

Mechanical and Thermal Properties of Chemically Modified Epoxy Resin

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ABSTRACT

Diglycidyl ether of bisphenol-A (DGEBA), having number average molecular weight (M_n) 375, was modified by incorporating the hydroxyl terminated polybutadiene (HTPB) based prepolymer using isophorone diisocyanate as a coupling agent. To increase the compatibility between the epoxy resin and HTPB part, polar groups were introduced in the later to achieve physical and chemical interactions between the two phases. The finally modified DGEBA system was cured with amine based hardener. FTIR and $^1\text{H-NMR}$ were used to monitor the whole modification procedure. The rubber particles size and distribution was monitored as a function of HTPB contents in the resin system using scanning electron microscopy (SEM). The mechanical, thermal and thermo-mechanical properties have shown that the tensile strength, toughness, ductility and impact strength of the modified cured system have been successfully increased at some optimum HTPB contents without affecting the inherent thermal and thermo-mechanical stability associated with DGEBA resin system. Some of the mechanical properties like flexural modulus, tensile modulus and compressive strength decreased with increasing rubber contents.

Keywords: DGEBA; HTPB; Impact Strength; Thermo-Mechanical; Mechanics Properties

1. Introduction

Thermo set resins form a rigid network which is dimensionally stable under many conditions, having good chemical and thermal resistance. As a result these polymers are very important engineering materials, accounting for nearly 20% of the polymer market, including use in composites, coatings and adhesive applications [1-3]. Epoxy resins are thermo sets with extraordinary adhesion accompanied by simple cures, good strength, creep resistance, heat tolerance, chemical durability and relatively low shrinkage. Adversely, these polymers are also brittle and have a high degree of cross linking. Toughening epoxy resins would allow them to be used in many additional applications including structural applications [3].

Toughening of thermosetting polymers can also be accomplished by adding a flexibilizer to the thermo set. Adding a flexibilizer will indeed increase the toughness, but it results in adverse effect such as lowering of the glass transition temperature (T_g) and modulus. Another method of toughness is inclusion of rubber particles into the primary phase. The secondary rubber can improve the impact strength without loss in polymer other properties [4].

Epoxy resins are frequently modified by dissolving in

a small proportion (10% - 20%) of a liquid rubber containing reactive end groups such as carboxyl-terminated acrylonitrile copolymer (CTBN) [5] and amine-terminated butadiene acrylonitrile copolymer (ATBN) [6]. Although CTBN and ATBN oligomers are very efficient in improving the fracture properties of epoxy resins but make the resultant material thermally unstable.

To avoid deterioration in the inherent stiffness and strength and a reduction in the glass-transition temperature of the resin, some engineering plastics, such as poly ether sulphone (PES) [7] and poly ether imide [8,9] have been used to produce systems containing rigid, ductile particles dispersed in epoxy resin. Particles of crystalline polymers, such as poly vinylidene fluoride (PVDF), poly butylenes terephthalate (PBT) and nylon 6 has been used for the toughening of an aromatic amine cured epoxy resin. It has been reported that nylon 6 and PVDF toughened epoxy resins to an extent similar to that of CTBN. The fracture toughness, however, was increased two fold by the inclusion of PBT over that achieved with nylon 6 and PVDF [10].

It has been reported that both poly ether ether ketone (PEEK) and PBT could form crystals in the form of triblock copolymers with amorphous PES. The most effective modifier for increasing toughness appeared to be the triblock PEEK-PES-PEEK system, which gave an almost

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single-phase structure [11]. Various carboxyl-terminated elastomeric acrylate oligomers have been used to toughen a DGEBA resin. Acrylate oligomers exhibited extremely good miscibility with conventional epoxy resins and cured castings exhibited enhancements in impact strength comparable to those of traditionally toughened epoxy systems. A different approach has been taken [12] to synthesize two polymers, one of which formed a network by simultaneous independent reactions in the same container. Intercross linking reactions were eliminated by the combination of free-radical (acrylate) and condensation (epoxy) polymerization. The mechanical properties of the resultant system improved when the extent of molecular mixing was minimized and hetero phase semi-interpenetrating polymer networks (semi-IPNs) were produced. Similar observations were reported in the work concerning the production of heterogeneous interpenetrating polymer networks (IPNs) of poly methyl methacrylate within a poly dimethyl siloxane elastomer [13].

Recently, epoxy resin acrylated polyurethane semi-IPNs [14] were synthesized that were compatible and sufficiently flexible. A great deal of literature has been devoted to the toughening of epoxy resins via polyurethane incorporation as a secondary phase in a specific matrix to form a grafted or un-grafted IPN [15-17]. Siloxane elastomers [18] have also been used as attractive alternatives to traditional toughening systems. For example, the addition of room temperature vulcanized (RTV) silicon rubber in amount up to two times that of the unmodified resin has been reported. Although some of these oligomers are quite expensive, these oligomers are immiscible in the resin systems and tend to migrate to the outside. To resolve this problem, epoxy resin has been chemically modified with functionally terminated poly dimethyl siloxane and poly dimethyl-co-diphenyl siloxane oligomers [19].

Rubber modification of bifunctional and tetrafunctional epoxy matrices by means of block co-polymer of poly dimethyl siloxane and poly oxyethylene elastomer or an anhydride-grafted polybutene [20] improved the impact strength for bifunctional epoxy systems but failed for tetrafunctional epoxy resin systems.

