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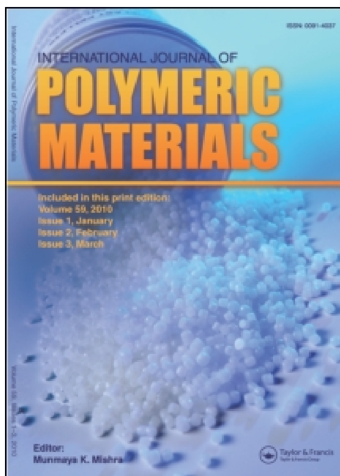

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Epoxy-Imide Resins from N-(4- and 3-Carboxyphenyl) Trimellitimides: Modified with Reactive Rubbers

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Epoxy-Imide Resins from N-(4- and 3-Carboxyphenyl) Trimellitimides: Modified with Reactive Rubbers

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Epoxy-imide resins obtained through the reaction of epoxy resins such as Araldite® GY 250/Araldite® EPN 1138 with N-(4- and 3-carboxyphenyl)trimellitimides (IDA-I and IDA-II, respectively) have been modified with 10 wt% of epoxidized hydroxyl-terminated polybutadiene (EHTPB), 10 phr of carboxyl-terminated butadiene-acrylonitrile liquid copolymer (CTBN-L), and 10 phr of carboxyl-terminated butadiene-acrylonitrile solid copolymer (CTBN-S) without sacrificing much of their performance at elevated temperatures. Adhesive lap shear strength on stainless steel substrate at room temperature and at 100, 125, and 150°C has been evaluated for the modified and unmodified systems. CTBN-S offers a remarkable increase of 13 MPa and 8 MPa in the room temperature adhesive strength of GY 250-based system and EPN 1138-based system, respectively. EHTPB gives only a marginal improvement and CTBN-L offers an improvement by 4 MPa for GY 250-based system whereas CTBN-L reduces the adhesive strength of EPN 1138-based system.

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SEM studies suggest that in general, the modification with EHTPB and CTBN-L results only in improving the ductility of epoxy-imide systems, whereas the modification with CTBN-S results in phase separation of rubber particles in the epoxy-imide matrix.

Keywords: epoxidized hydroxyl-terminated polybutadiene (EHTPB), carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN), epoxy-imide resins, rubber modified epoxy-imide resins

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INTRODUCTION

Important progress has been made over the last few years to combine the versatility of epoxy resins and the thermal stability of imide groups resulting in a class of polymers called epoxy-imide resins [1–17]. The authors' laboratory has developed several epoxy-imide resins and used them as adhesives [18–25] and matrix resins for unidirectional composites [25]. Although the incorporation of imide linkages in epoxy resins imparts stiffness to some extent, which in turn improved their thermal stability and adhesive strength at elevated temperatures, epoxy-imides are generally brittle in nature, which limits their room temperature adhesive strength. Usually the brittleness of epoxy resins is reduced by the addition of rubber toughening agents like epoxidized hydroxyl-terminated polybutadiene (EHTPB) [26], and carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) [27–32]. Thus, it would be of interest to study the modification of epoxy-imide resins with reactive liquid/solid rubbers.

In the present study, modification of epoxy-imide resins obtained from Araldite® GY 250/Araldite® EPN 1138 and N-(4- and 3-carboxyphenyl)trimellitimides (IDA-I and IDA-II, respectively) has been carried out via the addition of 10 wt% of epoxidized hydroxyl-terminated polybutadiene (EHTPB), 10 phr of carboxyl-terminated butadiene-acrylonitrile liquid copolymer (CTBN-L) and 10 phr of carboxyl-terminated butadiene-acrylonitrile solid copolymer (CTBN-S). While modifying these epoxy-imide resins, attention is focused on improving the room temperature adhesive strength without sacrificing much the high temperature adhesive strength. Adhesive lap shear strength on stainless steel substrate at room temperature and at 100, 125, and 150°C has been evaluated. The adhesive and thermal properties of the modified systems were compared with those of the unmodified systems. Morphological studies of the fractured surfaces of the modified and unmodified systems were carried out by using scanning electron microscopy.

EXPERIMENTAL

Materials

EHTPB (epoxy value = 5.4 eqv/kg; polyfunctional, internal epoxy resin) [20–21,26] and imide-diacids, namely, N-(4- and 3-carboxyphenyl)trimellitimides (IDA-I and IDA-II, respectively) [19] were synthesized by the procedure reported earlier. Methyl ethyl ketone (Nice Chemicals, Cochin, India) and triphenyl phosphine (SISCO Research Lab., Mumbai, India) were used as received. Solid carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN-S)-Nipol 1072 [carboxyl content: 0.07-0.08 ephr (eq./100 parts of resin); M_n: 65,000 g/mol, acrylonitrile content: 26–28%, Zeon Chemicals, USA] and liquid-carboxyl-terminated butadiene-acrylonitrile copolymer (CTBN−L)-Hycar 1300 × 8 [carboxyl content: 0.05 ephr; M_n: 3500 g/mol, acrylonitrile content: 26–28%, B. F. Goodrich, USA] were used as received. Epoxy resins, namely, Araldite® GY 250 (diglycidyl-ether of bisphenol-A; epoxy value = 5.0–5.5 eqv/kg; difunctional) and Araldite® EPN 1138 (Novolac epoxy; epoxy value = 5.5–5.7 eqv/kg; polyfunctional) manufactured and supplied by M/s. Hindustan Ciba-Geigy, India Ltd., Mumbai, India were used as received. Structures of Araldite® GY 250, Araldite® EPN 1138, EHTPB, CTBN, IDA-I and IDA-II are given in Figure 1.

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Pre-Reaction of Epoxy Resins with CTBN-L or CTBN-S

To achieve effective toughening it is necessary to ensure that CTBN molecules are chemically bonded to epoxy resin. If they are not bonded to epoxy resin, they can migrate to the glue line and act as a weak boundary layer resulting in the reduction of adhesive strength [33]. Thus, it is necessary to pre-react CTBN with epoxy resin. The resultant product obtained after pre-reaction is an epoxy terminated CTBN (Scheme 1). CTBN-L and CTBN-S were pre-reacted with excess amount of Araldite® GY 250 or Araldite® EPN 1138 prior to making the adhesive formulation of toughened epoxy-imide resins.

Pre-reaction of CTBN-L with GY 250 or with EPN 1138 was carried out as follows: 0.05 g of triphenyl phosphine (TPP) (0.25 parts per 100 g of CTBN-L) was added to 100 ml of methyl ethyl ketone (MEK) taken in a 500 ml round bottom flask fitted with a water condenser, mechanical stirrer, and a water bath. The temperature of the bath was raised to 80°C. On complete dissolution of TPP in MEK, 20 g of CTBN-L and 20 g of GY 250 or EPN 1138 were added to it under constant stirring. The contents were stirred for 6 h at 80°C. MEK was partially removed from the solution by distillation under vacuum. The solid content of

