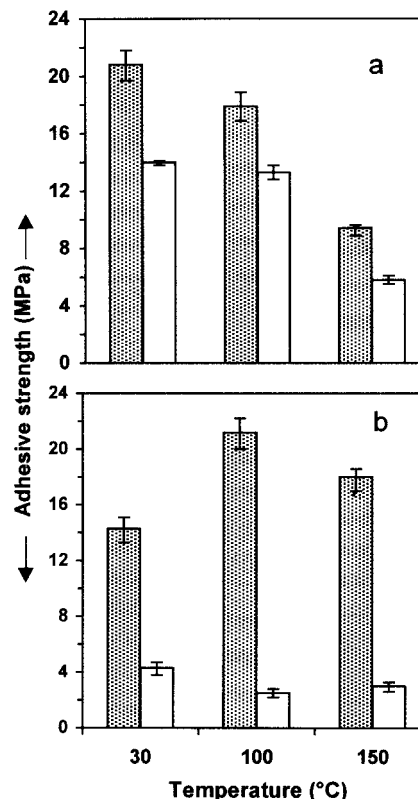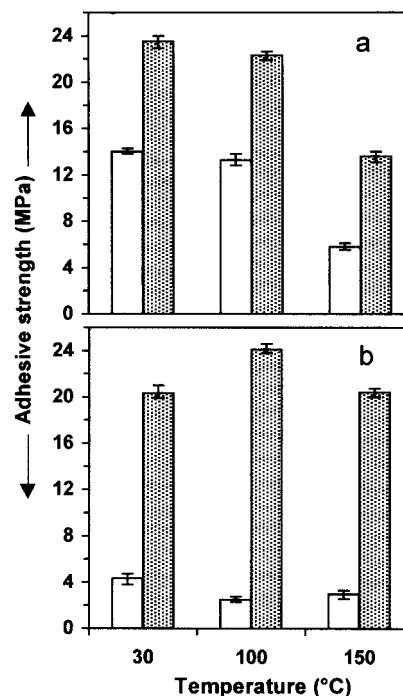

Figure 5 Adhesive strength of (a) GY 250–DIDA-V and (b) EPN 1138–DIDA-V systems at different temperatures: stippled bar: carboxyl equiv to epoxy equiv ratio 0.5; open bar: carboxyl equiv to epoxy equiv ratio 1.0.

Figure 6 Effect of solvent on the room temperature adhesive strength of the GY 250–DIDA-V system for carboxyl equiv to epoxy equiv ratio 0.75:1.

substrate by DMAc and diglyme would be more when compared to THF. This would mean a reduction in the wetting of the substrate by the GY 250–DIDA-V mixture. (4) Since DIDA-V is readily soluble in THF than in DMAc or diglyme, the GY 250–DIDA-V mixture is more homogeneous when THF is used.

As THF improves the adhesive strength for the GY 250–DIDA-V system, attempts were made to improve the adhesive strength of the EPN 1138–DIDA-V system using this solvent in the adhesive formulation. Adhesive lap shear strength values of both systems by using THF in the adhesive formulation are given in Table I for the carboxyl equiv to epoxy equiv ratios 0.75 and 1.0. It is noticed that for both the systems, maximum adhesive lap shear strength is obtained when carboxyl equiv to epoxy equiv ratio is 1.0. Adhesive strength values of GY 250/EPN 1138–DIDA-V systems for the ratio 1.0 at different temperatures with and without the addition of THF in the adhesive formulation are compared in Figure 7. When THF is used in the adhesive formulation, for the GY 250–DIDA-V system there is a 68, 68, and 134% improvement in adhesive strength at room temperature and at 100 and 150°C, respectively, that is noticed when compared to the corresponding system without THF. In the case of

Figure 7 Adhesive strength of (a) GY 250–DIDA-V and (b) EPN 1138–DIDA-V systems for carboxyl equiv to epoxy equiv ratio 1.0 at different temperatures with (stippled bar) and without (open bar) using THF in the adhesive formulation.

the EPN 1138–DIDA-V system, 372, 864, and 580% improvement in adhesive strength at room temperature and at 100 and 150°C, respectively, is observed when compared to the corresponding system without THF. Thus, it can be seen that the improvement in the adhesive strength values when THF is used in the adhesive formulation is more pronounced for the EPN 1138-based system than for the GY 250-based system. As discussed earlier, EPN 1138 has higher viscosity when compared to GY 250, and hence the effect of solvent is more pronounced for the epoxy–imide system based on EPN 1138.