Within this framework, the main objective of the present work is to toughen epoxy resins by chemically incorporating hydroxyl terminated poly butadiene (HTPB) into the backbone of epoxy resin and its characterization. Different ratio by weight of epoxy terminated HTPB based prepolymer was used as a reactive modifier and its effect on the particle morphology, impact strength, toughness, flexibility and other mechanical, thermal and thermo-mechanical properties of the final system was studied.

2. Experimental

2.1. Materials and Preparation of Epoxy Terminated Htpb Based Prepolymer

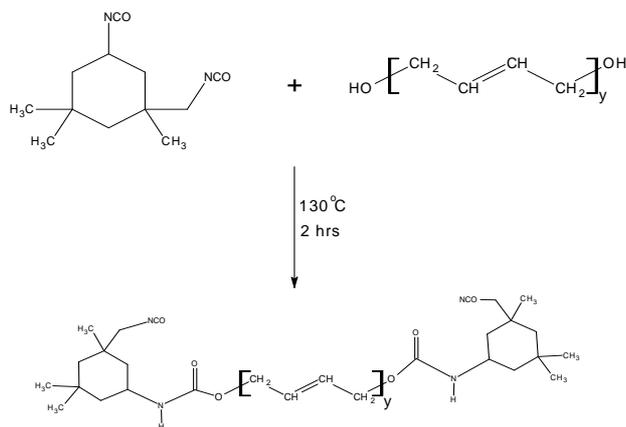
The epoxy resin synthesized in our lab was a diglycidyl ether of bisphenol-A (DGEBA) with an epoxy equivalent weight of 194g/eq. and M_n of 375 g/mol. Hydroxyl terminated polybutadiene (HTPB, supplied by Aldrich) with M_n 2800 (M_n stands for number average molecular weight of the polymer and does not have units) and OH content of 0.72 m eq./g was used as a rubber modifier. Isophorone diisocyanate (IPDI, with 99% purity, supplied by Sigma) was used as a coupling agent between epoxy resin and HTPB.

N-(3-dimethylaminopropyl)-1,3-propylene diamine (Araldite 2011B, supplied by Ciba-Giegy) was used as a hardener. Tetrabutyl ammonium chloride (TBAC, supplied by BDH, 98%) was used as a catalyst for the reaction between epoxide and isocyanate groups.

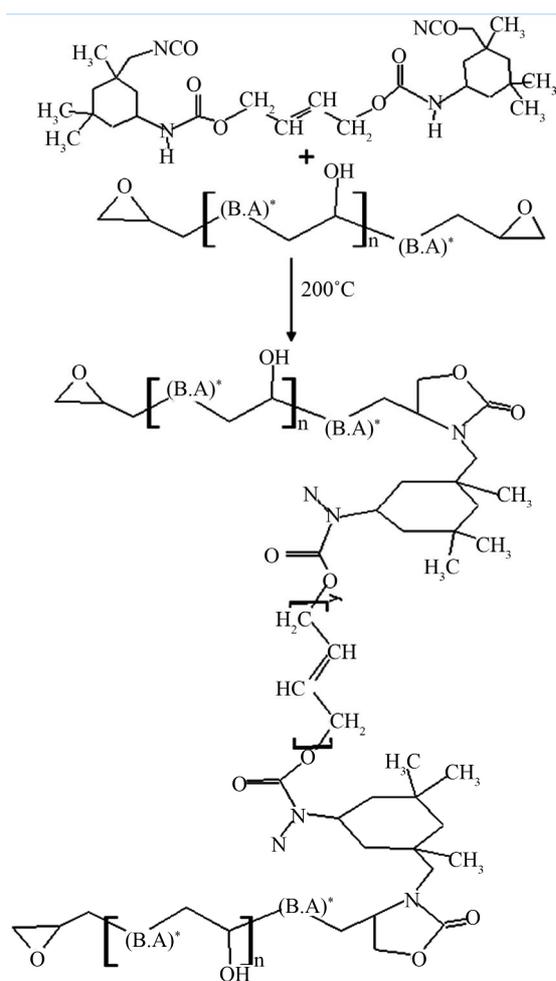
In the first step of reaction, IPDI and HTPB were charged in 1L reaction kettle. The mixture was continuously stirred while the temperature was raised to 130°C that was kept constant for two hr under nitrogen atmosphere. The hydroxyl group of HTPB reacted with the -NCO group of IPDI to produce a urethane linkage (see **Scheme 1**). Unreacted -NCO groups were titrimetrically determined. After a series of experiments using different molar ratios of HTPB with IPDI, it was found that 53% of -NCO groups remain unreacted when 16 g (0.072 moles) of IPDI was mixed with 84 g (0.04 moles) of HTPB. In the second step of reaction, a small amount (5 g) of tetra butyl ammonium iodide was added into 750 g of DGEBA epoxy resin as a catalyst, which was mixed at 145°C ± 5°C. Then the temperature was raised to 200°C while vigorously stirring the mixture for 30 min. This results in the reaction between the epoxide group of DGEBA and the NCO group of IPDI-HTPB based telechelic polymer to form epoxy-terminated HTPB-based prepolymer (ETHTPB) with number average molecular weight (M_n) of 3553 as determined by vapour pressure osmometry (see **Scheme 2**). ETHTPB prepolymer was further diluted with different amount of DGEBA epoxy resin to get various concentrations on the basis of HTPB part of the polymer. For 0.1%, 0.3%, 0.7%, 1.0%, 1.5% and 2.0% the amount of ETHTPB prepolymer added per 100 g of resin was 100 mg, 300 mg, 700 mg, 10 mg, 15 mg and 20 mg respectively. Finally curing agent, N-(3-dimethylaminopropyl)-1,3-propylene diamine, was added into the mixture at a weight ratio of 100:100, followed by curing at 120°C for 10 hrs.