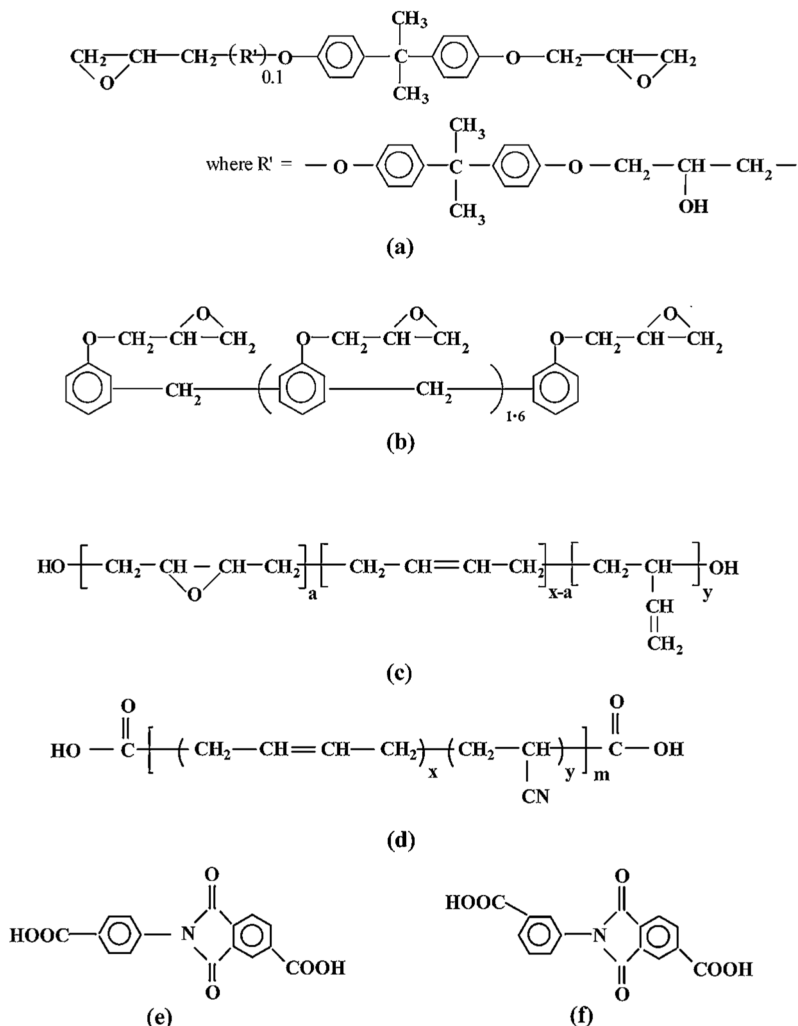

FIGURE 1 Structures of (a) Araldite GY 250, (b) Araldite EPN 1138, (c) EHTPB, (d) CTBN, (e) IDA-I, and (f) IDA-II.

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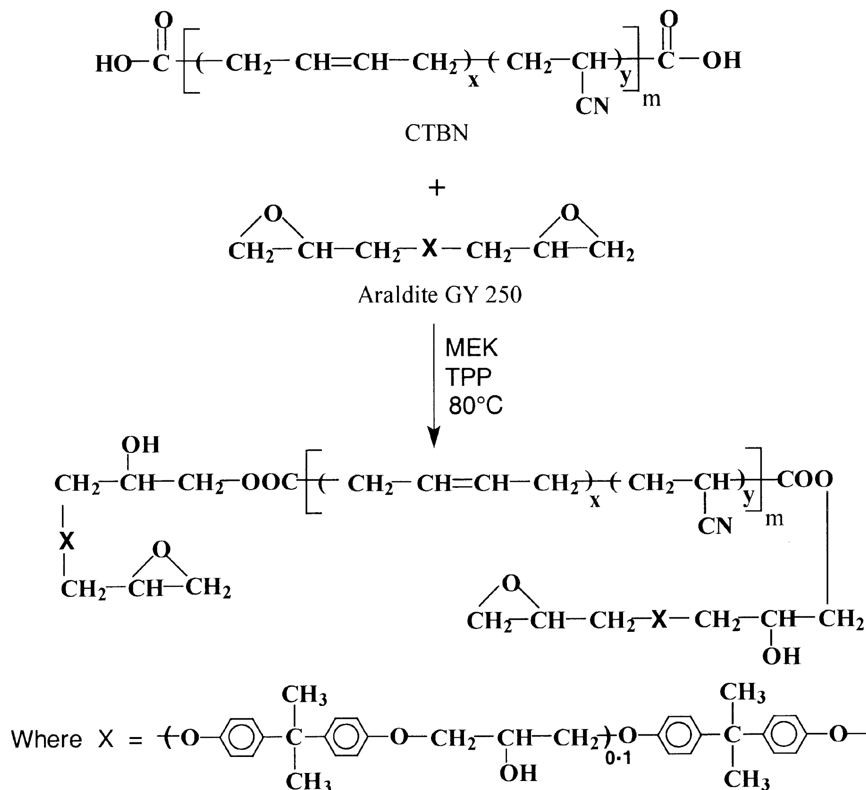
the remaining solution was determined by evaporating a weighed quantity of the solution to constant weight in a hot air oven at 100°C. The completion of the reaction was confirmed by monitoring the acid value. The acid value of the pre-reacted resin was found to be nil. In the case of CTBN-S, it was masticated in a two-roll mill and cut into small pieces and dissolved in MEK to get approximately



SCHEME 1 Pre-reaction of CTBN with Araldite GY 250.

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20% solution. The solid content of this solution was determined following the procedure described above. Required quantity of this solution to get 20 g of CTBN-S was reacted with 20 g of GY 250 or EPN 1138 in presence of TPP following the procedure described earlier.

During the pre-reaction, the carboxyl group of CTBN undergoes esterification with epoxy group to produce epoxy-end-capped CTBN by epoxy-carboxyl addition reaction as shown in Scheme 1.

Modification of Epoxy-Imide Resins with Reactive Liquid Rubbers

As the epoxy value of EHTPB is close to Araldite® GY 250/Araldite® EPN 1138, a part of GY 250/EPN 1138 used for making epoxy-imides is replaced by EHTPB. Thus, for modifying epoxy-imide resins with EHTPB, 10 wt% of EHTPB was blended with Araldite® GY 250 and

TABLE 1 Curing of Epoxy Resins with Imide-Diacids: DSC Studies

Sl. No.	System	Temperature (°C)		
		T_i	T_{max}	T_f
1	GY 250-IDA-I	150	200	230
2	GY 250-IDA-II	170	230	250
3	EPN 1138-IDA-I	170	230	270
4	EPN 1138-IDA-II	200	250	270

T_i: initial cure temperature; T_{max}: peak cure temperature and T_f: final cure temperature.

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Araldite® EPN 1138, and the blended resin was thoroughly mixed with IDA-I or IDA-II in a pestle and mortar in 1:1 carboxyl eqv to epoxy eqv (C/E) ratio. For modifying epoxy-imide resins with CTBN-L and CTBN-S, Araldite®GY 250 and Araldite® EPN 1138 were pre-reacted with CTBN-L and CTBN-S as explained earlier. The pre-reacted resin was then blended with the required quantity of the corresponding Araldite® GY 250 and Araldite® EPN 1138 to obtain 10 phr of CTBN in the blended resin, and the blended resin was thoroughly mixed with IDA-I or IDA-II in a pestle and mortar in 1:1 C/E ratio. The modified systems were cured following the cure schedule; T_i (30 min); T_{max} (1 h); T_f (30 min) (Table 1) adopted for the corresponding unmodified systems [19]. The cure reaction was followed by IR. The completion of the cure reaction is confirmed by the absence of the peak at 910 cm^{-1} (corresponding to epoxy group) in the IR spectra of the cured epoxy-imide systems.

Surface Preparation of Stainless-Steel Coupons

Surface preparation of stainless steel (AISI 304 SS cold roll) test pieces of dimension 100 mm × 25 mm × 1.6 mm was carried out following the procedure described elsewhere [18,20].

Measurements

IR spectra of the samples were recorded on a Nicolet 510P FT-IR in KBr pellets or as a smear on NaCl plate. 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 951 thermogravimetric analyser at a heating rate of 10°C/min in nitrogen atmosphere. Tensile lap shear strength of bonded stainless-steel coupons was measured using a universal testing machine

(Instron Model No. 4549) at a cross-head speed of 10 mm/min. The tensile lap shear strength at 100, 125, 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 five measurements, which fell in the range of ±1 MPa. Morphology of fractured surfaces of toughened epoxy-imide resins was examined using scanning electron microscopy (SEM). A Hitachi Model S-2400 SEM was used. This instrument has a resolution of 4 μm at an accelerating voltage of 25 KV and ultimate vacuum of 10^{-7} torr. The specimen surface was made electrically conductive by coating a thin layer of gold using the plasma vapor deposition technique in a Fine Coat Ion Sputterer JF-1100.

