

# Studies on the Effect of Concentration of Hydroxyl-Terminated Polybutadiene (HTPB) on the Physico-Thermal and Physico–Mechanical Properties of Blends of Isocyanate-Terminated Prepolymer from Epoxy Novolac Resin and HTPB

Kavita Srivastava<sup>1</sup>, Manoj Kumar Kaushik<sup>2</sup>, Deepak Srivastava<sup>3</sup>, and Santosh K. Tripathi<sup>4</sup>

Assistant Professor, Department of Chemistry, V.S.S.D. College, Kanpur, Uttar Pradesh, India<sup>1</sup>

Assistant Professor, Department of Chemistry, S.I.E.M., Mathura, Uttar Pradesh, India<sup>2</sup>

Professor, Department of Plastic Technology, H. B. Technological Institute, Kanpur, Uttar Pradesh, India<sup>3</sup>

Associate Professor, Department of Chemistry, V.S.S.D. College, Kanpur, Uttar Pradesh, India<sup>4</sup>

**ABSTRACT:** Six blend samples of isocyanate-terminated modified epoxy novolac (*IEN*) and varying concentration of hydroxyl-terminated polybutadiene (HTPB) ranging between zero to 15 wt% (i.e., 0, 3.0, 6.0, 9.0, 12, and 15% of HTPB) were prepared in two stages at 120°C for 120 min. The catalyst, tetra-*n*-butyl ammonium iodide (TBAI), was added (approximately 1% by weight of the mixture) at this stage and the temperature of the reaction mixture was kept at 160°C for another one and half-hours, and finally, the required sample with increased viscosity was obtained for further studies. The epoxy novolac resin (EN) was prepared by the reaction of epichlorohydrin and novolac resin (N) in presence of 40% methanolic sodium hydroxide as catalyst. The synthesized resin samples were characterized by FTIR analysis. The curing of the *IEN* samples was done dynamic differential scanning analyzer (DSC). Tensile strength, tensile modulus and elongation at-break were measured on UTM whereas the impact strength was measured on Izod impact tester. The relative thermal stability of the samples was checked by thermogravimetric analyzer (TGA).

**KEYWORDS:** Isocyanate-terminated modified epoxy novolac, HTPB, FTIR, DSC, TGA.

## I. INTRODUCTION

Cured epoxy resins are known to exhibit good engineering properties, such as high stiffness and strength, creep resistance and chemical resistance [1]. In common with all thermoset plastics, however, they are intrinsically brittle. To alleviate this deficiency epoxy resins are frequently modified by dissolving in the liquid system a small proportion (10-20%) of a liquid rubber containing reactive end groups and allowing the precipitation of cross-linked rubber particles during curing [2]. It is preferable that the modifying agent is a low molecular weight polymer to ensure that the viscosity of the resin is not increased excessively so that the processability of the system is not impaired [3]. In this way, carboxyl-terminated poly (butadiene-co-acrylonitrile) (CTBN) rubber [4, 5], acrylic elastomers [6, 7] and silicon rubber [8], used as toughening elastomers, have been successfully blended to improve the toughness of the epoxy resins. Attempts to toughen the epoxy matrix using hydroxy-terminated poly (butadiene-co-acrylonitrile) (HTBN) to the epoxy matrix, suffer from two disadvantages [9] – the poor selectivity of HTBN towards generating a hydroxylate anion under mild conditions and, secondly, the self-polymerization of epoxy resin on employing moderately high temperatures with a Lewis bases or acid catalyst. The preceding problems have already been overcome by using tolylene diisocyanate

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(TDI) in place of  $\text{BF}_3$ -tertiary amine complexes [9]. Up to best of my knowledge, none of the workers modified the epoxidized novolac resin matrix by hydroxyl- terminated polybutadiene (HTPB) as the reactive liquid rubber. Therefore, we have selected this problem in the present investigation. The problem proceeds with the synthesis of epoxidized novolac resins, and their blends, separately, with TDI and HTPB.