2.2. Measurements

FTIR and H^1NMR (300 MHz) were used in the whole process to monitor the reaction product while free NCO



Scheme 1. Synthesis of IPDI-HTPB-IPDI telechelic polymer.



Scheme 2. Reaction between telechelic polymer and DGEBA to synthesize prepolymer.

groups were determined by the usual chemical titration method. FTIR spectra were obtained using Thermo Electron Corporation IR 200 FT-IR spectrometer. All FTIR analysis were carried out in the range of 400 - 4000 cm^{-1}

using KBr pellets and CDCl_3 was used as a solvent during $^1\text{H-NMR}$ analysis. The microstructure of diamond-poxy nanocomposites was observed under scanning electron microscope (SEM, JED 2300). SEM was performed on the fractured surfaces after dipping the sample into liquid N_2 to make the material more brittle. Fractured surfaces were sputtered with gold and all the measurements were done using 10 kV voltage electron beam. Many important mechanical properties were also investigated including The Izod impact strength was measured using 64 mm long, 12.7 mm wide and 6.4 mm thick specimens on a pendulum impact testing machine according to the specification, ASTM D 256. The depth under the notch of a specimen is 10.2 mm. Drop height of pendulum was kept 1.46 meter with a striking velocity of 5.35 m/s. Tensile, flexural and compressive properties were measured using a universal testing machine, (Tometric, UK), at room temperature at a cross head speed of 5 mm/min, according to the specifications, ASTM 638 - 52, D-790, D-695, respectively. The Vickers hardness number (VHN) was calculated using micro-hardness testing instrument manufactured by M/s. Frank, UK. For hardness measurement at ambient conditions, films of uniform thickness (0.8 - 1.0 mm) were used. The hardness of a material was measured by forcing an indenter into the surface of the film with a constant speed. A force of 2.94N was applied slowly by pressing the indenter at 90° into the material surface being tested. The indenter material, in the form of square based pyramid made up of diamond was used for indentation. The indentation time was kept fixed (*i.e.* 30 seconds) for all samples. An empirical hardness number was then calculated by measuring the length of the diagonal through microscope attached with the instrument. To evaluate the effects of HTPB contents on the degradation behaviour of modified epoxies at various temperatures, thermogravimetric analysis was conducted on a Perkin Elmer Diamond TGA/DTA machine at a heating rate of $10^\circ\text{C}/\text{min}$. The dynamic mechanical thermal analysis measurements were performed in a temperature range of 50°C - 300°C using Perkin Elmer Diamond DTMA at a heating rate of $2^\circ\text{C}/\text{min}$ and at a frequency of 1Hz.

3. Results and Discussion

3.1. IPDI-HTPB-IPDI Telechelic Polymer

In the first step of modification process, *i.e.* the IPDI was always taken in excess of the equimolar ratio between NCO groups of IPDI and OH groups of HTPB. The concentration of IPDI studied was 16%, 20%, 24% and 32% w/w with respect to HTPB which correspond to 2:1; 2.5:1; 3.0:1 and 4.0:1 moles of NCO groups per mole of OH groups in IPDI and HTPB, respectively. The molar ratio 2:1 (16% w/w of IPDI with respect to HTPB) was

considered ideal as it could leave one NCO group free to react with one epoxide group of epoxy resin, in the second step of reaction. The peak in the FTIR spectrum appeared at 1720 cm^{-1} indicates the formation of urethane linkage between HTPB and IPDI, **Figure 1**. The peak due to unreacted NCO's is also present at 2260 cm^{-1} , while in $^1\text{H-NMR}$ the NH proton of urethane linkage appeared at δ 7.5 ppm and a doublet appeared at δ 2.9 ppm due to four protons in 2 CH_2 attached to nitrogen.

3.2. Epoxy Terminated HTPB Based Prepolymer

In the second steps i.e. the reaction of unreacted isocyanate groups of IPDI-HTPB-IPDI telechelic polymer with the epoxide groups of DGEBA results in the formation of oxazolidone linkage. The characteristic peak of carbonyl group appeared at 1749 cm^{-1} and 1723 cm^{-1} in FTIR spectrum due to oxazolidone and urethane linkage, respectively as shown in **Figure 1(b)**. The band appearing at 1456 cm^{-1} is attributed to the C-N linkage in oxazolidone. No peak appeared in FTIR spectrum at 2260 cm^{-1} corresponding to NCO's antisymmetric stretching indicating the completion of the reaction. While in $^1\text{H-NMR}$ the doublet at δ 4.19 ppm and multiplet at δ 5.70 ppm appeared due to four protons of 2CH_2 and two protons of 2CH in oxazolidone ring, respectively. While the formation of two tertiary nitrogen were confirmed by the appearance of multiplet at δ 3.58 ppm by the 2CH proton attached to tertiary nitrogen. The peaks observed at 967 cm^{-1} and 913 cm^{-1} are attributed to the stretching and bending vibration of cyclo-oxirane in FTIR spectrum.