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RESULTS AND DISCUSSION

Curing of epoxy resins, namely, GY 250 or EPN 1138 with imide-diacids proceeds through carboxyl-epoxy addition reaction at elevated temperatures [19]. Curing of modified epoxy-imide resins is also expected to proceed in a similar way. Because the epoxy value of EHTPB is close to that of GY 250/EPN 1138, a part of GY 250/EPN 1138 used for preparing epoxy-imides has been replaced by EHTPB. EHTPB present in the blend would undergo curing with IDA-I/IDA-II in the same way as that of GY 250/EPN 1138. The modification of epoxy-imides with CTBN has been carried out by the pre-reaction of CTBN-L/CTBN-S with excess amount of GY 250 or EPN 1138 as explained earlier, which resulted in epoxy-terminated CTBN-L or CTBN-S. The curing of epoxy-terminated CTBN-L or CTBN-S blended with the required quantities of GY 250 or EPN 1138 and imide-diacids is expected to proceed through the carboxyl-epoxy addition reaction at elevated temperatures. It is reported that CTBN is compatible with the epoxy-curative mixture in the initial stages of curing [33]. With the progress of curing the molecular weight increases that would result in a two-phase microstructure consisting of small rubber particles dispersed in and bonded to the epoxy matrix. These small rubber particles in the crosslinked epoxy matrix would absorb the mechanical energy applied, thereby effectively preventing local stress concentration.

The effect of modifiers such as EHTPB, CTBN-L, and CTBN-S on the adhesive strength, thermal stability, and the morphology of epoxy-imide resins has been studied in order to find out the best modifier for obtaining maximum room temperature adhesive strength with minimum sacrifice of their elevated temperature properties.

Adhesive Lap Shear Strength of Modified Epoxy-Imide Resins

The adhesive lap shear strength of GY 250-IDA-I/IDA-II and EPN 1138-IDA-I/IDA-II systems modified with 10 wt% of EHTPB, and 10 phr each of CTBN-L and CTBN-S was evaluated on stainless steel substrate at room temperature and at 100, 125, and 150°C. The adhesive strength of each modified system is compared with that of the corresponding unmodified system and is discussed in detail in the following sections.

Effect of Addition of EHTPB on the Adhesive Strength of GY 250–/EPN 1138-IDA-I/IDA-II Systems

The adhesive strength values at different temperatures of GY 250-IDA-I/IDA-II systems modified with 10 wt% of EHTPB are compared with those of the corresponding unmodified systems in Figure 2. It is observed that both systems follow a similar trend. For both systems, at 100°C an increase by 1 to 2 MPa is observed in the adhesive strength values. The adhesive strength value at 125°C of IDA-I-based system is comparable to that of the unmodified one, whereas for IDA-II-based system an increase by ≈2 MPa is observed at 125°C. Interestingly, for the systems modified with 10 wt.% of EHTPB, the adhesive lap shear strength values at 150°C are comparable to those of the unmodified systems.

In order to study the effect of EHTPB addition on the adhesive strength of a crosslinked system, EPN 1138-based systems were also modified with 10 wt% of EHTPB. Adhesive strength values at different temperatures of EPN 1138-IDA systems modified with 10 wt% EHTPB are compared with those of the unmodified ones in Figure 3. For the unmodified systems, adhesive strength values increase with the increase in the test temperature and in fact, more than 100% retention is observed at 150°C. This is attributed to the flexibility of the system arising due to the increased mobility of the crosslinked units at elevated temperatures. But this trend is not observed for the EHTPB-modified EPN 1138-based systems. This may be due to the presence of aliphatic linkages of EHTPB in the system. Although 100% retention of room temperature adhesive strength at elevated temperatures is not observed for EHTPB-modified systems, the absolute values at elevated temperatures are comparable to those of the unmodified systems.

By modifying epoxy-imides with 10 wt% of EHTPB, marginal improvement in the room temperature adhesive strength is achieved for both GY 250 and EPN 1138-based systems without reducing much of the absolute adhesive strength values at elevated temperatures.

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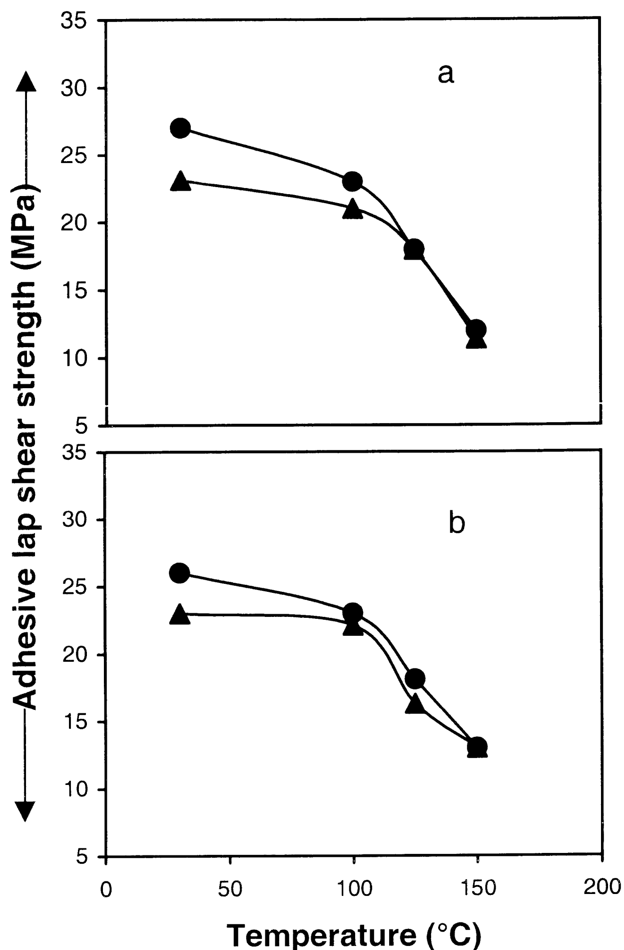

FIGURE 2 Adhesive lap shear strength values of unmodified and EHTPB (10 wt%) modified (a) GY 250-IDA-I system and (b) GY 250-IDA-II system at different temperatures: (▲) unmodified and (•) modified.

Effect of Addition of CTBN-L on the Adhesive Strength of GY 250–/EPN 1138-IDA-I/IDA-II Systems

Adhesive lap shear strength at room temperature, and at 100, 125, and 150°C of CTBN-L modified GY 250-IDA-I/IDA-II was evaluated on stainless steel substrate and the results are compared with those of the unmodified systems in Figure 4. For GY 250-IDA-I system an improvement in room temperature adhesive strength by $\approx$4 MPa is

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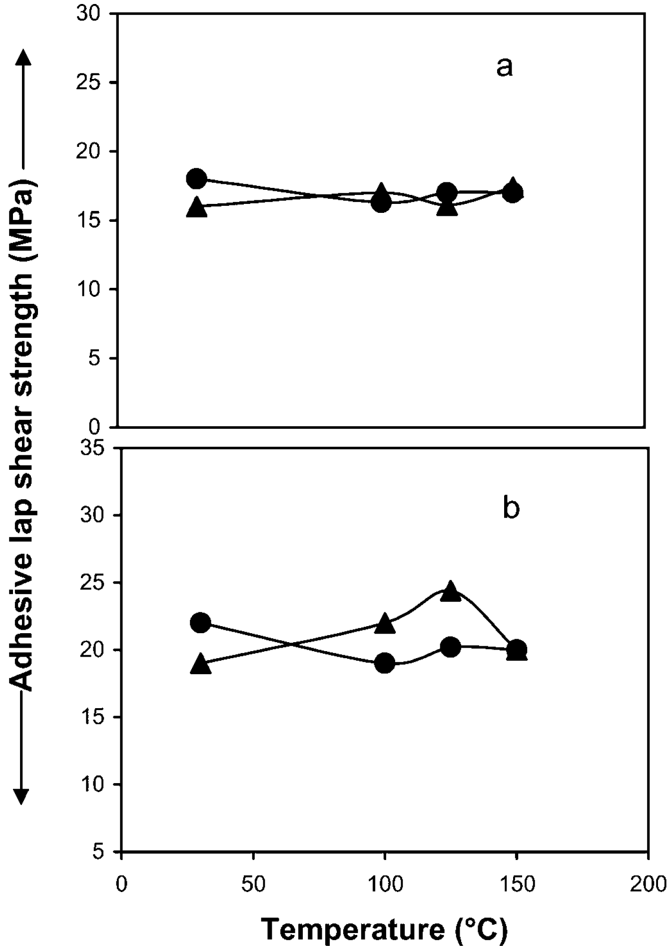