## II. MATERIALS AND METHODS

Epichlorohydrin, phenol, toluene diisocyanate (TDI), *o*-chloro benzyl chloride, tetra-*n*-butyl ammonium iodide (TBAI) (all procured from M/s Ranbaxy Laboratories Ltd, Punjab), formaldehyde (40% solution from M/s Qualikem Industries, New Delhi), *p*-toluene sulphonic (PTSA) obtained from E.Merck, New Delhi, sodium hydroxide, methanol (both from M/s BDH), hydroxy-terminated polybutadiene (HTPB) procured from M/s Petroflex Ind. Com. S. A., Rio de Janeiro, Brazil having number-average molecular weight  $3000 \text{ gmol}^{-1}$  with hydroxyl number 0.8 g/mequiv were used during the investigation. Diaminodiphenylmethane (DDM) (M/s Hindustan Ciba-Geigy Ltd., Bombay, India) was used as curing agent for epoxy resin.

Novolac resin with mole ratio 1:0.7 of phenol (*P*) to formaldehyde (*F*) was prepared using *p*-toluene sulphonic acid as catalyst (0.5% based on phenol) dissolved in 2 ml methanol under warm conditions by a method given in the past [10]. Samples were drawn at regular intervals of 45 minutes from the reaction mixture, taken in a three-necked round bottom (R.B.) flask, for determining the free-phenol (as per ASTM standard D 1312-56) and free-formaldehyde content (as per ISO standard 9397). The reaction product was cooled and dried under vacuum at  $60^\circ\text{C}$  overnight before purification by column chromatography. A resin solution prepared with *n*-hexane, charged to the silica gel column chromatographic purification, was adopted mainly to remove the unreacted components, impurities etc. from the methylolated phenol. Purification was effected using the eluent mixture of ethyl acetate-benzene (60:40). The novolac resin (*PN*), thus formed, was treated with molar excess of epichlorohydrin and 40% solution of sodium hydroxide at  $120^\circ\text{C}$  for about 10 hours. The formed product was vacuum distilled for the removal of excess of epichlorohydrin. The epoxide equivalent weight (*EEW*) of phenol-based epoxidized novolac resin (*PNE*) resin was found to be 320 eq/g (as determined by Pyridinium chloride method).

The synthesis of isocyanate-terminated prepolymer from epoxy novolac resin (*PNE*) with HTPB was carried out in two stages. In the first stage, a reaction between HTPB and TDI, in epoxy novolac resin as reaction medium, was carried out to produce the urethane links but leaving free isocyanates groups that would react afterwards with epoxy groups of the epoxy resin. The TDI was taken in excess of the equimolar ratio between -NCO groups and -OH groups in HTPB. The TDI concentration was 30% w/w in relation to HTPB which corresponds to 4:1 mole of -NCO groups per mole of -OH groups in HTPB. Approximately, 100 grams with epoxy - novolac resin (*PN*) of HTPB was taken in a three - necked round bottom (R.B.) flask fitted with reflux condenser, mechanical stirrer with controller, contact thermometer, and dry nitrogen inlet assembly. HTPB was degassed at  $90^\circ\text{C}$  for one hour to remove any moisture and volatile. The reaction medium was epoxidized novolac based on phenol (*PNE*). A few drops of *o*- chloro benzoyl chloride was added to the content and then about 30 grams of TDI was added in drops while stirring. The contents were heated to  $120^\circ\text{C}$  for two hours with stirring under dry nitrogen in the presence of epoxy - novolac atmosphere. Finally, we get the resin, i.e., isocyanate - terminated prepolymer.