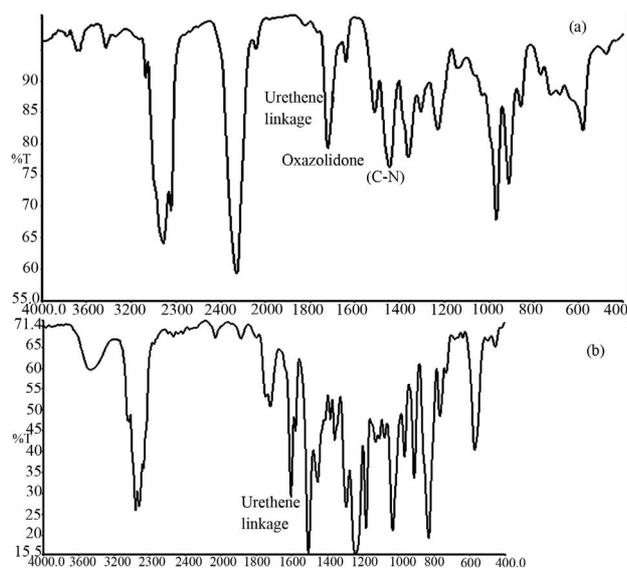


Figure 1. FTIR spectra of (a) IPDI-HTPB-IPDI telechelic polymer in transmission mode, (b) epoxy terminated HTPB based prepolymer.

SEM micrographs of the fractured surface of modified epoxy-amine system having different proportion of HTPB rubber i.e. 0.3 wt%, 0.7 wt%, 1.0 wt% and 2.0 wt% are shown in **Figures 2(A)-(D)**. The elastomer appeared as distinct particles in epoxy-amine network. These rubber particles were clearly observed to be homogeneously dispersed in the epoxy-amine matrix. The diameter of the particles was in the range of $0.2\text{ }\mu\text{m}$ to $2.6\text{ }\mu\text{m}$. Although boundaries were not very sharp but still the particles appeared as distinct constituents with separate boundaries, which confirmed that there was less chemical interaction between the two constituents. The diffused nature of the boundaries observed in the micrograph may be due to the physical interaction (hydrogen bonding etc.) between the two phases. It means that the polar groups that had been inserted in the rubber chains i.e., epoxide groups, -OH-groups and NCO-groups make the prepolymer compatible to large extent with the matrix creating physical interaction that assist the homogeneous distribution of rubber particles. Due to the presence of terminal epoxide group most of the prepolymer could become the part of the main polymer chains decreasing the number of distinct particles that could be expected, especially at lower concentration of prepolymer. According to the SEM results, the particle size increased with the increase of rubber contents in the matrix as shown in **Figure 3**. Initially the effect of elastomer concentration on the particle size was very small but after 0.7 wt% there was a steep incline suggesting that the rubber particles agglomerate when its concentration exceeded certain value and had pronounced effect on particle diameter.

3.3. Mechanical Properties

One of the reasons behind modifying epoxy-amine material was to improve its impact strength. Impact strength of neat epoxy-amine polymer was 2.3 kJ/m which was doubled by modifying the system with HTPB contents as shown in **Figure 4** (rectangular symbols). Impact strength was observed to increase linearly with increasing HTPB concentration up to 1.0%. At 1.0% HTPB contents the value of impact strength was found to be 4.23 kJ/m . Beyond 1.0% of HTPB the impact strength remained almost constant with a very little deviation and reached to 4.5 kJ/m when 2.0% HTPB contents were incorporated to the system. Same effect has been observed in the material prepared with an epoxy resin modified with hydroxyl terminated poly(butadiene-acrylonitrile) by Sankaran and Chandas [21].

To evaluate the hardness property, microhardness measurement were performed on both unmodified and modified samples at 25°C , using Vickers microhardness indentation. Hardness of modified system was also found

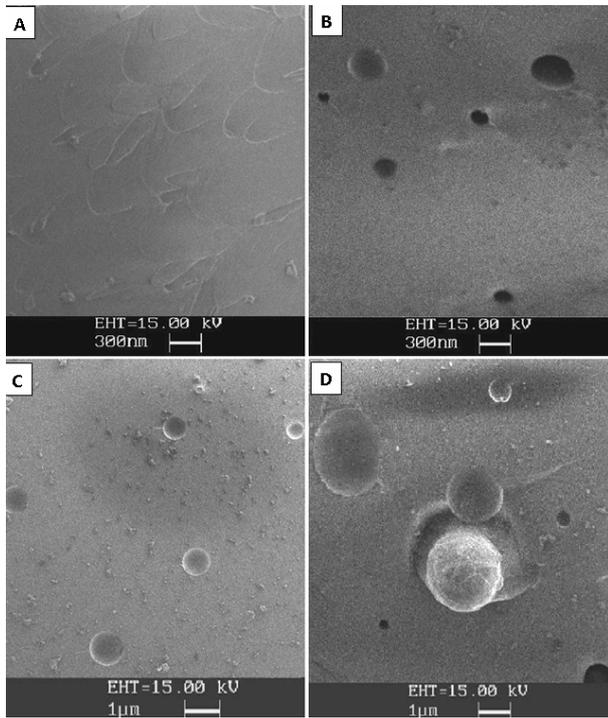


Figure 2. SEM micrograph of (A) 0.3% (B) 0.7% (C) 1.0% (D) 2.0% HTPB modified cured epoxy-amine system.