For the carboxyl equiv to epoxy equiv ratio 1:1 (by using THF in the adhesive formulation), 58% retention of adhesive strength is observed at 150°C, whereas for the EPN 1138-based system 100% retention is observed. This is attributed to the higher crosslinking

TABLE I
Effect of Imide Content on Adhesive Lap Shear Strength of Epoxy—Imide Resins Obtained
from GY 250/EPN 1138 and DIDA-V Using THF in the Adhesive Formulation

System	Composition (carboxyl equiv: epoxy equiv)	Adhesive strength (MPa) at		
		Room temperature	100°C	150°C
GY 250–DIDA-V	0.75	23.2 ± 0.4	22.3 ± 0.5	10.7 ± 0.6
	1.0	23.5 ± 0.6	22.3 ± 0.3	13.6 ± 0.5
EPN 1138–DIDA-V	0.75	16.0 ± 0.3	20.2 ± 0.3	18.2 ± 0.4
	1.0	20.3 ± 0.5	24.1 ± 0.4	20.4 ± 0.3
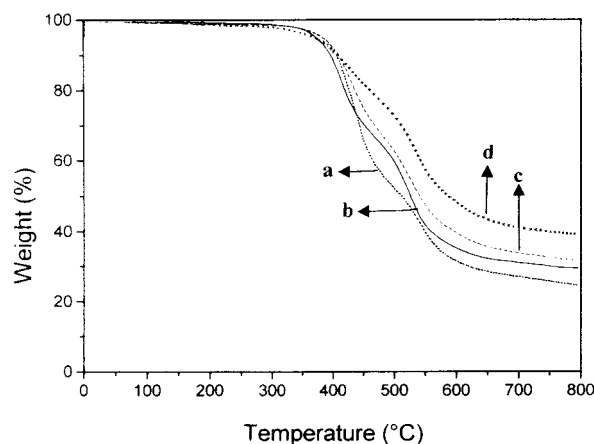
Figure 8 Thermograms of epoxy–imide resins for different carboxyl equiv to epoxy equiv ratios: (a) GY 250–DIDA-V (0.5:1), (b) GY 250–DIDA-V (1:1), (c) EPN 1138–DIDA-V (0.5:1), and (d) EPN 1138–DIDA-V (1:1)

possible in the EPN 1138-based system when compared to that of the GY 250-based system.

Preliminary studies on UD composites

UD composites were made using E-glass fiber as the reinforcement and GY 250/EPN 1138–DIDA-V epoxy–imides as matrix resins. The fiber content (weight %) of the composites was determined by the digestion method as detailed in the experimental section. The fiber content was found to be 65.3 and 65.4% for the GY 250–DIDA-V system prepared by using carboxyl equiv to epoxy equiv ratios 0.5 and 1.0 respectively, and 65.6% for the EPN 1138–DIDA-V system prepared by using carboxyl equiv to epoxy equiv ratio 1.0. For the GY 250–DIDA-V system, ILSS of 26.3 and 31 MPa was obtained for carboxyl equiv to epoxy equiv ratios of 0.5 and 1.0, respectively, at room temperature. This observation suggests that higher ILSS is obtained for the system having higher aromatic and imide content. Hence, for the EPN 1138–DIDA-V system, ILSS of glass fiber reinforced UD composite was evaluated for carboxyl equiv to epoxy equiv ratio 1.0. ILSS of the EPN 1138–DIDA-V system is found to be 26.4 MPa at room temperature. As in the case of ad-

hesive strength, ILSS of UD composite is lower for the EPN 1138-based system when compared to that of the GY 250-based system. This may be due to the higher crosslinking possible for the EPN 1138-based system when compared to that of the GY 250-based system.

Thermal properties

The thermograms of epoxy–imide resins are shown in Figure 8. The initial, maximum, and final decomposition temperatures, char residues at 800°C and the temperature at which 10, 20, and 30% weight loss occurs are given in Table II. It is observed that the char residue and overall thermal stability increase with an increase in imide content. EPN 1138-based systems have better thermal stability when compared to GY 250-based systems. The higher thermal stability and char residue of the former system is attributed to the higher crosslinking possible due to the polyfunctional nature of EPN 1138.

CONCLUSIONS

Epoxy–imide resins were prepared by curing Araldite® GY 250 and Araldite® EPN 1138 with the diimide–diacid, DIDA-V. The effect of variation of imide content on adhesive strength was studied. With the increase in imide content the room temperature adhesive strength decreases for both GY 250- and EPN 1138-based systems, and this has been attributed to the poor wetting of the substrate by the epoxy–diimide–diacid mixture. Use of a small amount of THF in the adhesive formulation results in improvement in both the room temperature and high temperature adhesive strength, and the improvement is more pronounced with the EPN 1138-based system. For both GY 250- and EPN 1138-based systems, maximum room temperature adhesive strength is obtained for carboxyl equiv to epoxy equiv ratio of 1.0 when THF is used in the adhesive formulation. In general, the retention of adhesive strength and the overall thermal stability are higher for EPN 1138-based systems than for GY 250-based systems, and this has been attributed to the higher crosslinking possible, with the former

TABLE II
TGA Data of Epoxy–Imide Resins[a]

System	Composition (carboxyl equiv to epoxy equiv)	T_i (°C)	T_{max} (°C)	T_f (°C)	10% Weight loss	20% Weight loss	30% Weight loss	Char residue at 800°C
GY 250–DIDA-V	0.5	380	530	580	403	430	450	27
	1.0	376	550	580	403	430	460	31
EPN 1138–DIDA-V	0.5	380	536	582	425	443	478	33
	1.0	370	540	636	425	470	520	41

[a] T_i: initial decomposition temperature; T_{max}: maximum decomposition temperature; T_f: final decomposition temperature.

system arising from the polyfunctional nature of Araldite® EPN 1138.

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