In the second stage, the prepolymer prepared in the first stage, was used for further reactions. The temperature of the reaction mixture, from first stage, was raised up to  $160^\circ\text{C}$  and kept at this temperature for an half an hour. The catalyst, tetra - *n* - butyl ammonium iodide (*TBAI*) was added (approximately 1% by weight of the mixture) at this stage and the temperature of the reaction mixture was kept for another one and half hours, during which time a substantial increase in viscosity was noted. Finally, the reaction mixture was cooled to room temperature and stored in a desiccator for further studies. The sample prepared under this category was termed as *IEN*. The modified epoxy novolac resin (*IEN*) suitably diluted with excess of epoxy novolac (i.e., *PNE*) to prepare the samples of different composition varying in their rubber content from zero to 15 percent of HTPB (i.e., 0.0, 3.0, 6.0, 9.0, 12, and 15% of HTPB designated as *IEN0*, *IEN3*, *IEN6*, *IEN9*, *IEN12*, and *IEN15*, respectively). The respective epoxy novolac resins were degassed in vacuum oven at a temperature of  $100^\circ\text{C}$  to remove any volatiles. To this was added the correct quantity of chemically reacted rubber/epoxy mixture of known rubber content. The mixture was heated to  $120^\circ\text{C}$  and stoichiometric quantity of curing agent, diaminodiphenylmethane (DDM), in powder form, was added in lots and stirred well till the curing agent was completely dissolved. The mixture was powdered to fill a metallic mold with a

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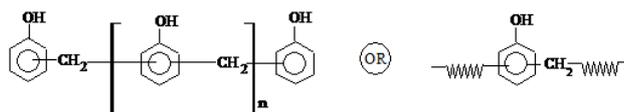
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teflon releasing surface, preheated to a temperature of 80 - 100°C. Enough care was taken to avoid air bubbles getting trapped inside. Curing was done in an air oven as per the cure temperatures obtained from differential scanning calorimetric (DSC) analysis.

The purified resins were subjected to Fourier-transform infra-red (FTIR) spectroscopic analysis, to monitor the various functional groups in the wavelength range of 400 to 4000  $\text{cm}^{-1}$  by Perkin Elmer FTIR, RX-1 spectrophotometer. Cure temperature of the prepared samples was observed by taking very little quantity of the sample into shallow aluminum pan sealed by an aluminum cover of differential scanning calorimetric (DSC) (TA, Instrument, USA; Model DSC 2920). This was placed in sample cell of the instrument. The starting temperature, programmed rate and final temperature were taken at heating rate of 10°C/min. Dynamic scans were obtained which were used for assuming the cure temperature. Dumbbell-shaped cured IEN-series samples (size : 7.5 x 3/4 x 1/8 inch) were used for the determination of tensile strength and elongation-at-break according to the ASTM D 638 standard on a Universal Testing Machine (UTM)(M/s Patiwana Group, Star Testing Systems, Mumbai, India). The crosshead speed of the machine was kept at 25  $\text{mm min}^{-1}$ . The impact strength of the specimen was determined by using Izod Mandate Tensometer using rectangular specimen of 75mm x 15mm x 3mm according to ASTM D-256 standards. The percent weight loss and thermal degradation characteristic of prepared sample was evaluated by thermogravimetric analyzer (TGA) recorded on TA Instrument (Model Hi. Res. 2950) TGA unit interfaced with TA instruments Inc. Thermal Analyst 2100 (Du Pont) control unit. The TGA cell was purged with nitrogen at 60 $\text{mLmin}^{-1}$  during degradation runs. The amount of sample taken was approximately 5-10 mg in a platinum sample pan. The heating rate in each run was kept at 10°C $\text{min}^{-1}$  and the temperature range was ambient to 800°C.

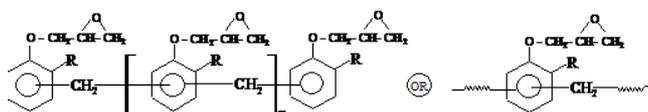
### III. RESULTS AND DISCUSSION

On the basis of discussion based on FTIR and NMR spectroscopic analysis, as discussed elsewhere in our previous publication [10], the average phenol functionality,  $f$ , and  $M_n$  were found to be 2.55 and 256g  $\text{mol}^{-1}$ , respectively. The following structure of phenolic novolac (PN) (Scheme 1) and epoxy novolac resin (EPN) (Scheme 2) resins may be proposed :