FIGURE 3 Adhesive lap shear strength values of unmodified and EHTPB (10 wt%) modified (a) EPN 1138-IDA-I system and (b) EPN 1138-IDA-II system at different temperatures: (▲) unmodified and (•) modified.

observed. The adhesive strength values at 100 and 125°C are comparable to those of the unmodified systems. In the case of GY 250-IDA-II systems, the adhesive strength values at room temperature and at 100°C increase by about 3 MPa whereas the adhesive strength at 125°C increases by ≈7 MPa. For both systems, modification with CTBN-L brings down the adhesive strength at 150°C by 2 to 3 MPa.

The adhesive strength values of EPN 1138-IDA-I/IDA-II systems at room temperature and at 100, 125, and 150°C are compared with those

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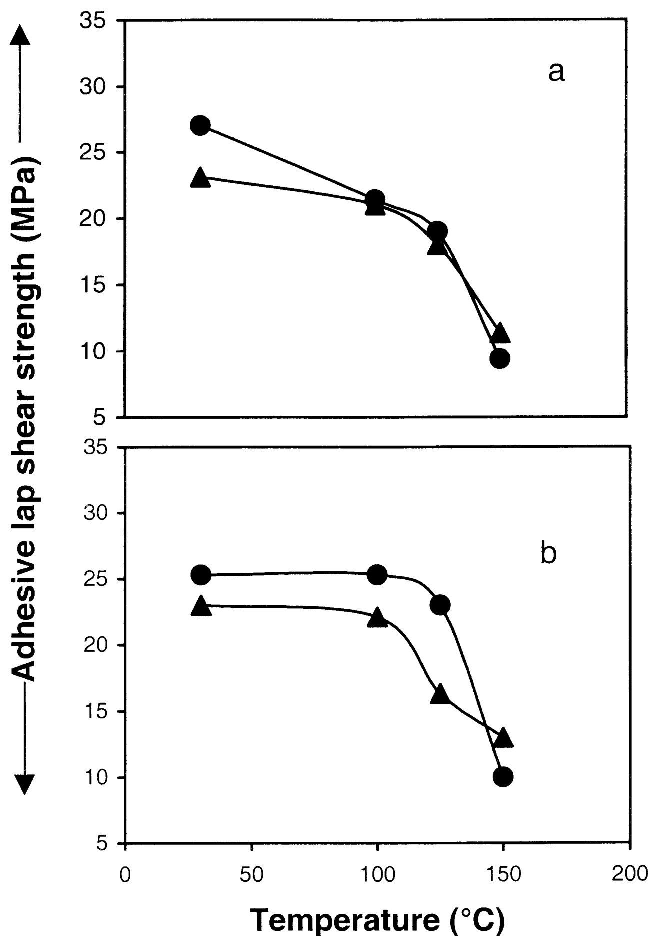

FIGURE 4 Adhesive lap shear strength values of unmodified and CTBN-L (10 phr) modified (a) GY 250-IDA-I system and (b) GY 250-IDA-II system at different temperatures: (▲) unmodified and (•) modified.

of the unmodified ones in Figure 5. It is observed that for both EPN 1138-IDA-I and EPN 1138-IDA-II systems, adhesive strength decreases when they are modified with CTBN-L and the decrease is more pronounced with the latter system. It is reported that effective toughening may not be possible for highly crosslinked systems such as EPN 1138-based ones with CTBN-L [34–35]. In the absence of toughening, CTBN-L addition to EPN 1138-based systems probably plays the role of a diluent. Because CTBN-L itself is not a good

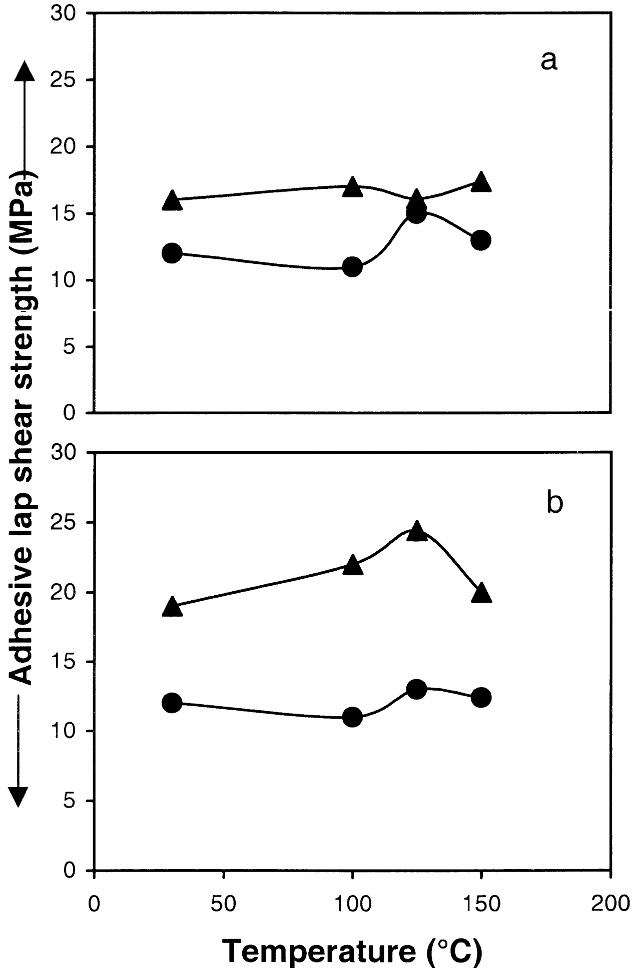

FIGURE 5 Adhesive lap shear strength values of unmodified and CTBN-L (10 phr) modified (a) EPN 1138-IDA-I system and (b) EPN 1138-IDA-II system at different temperatures: (▲) unmodified and (•) modified.

adhesive system, its presence probably reduces the adhesive strength of the modified systems.

Effect of Addition of CTBN-S on the Adhesive Strength of GY 250–/EPN 1138-IDA-I/IDA-II Systems

Adhesive strength at different temperatures of CTBN-S modified GY 250-IDA-I/IDA-II systems was studied. The results are compared

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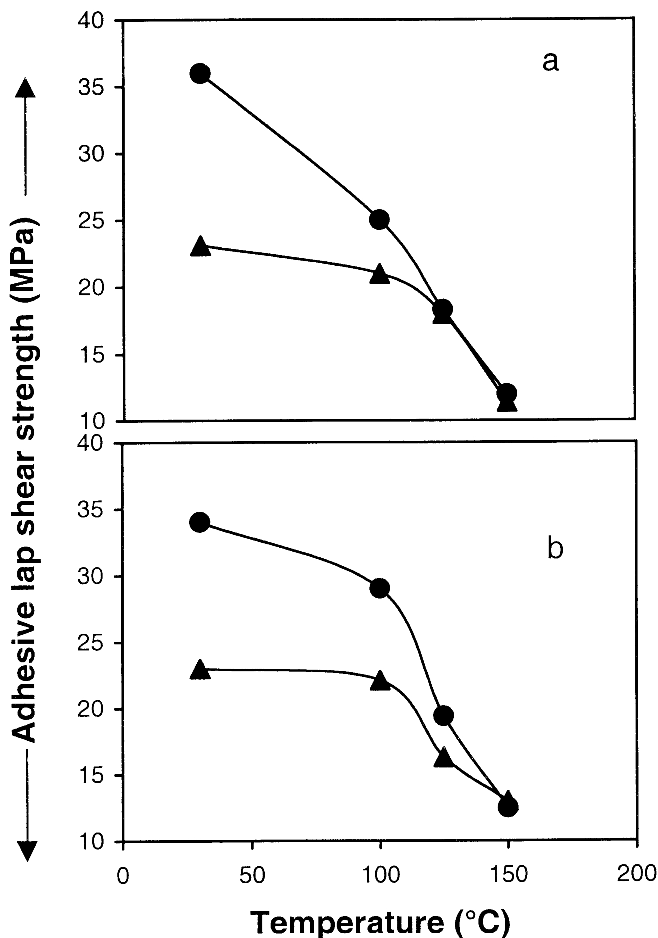

FIGURE 6 Adhesive lap shear strength values of unmodified and CTBN-S (10 phr) modified (a) GY 250-IDA-I system and (b) GY 250-IDA-II system at different temperatures: (▲) unmodified and (•) modified.