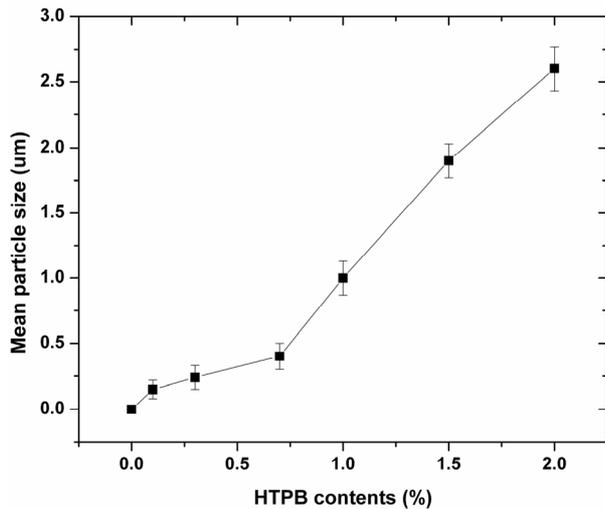


Figure 3. Mean particle size as a function of HTPB concentration in the epoxy-amine system.

to be decreased due to the incorporation of soft prepolymer contents. Vicker's hardness number decreased from 13.9 to 2.7 from neat system to 2.0% modified system as shown in **Figure 4** with circular symbols.

The tensile properties like fracture strength, Young's modulus, and elongation at break were calculated as shown in **Figure 5**. Fracture strength of unmodified system observed in case of neat system is 31.72 MPa (**Figure 5(a)** shown with colour square symbol). This low strength value of epoxy-amine system is due to the in-

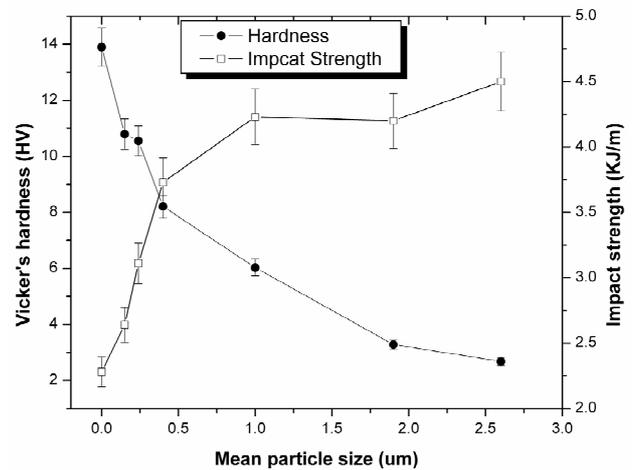


Figure 4. Vicker's hardness and Impact strength as a function of HTPB concentration in the modified epoxy-amine system.

herent brittleness of the system. The fracture strength of the system was increased by the addition of prepolymer. Maximum values *i.e.*, 42 - 44 MPa were achieved when 0.3% - 1.0% HTPB was incorporated into the epoxy-amine system. It can be attributed to the increase in fracture energy and resistance to the crack propagation when flexible HTPB parts are introduced to the brittle system. Beyond 1.0% addition of HTPB adversely affects the fracture strength of the resulting system, because HTPB itself is low strength material. As the percentage of rubbery segment increases the resulting material acquires intermediate properties of both the components resulting in the decrease in ultimate strength of the material. Young's modulus also showed a decrease with increase in HTPB contents ((**Figure 5(a)** shown with blank square symbol). However initially the addition of only 0.1% of HTPB in the system lowered its tensile modulus by about 700 MPa. Further addition of HTPB has very insignificant effect on the Young's modulus of the system. The ductility of the material was found to be increased by increasing rubber contents in the resulting material. The tensile elongation of unmodified epoxy-amine system was 1.7% at break (**Figure 5(b)**). Up to 0.3% HTPB concentration there was a steep incline in the ductility where the ductility reached to 5.5% with 0.3% HTPB incorporation. Beyond 0.3% to 2.0% HTPB contents the increase in ductility of material was comparatively slow and the final ductility of material reached to 8.7% before the failure of material by the applied pulling force. HTPB based flexible pre polymer in the main chain are probably responsible for increase in the ductility of the resulting material by reducing the cross-linking density and facilitating the chains to slide-pass each other. Rubber contents removed the inherent brittleness thus resisting the crack initiation with the applied external force, while

initial strength of the material was decreased. Rubber particles that were weakly bonded to the epoxy-amine system started agglomerating at high concentration of prepolymer, as supported by SEM results, which increased the ductility but decreased the modulus and tensile strength of the material.

Flexural properties of the material were determined by applying force in 3-point bending mode. The flexural strength and flexural modulus of the system was found to be decreased as rubber content in the modified system was gradually incorporated, as shown in **Figure 5(c)**. Similar results have been obtained by C. Kaynak and coworkers [22]. The value of flexural modulus in elastic region was always smaller than tensile modulus for any concentration of HTPB in epoxy-amine system. It suggests that the deformation produced in modified or unmodified material is greater in 3-point bending mode than tensile mode.

Compressive strength measure the ability of material to resist the crushing force. When a compressive force was applied on the sample the material bulged out from sides and adopted a barrel shape with cracks on sides as shown in **Figure 6(b)**. Compressive strength also decreased linearly with increase in HTPB contents as shown in **Figure 6(a)**. Compressive strength of unmodified epoxy-amine system was observed to be 132.3 MPa which decreased by 54 MPa by incorporating 2.0 % HTPB contents in the system. The decrease in compressive strength can be attributed to the decrease in crosslink density and increase in flexible aliphatic character in resulting modified epoxy-amine system.

3.4. Thermo-Mechanical Properties

The general trend of pyrolysis for all the samples including unmodified system are similar showing one step degradation starting with the weight loss from about 300°C upto about 500°C (**Figure 7(a)**). It was indicated that the mechanical performance has been improved by adding elastomer or rubber, but it has no adverse effect on the inherent thermal stability of the epoxy-amine thermo set resin. This can be attributed to the fact that the thermally less stable rubber contents are very small in quantity as compared to the matrix system to affect its thermal stability and secondly the rubber contents might have been well masked by the network of thermally stable epoxy-amine network. There were very small changes in percent weight loss at various temperatures with increasing rubber contents. The variation in thermal stability at higher temperatures can not be correlated with increasing rubber contents. The maximum rate of decomposition (T_{max}) calculated from the peak of the differential of the TGA curve and char content for each formulation of un-

modified and modified system was also calculated as shown in **Table 1**.