Where  $n = 0.55$

Scheme 1



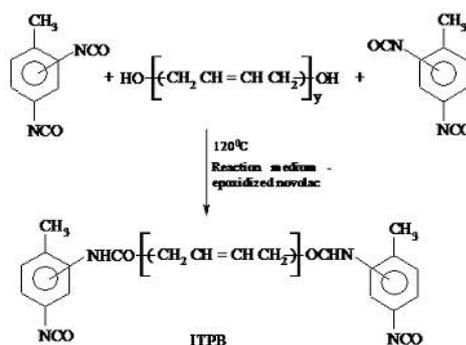
Scheme 2

The blending of epoxidized novolacs and hydroxyl-terminated polybutadiene (HTPB) liquid rubber may be done by the incorporation of toluene diisocyanate (TDI). This may be thought as chemical blending, in contrast to physical blending, where constituents are added and blended by some physical means, or chemically modifying of HTPB and to subsequently link it to be the epoxy resin. The reactions might occur in two stages. In the first stage, there could be a reaction between HTPB and TDI which might produce urethane links, but leaving free isocyanate groups that could react after wards with epoxy groups of the novolac epoxy. The possible reactions of first stage may be shown in Scheme 3.

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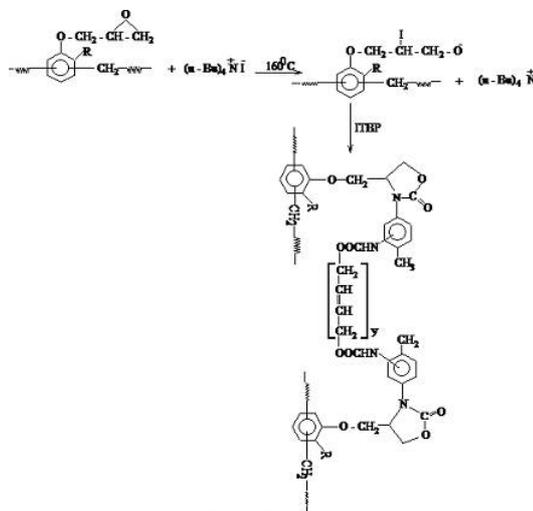
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Scheme 3

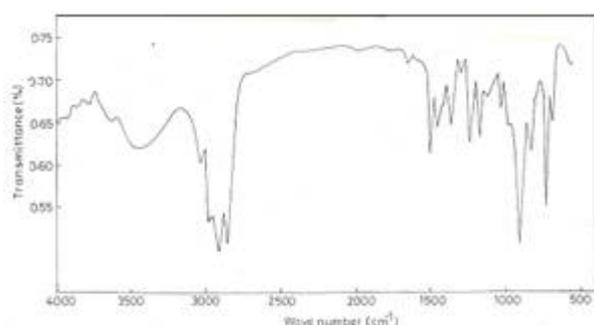
The reactions shown in Scheme 3 might result in isocyanate-terminated polybutadiene (*ITPB*) elastomer and this could be dissolved in the reaction medium. In the second stage, the end isocyanate groups of the elastomer chain might react with the epoxy groups of novolac epoxy by adding tetra-*n*-butyl ammonium iodide (the catalyst) to the reaction mixture after the first stage was over. The temperature at this stage was raised to 160°C. The possible reactions may be shown in Scheme 4. The amount of catalyst would depend on the epoxide equivalent weight (*EEW*) of the considered epoxidized novolac resin. Also, some of the epoxy groups might be unreacted.



Scheme 4

Of these two reactions the first stage reaction, i.e., the reaction of HTPB with excess of difunctional isocyanates might occur very rapidly to yield a stable prepolymer with isocyanate groups. Such a reaction with the polybutadiene diol has been successfully used in polyurethane elastomer. The second reaction between the isocyanate and the epoxy is also a known reaction in the chemistry of polyoxazolidones. It is reported that the reaction between epoxy and isocyanate took place at high temperatures with [11] and without [12] catalysts to form oxazolidones.

Fig. 1 and Fig. 2 showed the infra-red spectra of pure HTPB and its prepolymer with TDI, respectively. A very strong absorption band near 3400  $\text{cm}^{-1}$  which might be due to  $-\text{OH}$  stretching vibration of HTPB. The conspicuous reduction in the intensity of this band was observed in Fig. 1.