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in Figure 6. For GY 250-IDA-I modified with CTBN-S, improvement in adhesive strength at room temperature and at 100°C by 56% and 19%, respectively, is observed when compared to the unmodified system. The adhesive strength at 125 and 150°C of the modified system is comparable to that of the unmodified system. For GY 250-IDA-II system modified with CTBN-S improvement by 48, 31, and 19% is observed for the adhesive strength at room temperature, 100 and at 125°C, respectively, when compared to the unmodified system. At 150°C the

adhesive strength of the modified system is comparable to that of the unmodified system.

Adhesive strength values at room temperature, and at 100, 125, and 150°C of CTBN-S modified EPN 1138-IDA-I/IDA-II systems are compared in Figure 7. Unlike the modification of EPN 1138-IDA systems with CTBN-L, modification with CTBN-S has resulted in remarkable improvement in the room temperature and elevated temperature adhesive strength of EPN 1138-IDA systems. For EPN 1138-IDA-I

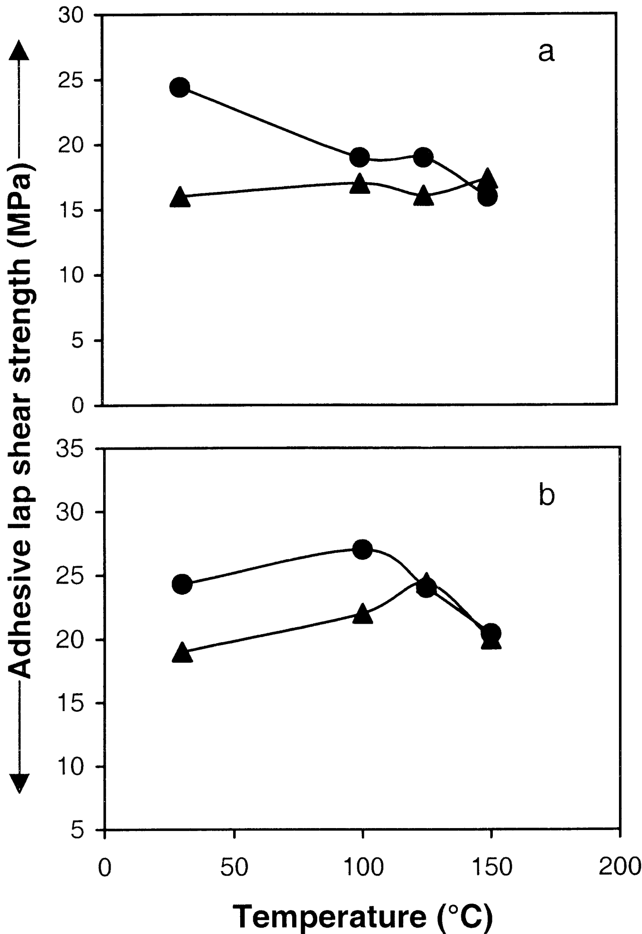

FIGURE 7 Adhesive lap shear strength values of unmodified and CTBN-S (10 phr) modified (a) EPN 1138-IDA-I system and (b) EPN 1138-IDA-II system at different temperatures: (▲) unmodified and (•) modified.

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system modified with CTBN-S, improvement by 53, 12, 12, and 7% is observed in the adhesive strength at room temperature, 100, 125, and at 150°C, respectively, when compared to the unmodified systems.

In the case of EPN 1138-IDA-II systems modified with CTBN-S, 28 and 23% improvement is observed for the adhesive strength at room temperature and at 100°C, respectively. The adhesive strength of the modified system at 125 and 150°C is comparable to that of the unmodified system.

Thermal Stability of Modified Epoxy-Imide Resins

For understanding the effect of modification of epoxy-imide resins on the thermal stability, epoxy-imide resins based on IDA-I were chosen to be studied. Thermal stability of the modified and unmodified epoxy-imide systems has been evaluated in nitrogen atmosphere at a heating rate of 10°C/min and are discussed in detail in the following sections.

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Thermal Stability of EHTPB-Modified Epoxy-Imide Systems

The thermograms of unmodified and EHTPB (10 wt%) modified GY 250-/EPN 1138-IDA-I systems are compared in Figure 8. It is noticed that the modification with EHTPB brings down to some extent the overall thermal stability of GY 250-IDA and EPN 1138-IDA systems. This is due to the incorporation of aliphatic linkages in the epoxy-imide systems.

It is interesting to note that the decrease in thermal stability on modification with EHTPB is more pronounced with EPN 1138-based systems than with GY 250-based systems. EHTPB is a polyfunctional resin and hence, modification of GY 250-based systems with EHTPB results in the incorporation of crosslinks and aliphatic linkages and thus, the decrease in the thermal stability caused by the incorporation of aliphatic linkages is probably partly compensated by the additional crosslinks. In the case of EPN 1138-based systems, modification with EHTPB would not result in additional crosslinks, as EPN 1138 is already a polyfunctional resin and it would result in the incorporation of aliphatic linkages only. Hence, the decrease in the overall thermal stability on modification with EHTPB is more pronounced for EPN 1138-based systems than for GY 250-based systems.

Thermal Stability of CTBN-L-Modified Epoxy-Imide Systems

Thermograms of unmodified and CTBN-L-modified GY 250-/EPN 1138-IDA-I systems are compared in Figure 9. Though the weight loss

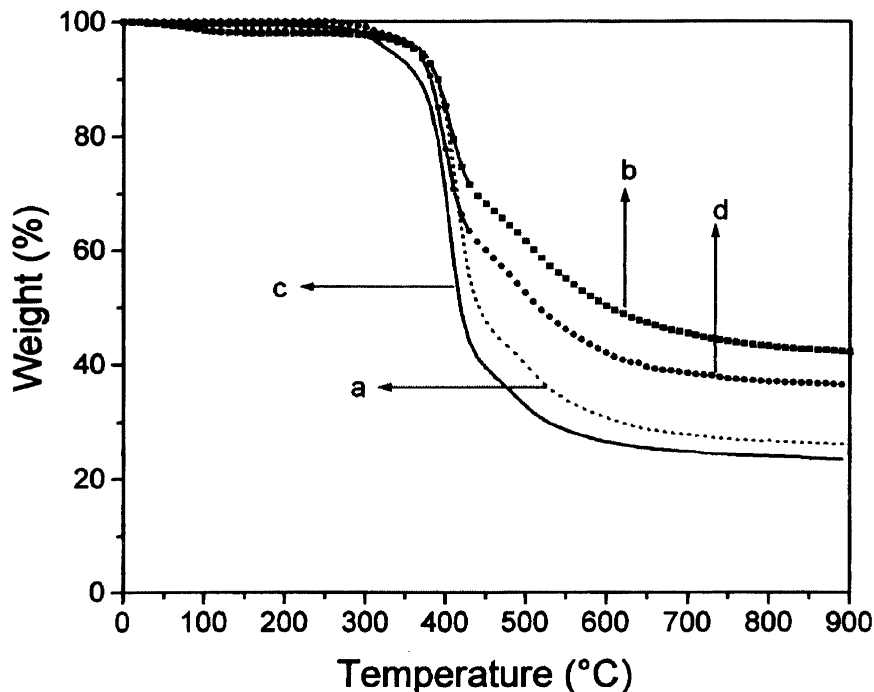

FIGURE 8 Thermograms (in nitrogen atmosphere) of unmodified and EHTPB (10 wt%) modified GY 250-/EPN 1138-IDA-I systems: (a) GY 250-IDA-I, (b) EPN 1138-IDA-I, (c) GY 250-IDA-I-EHTPB, and (d) EPN 1138-IDA-I-EHTPB.