Glass transition temperature (T_g) was calculated from the peak of $\tan\delta$ curve (**Figure 7b**) during DTMA analysis

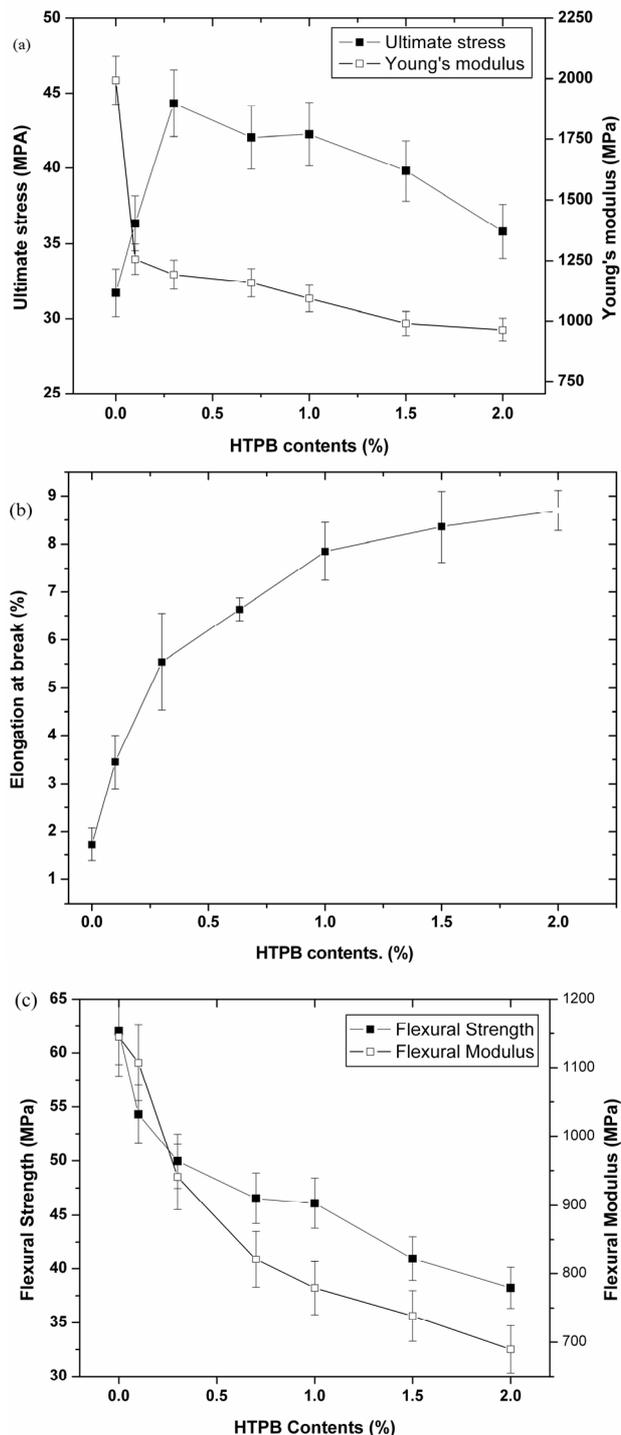


Figure 5. Variation in (a) ultimate stress and Young's modulus, (b) elongation at break, and (c) Flexural strength and Flexural modulus with increase in HTPB content in epoxy-amine system during tensile test.

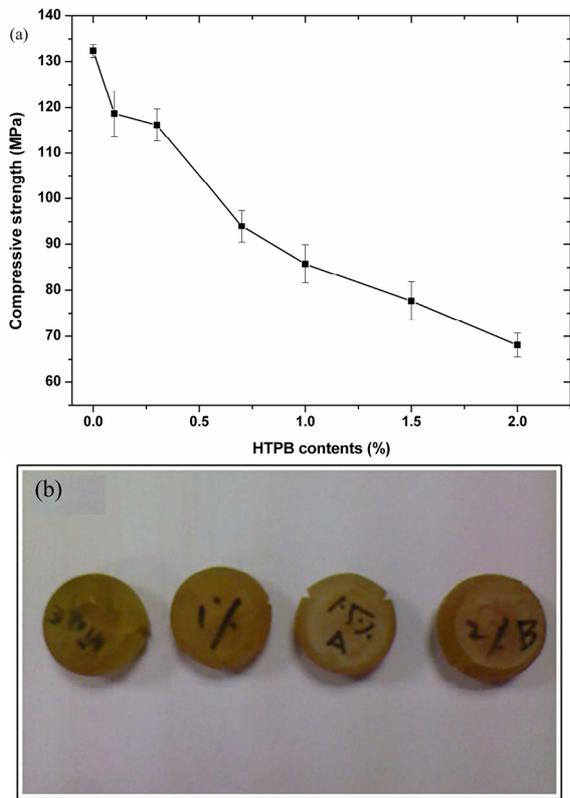


Figure 6. (a) Compressive strength as a function of HTPB in the epoxy-amine system; (b) Samples after compressive testing become barrel shaped with visible large cracks on sides.