This might be due to the conversion of the hydroxyl to urethane by reaction with the isocyanate of TDI. The formation of urethane linkage could be seen by the appearance of new peak in the region  $3310\text{ cm}^{-1}$  (-NH stretching) which was further confirmed by the appearance of peak near  $1720\text{ cm}^{-1}$ . The absorption band at  $1740\text{ cm}^{-1}$  also appeared in the spectrum (Fig. 2) which might be due to carbonyl type stretching vibration of the ester linkages formed during the reaction of TDI and HTPB in the first stage. As there existed epoxy medium with the reaction mixture, all the absorption bands related to epoxidized novolac (Sample *PNE*) were also seen in the spectrum (Fig. 2). A broad peak centered at  $2260\text{ cm}^{-1}$  appeared in spectrum of *ITPB* (Fig. 2) which might be due to presence of  $\text{-N=C=O}$  vibration from the isocyanate-terminated elastomer (i.e., *ITPB*) formed in stage-I of reaction (Scheme 3).

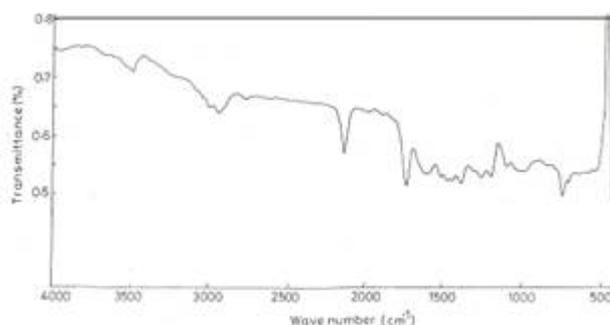


Fig. 2. : FTIR spectrum of isocyanate terminated prepolymer

Fig. 3 represented the infra-red spectrum of sample, *IEN9*. This was the product from the second stage (Scheme 4). There appeared the characteristics bands of oxazolidone besides the urethane bands, that is a carbonyl absorption at  $1754\text{ cm}^{-1}$  and a band at  $1412\text{ cm}^{-1}$  attributed to C-N linkages present in the sample *IEN9*. The formation of oxazolidone could also be indirectly inferred from the change in the shape and intensity of the peak at  $1740\text{ cm}^{-1}$  in Fig. 2 compared to Fig. 3.

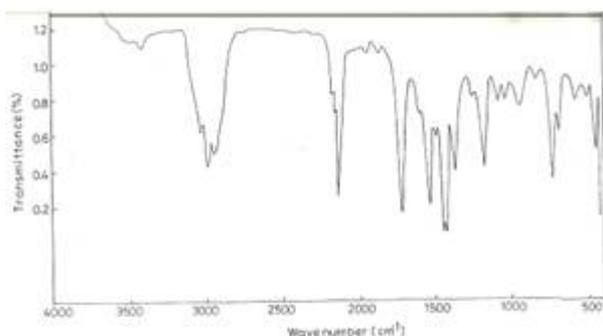


Fig. 3. : FTIR spectrum of blend sample *IEN9*.

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The results of infra-red spectroscopic analysis confirmed the formation of links as shown in Schemes 3 and 4. The results also revealed that epoxy was linked to HTPB-TDI by the formation of two functional groups, respectively, urethane and oxazolidone.

The modified epoxy novolac resin (Sample *IEN*) was suitably diluted with excess of respective epoxy novolac (i.e., *PNE*) so that the final mixture contained the concentration of HTPB ranging between zero and 15 percent of HTPB. These diluted samples were cured at 120°C with stoichiometric amount of curing agent, DDM. The cure temperature (i.e., 120°C) was from the dynamic scan at 100°C min<sup>-1</sup> by DSC.