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in the temperature range 550–900°C for CTBN-L-modified GY 250-IDA-I system is the same as that of the unmodified system, T_i and T_{max} decrease by 30 and 50°C, respectively when compared to the unmodified system. For EPN 1138-IDA-I system modified with CTBN-L, T_i and T_{max} are almost the same as those of the unmodified system. However, the weight loss in the temperature range 400 to 900°C is higher (by $\approx$6%) for the modified system when compared to the unmodified system. Thus, it is noticed that modification with CTBN-L marginally reduces the thermal stability of GY 250-/EPN 1138-IDA-I systems and this may be due to the aliphatic linkages present in CTBN-L.

Thermal Stability of CTBN-S-Modified Epoxy-Imide Resins

Thermograms of unmodified and CTBN-S modified GY 250-IDA-I and EPN 1138-IDA-I systems are compared in Figure 10. For both GY 250

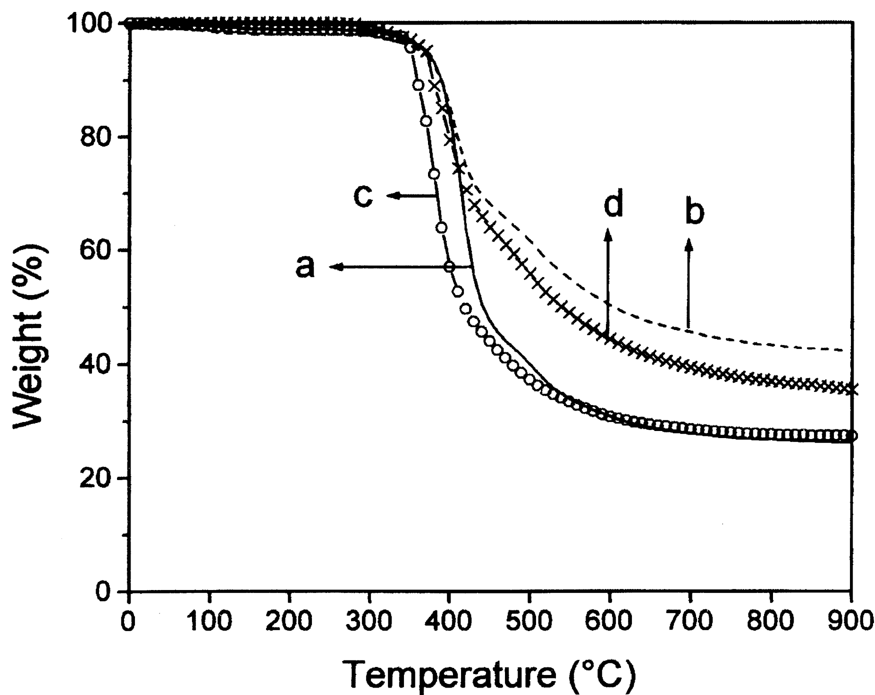

FIGURE 9 Thermograms (in nitrogen atmosphere) of unmodified and CTBN-L (10 phr) modified GY 250-/EPN 1138-IDA-I systems: (a) GY 250-IDA-I, (b) EPN 1138-IDA-I, (c) GY 250-IDA-I-CTBN-L, and (d) EPN 1138-IDA-I-CTBN-L.

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and EPN 1138-based systems T_i and T_{max} decrease marginally on modification with CTBN-S. This is due to the incorporation of aliphatic linkages into epoxy-imide resins.

It is interesting to note that in the temperature range of 450–900°C, the thermal stability of CTBN-S modified GY 250-IDA-I is slightly better than the unmodified system. On the other hand, for EPN 1138-IDA-I system in the same temperature range the thermal stability of the modified system is considerably less than that of the unmodified system. The unmodified EPN 1138-IDA-I system gives a char residue of 42% at 900°C whereas the modified system gives a char residue of 25% at this temperature. The earlier observations suggest that modification with CTBN-S influences the thermal stability of highly crosslinked EPN 1138-IDA-I system more than uncrosslinked/less crosslinked GY 250-IDA-I system.

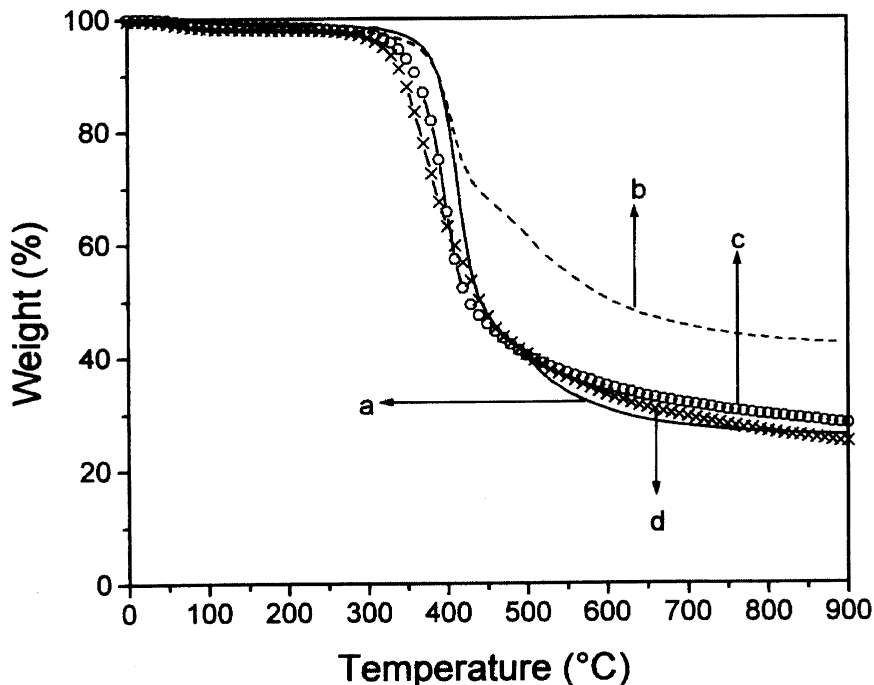

FIGURE 10 Thermograms (in nitrogen atmosphere) of unmodified and CTBN-S (10 phr) modified GY 250-/EPN 1138-IDA-I systems: (a) GY 250-IDA-I, (b) EPN 1138-IDA-I, (c) GY 250-IDA-I-CTBN-S, and (d) EPN 1138-IDA-I-CTBN-S.

Morphological Studies of Epoxy-Imide Resins

Morphological studies of the fractured surfaces of epoxy-imide systems modified with EHTPB, CTBN-L, and CTBN-S and those of the unmodified epoxy-imide systems were carried out by using scanning electron microscopy. As in the case of thermal properties, morphological studies were carried out only for IDA-I-based epoxy-imide systems.

Morphological Studies of the EHTPB-Modified Epoxy-Imide Systems

SEM studies of unmodified GY 250-IDA-I and EPN 1138-IDA-I are given in Figures 11(a) and (b), respectively. Both systems show morphology typical of brittle systems. In the case of GY 250-IDA-I systems a river-bed like morphology is observed. On the other hand, continuous deep cracks are seen in the micrograph of EPN 1138-IDA-I system.