Table 1. Maximum decomposition temperature, T_{max} , and char portion at 700°C for HTPB modified and unmodified systems.

| Sample ID | T_{max} (°C) | Char Portion (%) |
|-----------|----------------|------------------|
| Neat | 375.0 | 4.31 |
| 0.1% | 369.2 | 4.10 |
| 0.3% | 370.0 | 4.01 |
| 0.7% | 370.1 | 3.59 |
| 1.0% | 370.0 | 4.05 |
| 1.5% | 370.0 | 4.01 |
| 2.0% | 368.5 | 2.15 |

as shown in Figure 7(c). T_g of 2% HTPB modified system is about 6°C lower as compared to the unmodified system and T_g was observed to be inversely related with HTPB concentration in the modified epoxy-amine system, Figure 7(c). This could be explained by taking into account the free volume concept. However there is a very small change in the glass transition temperature at various rubber concentrations in the modified. From thermal and thermo-mechanical data it is inferred that improved mechanical properties can be achieved by modifying the system with HTPB based elastomer without having sig-

nificant effect on the thermal and thermo-mechanical properties of epoxy-amine system.

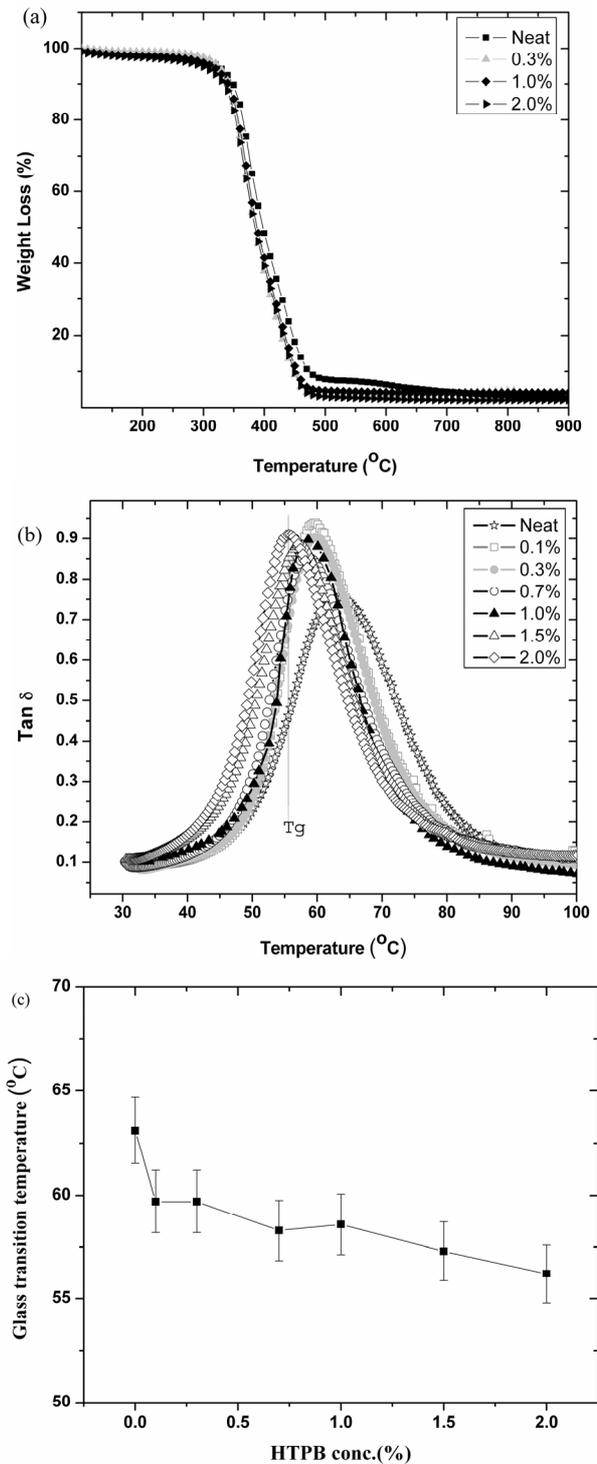


Figure 7. (a) Thermogravimetric curves showing the thermal stability of the modified epoxy-amine systems containing different HTPB concentrations; (b) $\tan \delta$ curves of the modified epoxy-amine systems containing different HTPB concentrations; (c) Glass transition temperatures (T_g) from $\tan \delta$ maxima as a function of HTPB conc. as determined by DMTA at frequency 1Hz.

4. Conclusion

The toughening of epoxy resin, DGEBA, with hydroxyl-terminated polybutadiene (HTPB) was success fully conducted. A chemical linkage between the elastomer and resin was developed by employing isophorone diisocyanate (IPDI) as a coupling agent to synthesize epoxy terminated HTPB based prepolymer. Test results showed increases in some of the important mechanical properties like toughness and impact strength by 100% with only 1% - 2% HTPB concentration. Other mechanical properties like flexural strength, flexural modulus, stiffness, and compressive strength decrease linearly with increasing rubber concentration. The toughening of epoxy resin, DGEBA, with hydroxyl-terminated polybutadiene (HTPB) was success fully conducted. A chemical linkage between the elastomer and resin was developed by employing isophorone diisocyanate (IPDI) as a coupling agent to synthesize epoxy terminated HTPB based prepolymer.