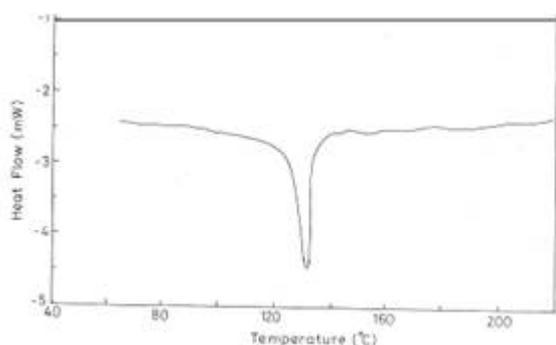


Fig. 4 : DSC scan of blend sample *IEN0*

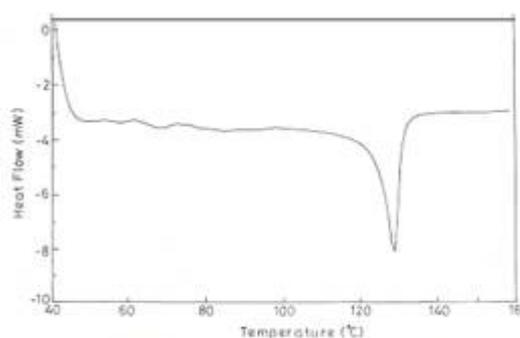


Fig. 5 : DSC scan of blend sample *IEN9*

Figs. 4 and 5 showed by dynamic DSC scans of blend samples *IEN0* and *IEN9*, respectively. It is clear from the figures that the exotherms were observed at 130°C and 128°C for blend samples *IEN0* and *IEN9*, respectively. With the cure temperature at 120°C, all the blend samples were cured in air oven. The cure time data as given in Table 1 revealed that the cure times for all the blend samples were almost the same.

Table 1. : Variation of cure time with HTPB concentration in the blend systems containing epoxidised phenolic novolac resin and HTPB at 120°C.

S.No.	Sample Code	Cure time (min)
1.	<i>IEN0</i>	136
2.	<i>IEN3</i>	132
3.	<i>IEN6</i>	132
4.	<i>IEN9</i>	130
5.	<i>IEN12</i>	133
6.	<i>IEN15</i>	134

Table 2 shows the data related to tensile strength, elongation-at-break, and tensile modulus with HTPB concentration in the blend sample. It is clear from the Table 4 that the tensile strength first decreased up to 12 percent level of HTPB in the blend samples and increased thereafter. It was found that there was a slow increase in the value of elongation-at-break up to 9 percent level of HTPB in the blend (refer Table 2). The further increase of concentration of HTPB in the blend, an abrupt increase was seen. The variation of tensile modulus of cured blend samples with HTPB concentration in the blends has been shown in Table 2. The table clearly indicated that a similar behavior in tensile modulus of blend samples with HTPB concentration was seen as observed for tensile strength.

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Table 2. : Variation of mechanical properties with HTPB concentration in the blend

S. No.	Conc. of HTPB (wt%)	Sample Code	Tensile strength (MPa)	Elongation-at-break (%)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (Jm <sup>-2</sup> )
1.	0	IEN0	25.7	21.8	1.61	62.6	1723	4.2
2.	3	IEN3	24.1	22.1	1.88	85.3	1617	5.8
3.	6	IEN6	21.7	25.8	2.03	90.4	1574	6.3
4.	9	IEN9	18.4	27.9	2.14	97.7	1101	6.9
5.	12	IEN12	16.2	29.7	1.72	69.1	1326	6.1
6.	15	IEN15	17.6	37.8	1.48	58.4	1491	5.4

From the preceding discussion, it can be concluded that inclusion of HTPB in the epoxy matrix below 12% decreased the tensile strength whereas the elongation-at-break continuously increased up to 15 percent rubber inclusion in the blend. The tensile modulus of the cured blend samples increased up to 9 percent HTPB inclusion in the blend and decreased thereafter. This might occur due to increase in the crosslink density, up to 9 percent HTPB inclusion, which could result from the proposed side reactions in the modification procedure, of hydroxyl group of epoxy resin with the isocyanate group of TDI forming a urethane linkage. The other isocyanate group of the TDI molecule might have got linked to another epoxy molecules either through an oxazolidone formation (in case the epoxy has reacted with the -NCO) or through urethane linkage (in case -OH of the epoxy had reacted with the -NCO). The data related to variation of HTPB inclusion, in the modified novolac epoxy, on impact strength has been presented in Table 2. It is evident from the table that the impact strength of blend samples, initially, increased to value of 6.9 Jm<sup>-2</sup> (refer Table 2) for blend sample IEN9. Merely, 3 percent HTPB inclusion increased the value of impact strength to about 38 percent of blend sample IEN0.