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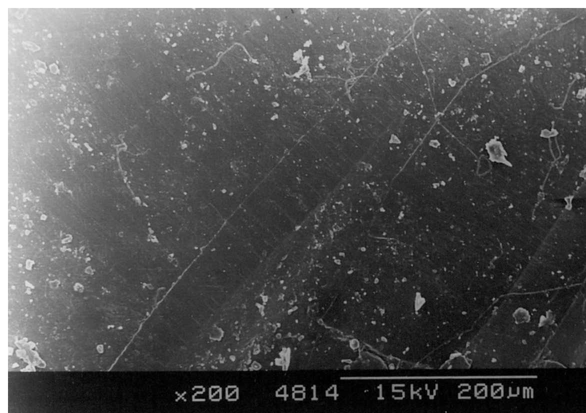
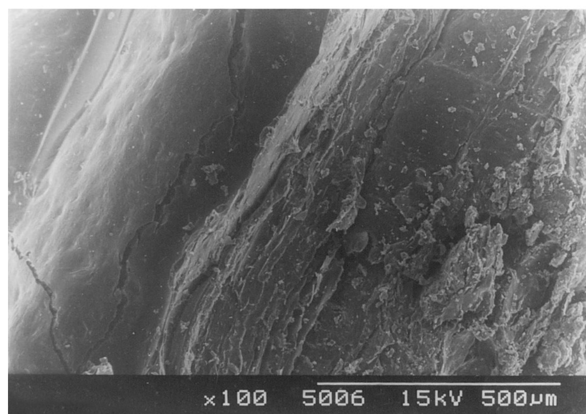


(a)



(b)

FIGURE 11 (a) SEM of unmodified GY 250-IDA-I system and (b) SEM of unmodified EPN 1138-IDA-I system.

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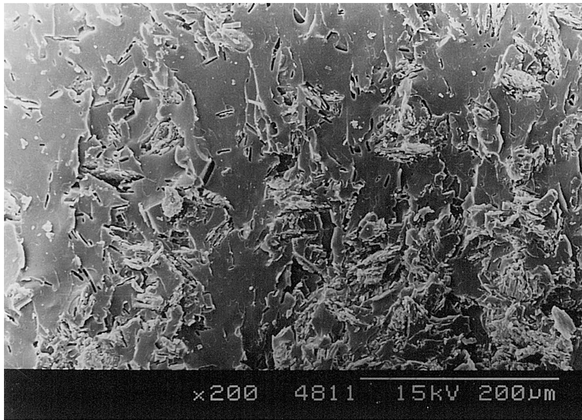
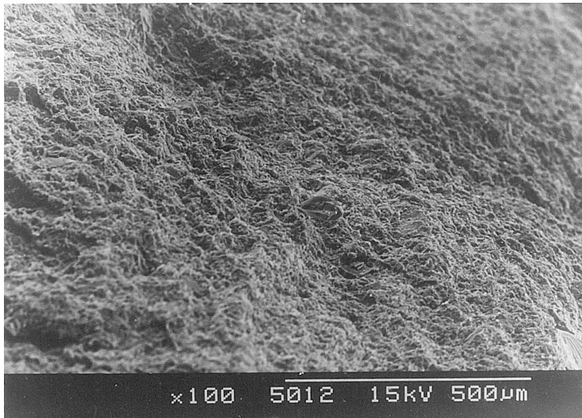
Comparison of micrographs of GY 250-IDA-I and EPN 1138-IDA-I suggests that the latter system is more brittle than the former. EPN 1138-IDA-I is highly crosslinked due to the polyfunctional nature of EPN 1138 and hence, it is a more brittle system.

The micrographs of EHTPB-modified GY 250-IDA-I and EPN 1138-IDA-I systems are shown in Figures 12(a) and (b), respectively. It is observed that for both GY 250-IDA-I and EPN 1138-IDA-I systems, addition of EHTPB reduces the brittleness and thereby making these systems somewhat ductile in nature. From Figures 11(a) and 12(a) it is



(a)



(b)

FIGURE 12 (a) SEM of EHTPB (10 wt%) modified GY 250-IDA-I system and (b) SEM of EHTPB (10 wt%) modified EPN 1138-IDA-I system.

observed that the morphology of the fractured surface of GY 250-IDA-I system changes from river-bed like pattern to ductile pattern when the system is modified with EHTPB. Comparison of Figures 11(b) and 12(b) suggests that modification of EPN 1138-IDA-I system with EHTPB reduces the brittleness of the system as evidenced by the absence of cracks in the micrograph of the modified system. However, phase separation of rubber particles in the epoxy-imide matrix has not been observed. The incorporation of EHTPB in the epoxy-imide systems proceeds mainly through the participation of epoxy groups

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present in EHTPB. As EHTPB, GY 250 and EPN 1138 undergo curing with IDA in the same temperature range, the EHTPB added to GY 250-/EPN 1138-IDA system probably undergoes co-curing resulting in a more homogeneous system.

Morphological Studies of CTBN-L-Modified Epoxy-Imide Systems

SEM studies of CTBN-L–modified epoxy-imide systems were carried out to understand the role played by CTBN-L. Micrographs of CTBN-L-modified GY 250-IDA-I and EPN 1138-IDA-I are shown in Figures 13(a) and (b), respectively. Comparison of micrographs of unmodified and CTBN-L modified GY 250-IDA-I suggests that the addition of CTBN-L reduces the brittleness of this system and makes it more ductile. No phase separation of rubber particles is observed. It appears that CTBN-L is distributed uniformly throughout the matrix.

In the case of EPN 1138-IDA-I system, modification with CTBN-L has not been able to reduce the brittleness of the system or toughen the system as evidenced by the presence of macro- and micro-cracks. This is reflected in the adhesive properties of this system. SEM studies and adhesive properties of CTBN-L modified EPN 1138-IDA-I system suggest that for a highly crosslinked EPN 1138-IDA-I system toughening does not take place with CTBN-L. Similar observations were made by Hodgin et al. [34] and Bucknall and Patridge [35] for CTBN-L modified highly crosslinked epoxy systems.

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Morphology Studies of CTBN-S-Modified Epoxy-Imide Resins

Micrographs of GY 250-IDA-I and EPN 1138-IDA-I systems modified with CTBN-S are shown in Figures 14(a) and (b), respectively. At lower magnification no meaningful information could be observed. At higher magnification, the presence of phase separated rubber particles is observed both in GY 250-IDA-I and EPN 1138-IDA-I systems modified with CTBN-S. It is reported that phase separated rubber particles present in epoxy systems effectively toughen the systems, thereby improving the fracture toughness and other mechanical properties considerably [36]. Evaluation of the adhesive properties of EHTPB, CTBN-L, and CTBN-S modified GY 250/EPN 1138-IDA systems suggests that remarkable improvement in room temperature adhesive strength is observed only when CTBN-S is used as the modifier. The improvement in adhesive strength of CTBN-S modified system is attributed to the effective toughening caused by phase separated CTBN-S particles.

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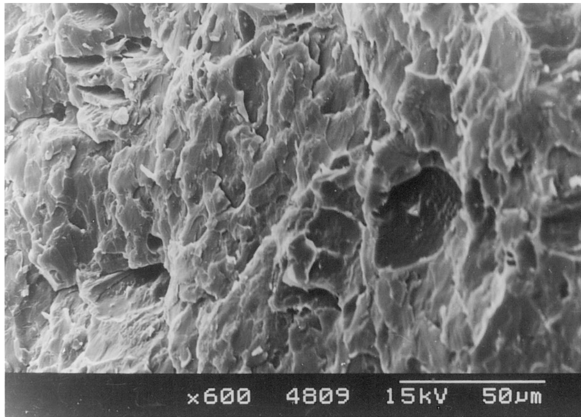
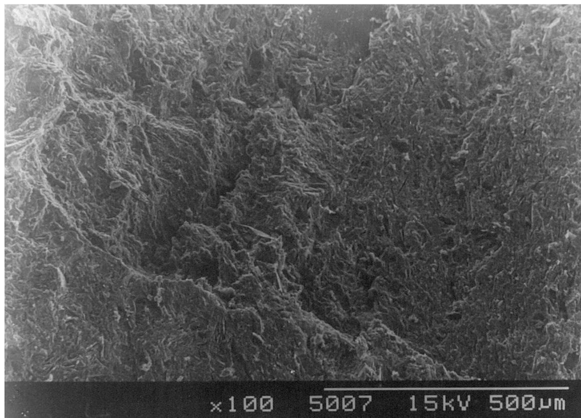


(a)



(b)

FIGURE 13 (a) SEM of CTBN-L (10 phr) modified GY 250-IDA-I system and (b) SEM of CTBN-L (10 phr) modified EPN 1138-IDA-I system.