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REFERENCES

- [1] E. W. Crandall and W. Mih, "Chemorheology of Thermosetting Polymers," American Chemical Society, Washington DC, 1983.
- [2] G. Odian, "Principles of Polymerization," 3rd Edition, John Wiley & Sons, New York, 1991.
- [3] J. R. Fried, "Polymer Science and Technology", Prentice Hall, Upper Saddle River, 1995.
- [4] F. J. McGarry, "Rubber in Crosslinked Glassy Polymers," *Proceedings from ACS Rubber Division 129th Meeting*, Paper No. 86. 1986.
- [5] Y. Huang, *et al.* "Mechanisms of Toughening Thermoset Resins," *Advances in Chemistry*, Vol. 233, 1993, pp. 1-35.
- [6] F. J. McGarry and A. M. Willner, "Toughening of an Epoxy Resin," Wiley Interscience, New York, 1968.
- [7] S. C. Kunz, J. A. Sayre and R. A. Assink, "Morphology and Toughness Characterization of Epoxy Resins Modified with Amine and Carboxyl Terminated Rubbers," *Polymer*, Vol. 23, 1982, pp. 1897-1906.
- [8] R. S. Raghava, *Proceedings of the 28th National AMPLE Conference*, Azusa, 1983, 367.
- [9] C. B. Bucknall and I. K. Partridge, "Phase Separation in Epoxy Resins Containing Polyethersulphone," *Polymer*, Vol. 24, No. 5, 1983, pp. 639-644.
[doi:10.1016/0032-3861\(83\)90120-9](https://doi.org/10.1016/0032-3861(83)90120-9)
- [10] A. H. Gilbert and C. B. Bucknall, "Epoxy Resins Toughened With Thermoplastic," *Makromolekulare Chemie. Macromolecular Symposia*, Vol. 45, No. 1, 289, 1991, pp. 289-298.
- [11] J. K. Kim and R. E. Robertson, "Toughening of Thermoset Polymers by Rigid Crystalline Particles," *Journal of Materials Science*, Vol. 27, No. 1, 1992, pp. 161-174.
[doi:10.1007/BF02403659](https://doi.org/10.1007/BF02403659)
- [12] A. K. Banthia, P. N. Chaturvdi, V. Jha and V. N. S. Pendyala, "Rubber Toughened Plastics," American Chemical Society, Washington DC, 1989.
- [13] R. E. Tonghsaent, D. A. Thomas and L. H. Sperling, "Toughness and Brittleness of Plastics," American Chemical Society, Washington DC, 1976.
- [14] L. H. Spelling and H. D. Sarge, "Joined and Sequential Interpenetrating Polymer Networks Based on Poly (dimethylsiloxane)," *Journal of Applied Polymer Science*, Vol. 16, No. 11, 1972, pp. 3041-3046.
[doi:10.1002/app.1972.070161128](https://doi.org/10.1002/app.1972.070161128)
- [15] R. K. Samal, B. K. Senapati and T. B. Behuray, "Synthesis and Characterization of Some Novel Copolymer Resins III," *Journal of Applied Polymer Science*, Vol. 68, No. 13, 1998, pp. 2183-2187.
[doi:10.1002/\(SICI\)1097-4628\(19980627\)68:13<2183::AID-APP15>3.0.CO;2-0](https://doi.org/10.1002/(SICI)1097-4628(19980627)68:13<2183::AID-APP15>3.0.CO;2-0)
- [16] H. H. Wang and J. C. Chen, "Modified Diglycidyl Ether of Bisphenol A with Modification of Matrix Resin Networks with Engineering Thermoplastics," *Polymer Engineering & Science*, Vol. 35, No. 18, 1995, pp. 1468-1475.
[doi:10.1002/pen.760351807](https://doi.org/10.1002/pen.760351807)
- [17] H. Harani, S. Fellahi and M. Baker, "Toughening of Epoxy Resin Using Synthesized Polyurethane Prepolymer Based on Hydroxyl-Terminated Polyesters," *Journal of Applied Polymer Science*, Vol. 70, No. 13, 1998, pp. 2603-2618.
[doi:10.1002/\(SICI\)1097-4628\(19981226\)70:13<2603::AID-APP6>3.0.CO;2-4](https://doi.org/10.1002/(SICI)1097-4628(19981226)70:13<2603::AID-APP6>3.0.CO;2-4)
- [18] H. H. Wang and J. C. Chen, "Toughening of Epoxy Resin by Functional-Terminated Polyurethanes and/or Semicrystalline Polymer Powders," *Journal of Applied Polymer Science*, Vol. 82, No. 12, 2000, pp. 2903-2912.
- [19] E. L. Warrick, O. R. Piece, K. E. Polmanteer and J. C. Saam, "The Influence of Fumed Silica Properties on the Processing, Curing, and Reinforcement Properties of Silicone Rubber," *Rubber Chemistry and Technology*, Vol. 52, 1974, 937.
- [20] E. M. Yorkgitis, N. S. Eiss, G. Zhilkes and J. E. McGrawth, "Siloxane-Modified Epoxy Resins," *Epoxy Resins and Composites I*, Vol. 72, 1985, pp. 79-109.
[doi:10.1007/3-540-15546-5_4](https://doi.org/10.1007/3-540-15546-5_4)
- [21] S. Sankaran and M. Chanda, "Chemical Toughening of Epoxies. I. Structural Modification of Epoxy Resins by Reaction with Hydroxy-Terminated Poly (Butadiene-co-Acrylonitrile)," *Journal of Applied Polymer Science*, Vol. 39, No. 7, 1990, pp. 1459-1466.
[doi:10.1002/app.1990.070390704](https://doi.org/10.1002/app.1990.070390704)
- [22] C. Kaynak, A. Ozturk and T. Tincer, "Flexibility Improvement of Epoxy Resin by Liquid Rubber Modification," *Polymer International*, Vol. 51, No. 9, 2002, pp. 749-156.