Figs. 6 and 7 showed the dynamic thermograms of blend of modified epoxidized phenolic novolac resin (IEN0), without or with 9 wt% HTPB inclusion, respectively.

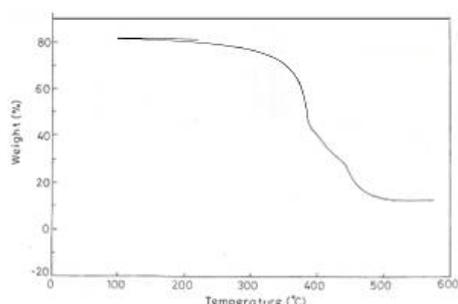


Fig. 6. : TGA trace of blend sample IEN0

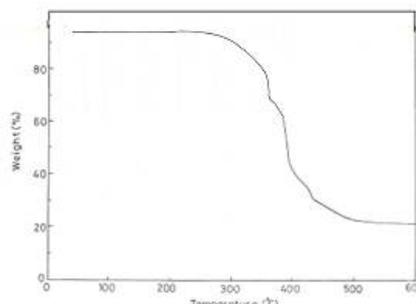


Fig. 7. : TGA trace of blend sample IEN9

Table 3 presented the initial degradation temperature (IDT), degradation temperature for 50 percent weight loss (DT<sub>50</sub>), final degradation temperature (FDT) and percent char yield for blend samples. From Table 3, it is observed that the value of IDT of blend sample without dilution with epoxy resin i.e., sample IEN0, has been found to be 260°C whereas the value of IDT for blend sample containing 9 wt% HTPB (sample IEN9) was found to be 275°C. The initial degradation temperatures (IDTs), a measure of thermal stability, increased with the inclusion of HTPB in the blend systems. Therefore, the thermal stability was improved by incorporating HTPB in the blends.

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**Table 3. :** Summary of the results obtained from TG-thermograms for thermal decomposition of blends samples with and without dilution with epoxidized novolac resins

Sample Code	IDT <sup>a</sup> (°C)	DT <sub>50</sub> <sup>b</sup>	FDT <sup>c</sup> (°C)	CY <sup>d</sup> (%)
IE <sub>ND</sub>	260	412	537	25.8
IE <sub>9</sub>	275	391	525	18.0

<sup>a</sup>Initial degradation temperature.  
<sup>b</sup>Degradation temperature for 50 percent weight loss.  
<sup>c</sup>Final degradation temperature, <sup>d</sup>Char yield.

## IV. CONCLUSIONS

The structures of the synthesized novolacs, epoxidised novolacs and their blends with HTPB have been ascertained on the basis of the appearance of various functional groups in their native region through FTIR spectroscopic analysis. There occurred a very little variation in cure times with HTPB concentration in the blend. The least cure time was observed with blend sample containing 9 wt% HTPB in the blend sample. This can be attributed to the fact that the rate of formation crosslink networks. Tensile strength showed a changing behavior beyond 9 percent HTPB inclusion in the blend samples series prepared from phenolic novolac whereas the elongation-at-break continuously increased up to 15 percent rubber inclusion in the blend. This might occur due to increase in the crosslink density, up to 9 percent HTPB inclusion, which could result from the proposed side reactions in the modification procedure, of hydroxyl group of epoxy resin with the isocyanate group of TDI forming a urethane linkage. The other isocyanate group of the TDI molecule might have got linked to another epoxy molecules either through an oxazolidone formation (in case the epoxy has reacted with the -NCO) or through urethane linkage (in case -OH of the epoxy had reacted with the -NCO). It may be concluded that the variation flexural modulus and flexural strength was opposite with HTPB inclusion. Finally, the thermal stability was improved by incorporating HTPB in the blends.

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