For CTBN-S toughened epoxy resin systems, scanning electron micrographs of fractured surface usually show the presence of cavities caused by the pullout of precipitated rubber particles. However, in the micrographs of CTBN-S modified GY 250-/EPN 1138-IDA-I systems, a fractured surface of precipitated rubber particles is seen. For epoxy-imides toughened with CTBN-S, there were practical difficulties in preparing samples for SEM analysis. As the imide-diacid and epoxy resin tend to separate out during curing, it was difficult to get CTBN-S modified epoxy-imide samples of reasonably large size

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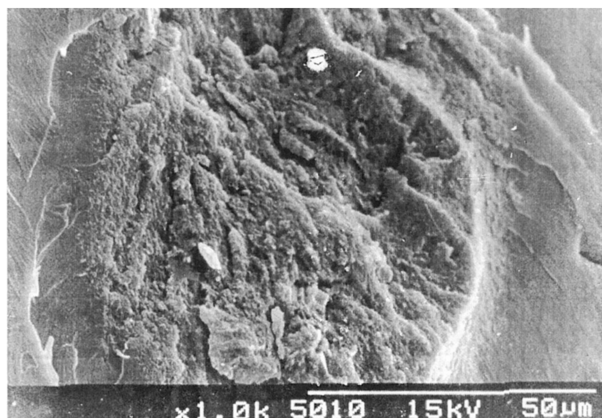
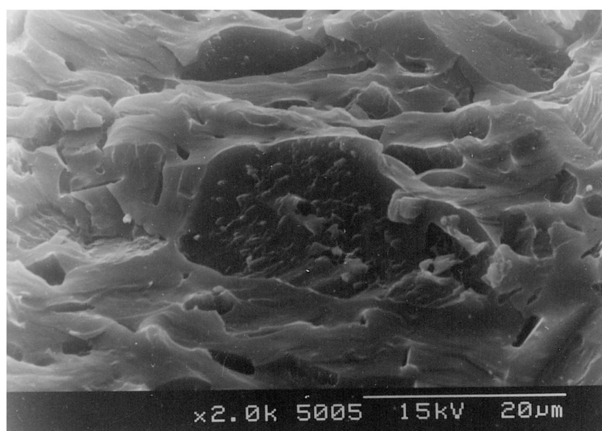


(a)



(b)

FIGURE 14 (a) SEM of CTBN-S (10 phr) modified GY 250-IDA-I system and (b) SEM of CTBN-S (10 phr) modified EPN 1138-IDA-I system.

having uniform composition. Hence, the sample size was limited to $1\,mm \times 2\,mm \times 2\,mm$. It was difficult to fracture the samples of this size and hence, the samples were soaked in liquid nitrogen and fractured by hammering. When soaked in liquid nitrogen, rubber particles would have become brittle and undergone fracture when hammered. Thus, in the micrographs of CTBN-S modified epoxy-imide systems, fractured rubber particles are seen instead of cavities formed due to the pull out of rubber particles.

Comparison of Adhesive Strength of Epoxy-Imides Modified with EHTPB, CTBN-L, and CTBN-S

In order to have a comparative evaluation of the effect of modifiers on the adhesive strength of epoxy-imide systems, the relative percentage increase or decrease in the adhesive strength values at room temperature and at 150°C of GY-250-IDA-I and EPN 1138-IDA-I systems when modified with EHTPB, CTBN-L, and CTBN-S are compared in Figure 15. It is observed that for GY 250-IDA-I system the room temperature adhesive strength increases by ≈17% when the system is modified with EHTPB and CTBN-L whereas remarkable improvement

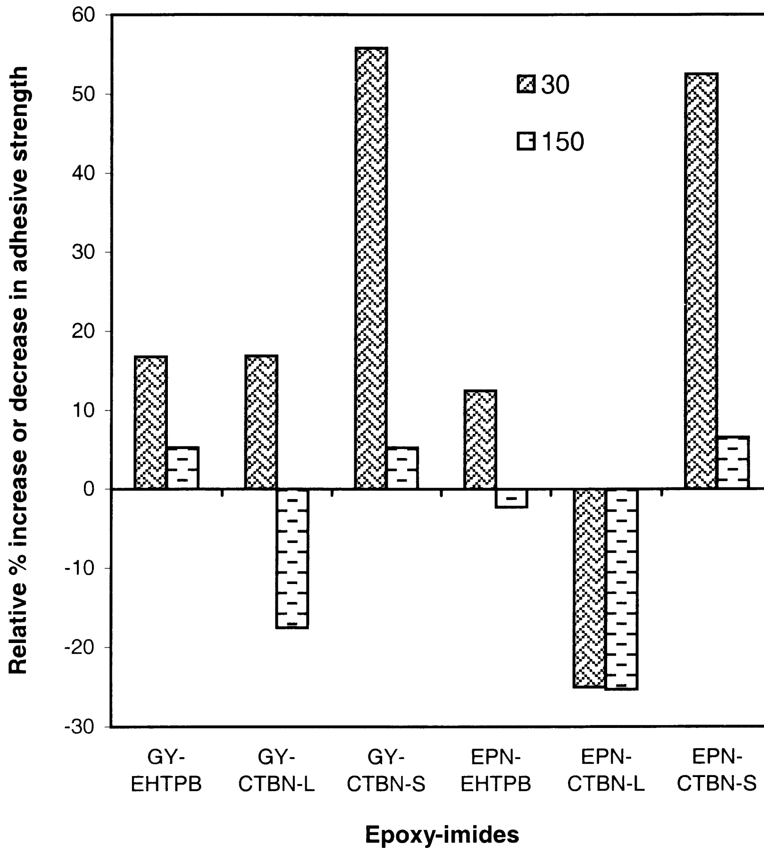


FIGURE 15 Relative percentage increase or decrease of adhesive lap shear strength of unmodified and EHTPB–, CTBN–L–, and CTBN–S– modified GY 250–IDA–I and EPN 1138–IDA–I systems.

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in adhesive strength (by ≈56%) is observed when the system is modified with CTBN-S.

It is noticed that for GY 250-IDA-I system modified with CTBN-L, the adhesive strength at 150°C is less than that observed for the unmodified system. But for GY 250-IDA-I system modified with EHTPB and CTBN-S, the adhesive strength at 150°C is increased by ≈5%. Similar observations are made with EHTPB, CTBN-L, and CTBN-S modified GY 250-IDA-II systems.

Modification of EPN-1138-IDA-I systems with CTBN-L reduces the adhesive strength by 25% at room temperature and at 150°C when compared to the unmodified system. As in the case of GY 250-based systems, modification with EHTPB offers only a marginal improvement in room temperature adhesive lap shear strength whereas the modification with CTBN-S offers improvement by ≈53%. For CTBN-S modified systems the adhesive strength at 150°C is comparable to that of the unmodified systems. Similar observations are made with EPN-1138-IDA-II based modified systems.

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CONCLUSIONS

Based on the results presented in this article it is evident that the modification with CTBN-S is rather effective for improving the room temperature adhesive lap shear strength of GY 250/EPN 1138-IDA-I/IDA-II systems. SEM studies suggest that, in general, the modification with EHTPB and CTBN-L does not result in phase-separated morphology and results in only improving the ductility of epoxy-imide systems. On the other hand, when the modification is carried out with CTBN-S precipitation of rubber particles is observed that enhances the toughness of the epoxy-imide systems.

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