Mechanical properties of multifunctional epoxy resin/glass fiber reinforced composites modified with poly(ether-imide)

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ABSTRACT

In the present paper effect of thermoplastic on various mechanical and thermal properties of multifunctional epoxy resin have been studied. Epoxy phenol novolac resin has been cured with hardner diamino, diphenyl sulfone. Changes in mechanical and thermal properties of epoxy phenol novolac resin with engineering thermoplastic poly (ether imide) have been investigated. Specimens were prepared using different mixing orders for multifunctional epoxy resin with poly (ether imide). Effect on glass transition temperature (Tg) were observed by using DSC measurements. Variation in mechanical properties viz. Tensile strength, flexural strength, flexural modulus, interlaminar shear strength and impact strength have been observed. With the thermoplastic modification of thermoset matrix material, improvement in mechanical properties of epoxy-glass fiber reinforced composites have been expected. Changes in storage modulus and loss modulus of all specimens were also evaluated by dynamic mechanical analysis (DMA). Scanning electron microscopy (SEM) was used to investigate the relationship between the morphological study of the fractured epoxy resins and mechanical properties of the modified epoxy resins and glass fiber reinforced composites. If the polymer matrix is fairly brittle (unmodified epoxy), there may be a corresponding reduction in mechanical properties. Incorporation of engineering thermoplastic Poly (ether-imide) has resulted in improvement of above stated mechanical properties. All results indicated that thermoplastic modified multifunctional epoxy resin proved to be a good matrix material which enhances the mechanical properties of glass fiber reinforced composites. Copyright © 2013 VBRI press.

Keywords: Composites; mechanical properties; polymer blends; thermoplastics; thermosets.

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Introduction

Epoxy resins are relatively low molecular weight pre polymers capable of being processed under a variety of conditions. The most frequently used epoxy resin types are bifunctional resin based on diglycidyl ether of bisphenol-A (DGEBA). However, the increment of the resin functionality has resulted in a new group of materials with improved properties regarding bifunctional resin. Multifunctional resins are characterized by a functionality degree between 3 and 5 which provides high crosslink density and higher glass transition temperature as well as improvements in the mechanical, physical and adhesive properties [1]. Well balanced multifunctional epoxy resins, which retain high modulus and high strength at relatively high temperatures, make the material suitable for these applications. However, these resins have the major drawback of brittleness, due to their tightly crosslinked structure. Multifunctional epoxy-novolac resins were commercialized in late 1950's. Better chemical resistance and heat distortion temperature are obtained with these resins. Extensive development has taken place with epoxy phenol novolacs in terms of quality improvement and reduction of ionic and chlorohydrin impurities for applications in electronic markets. Epoxy phenol novolc (EPN) resins have commercial importance. It is made by epoxidation of phenol formaldehyde condensates (novolacs) obtained from acid catalyzed condensation of phenol and formaldehyde [2]. However, these resins have a major drawback of brittleness, due to their tightly crosslinked structure. Moreover, low toughness and brittle behavior limit the use of epoxy resin for some critical areas. The use of high performance thermoplastics to modify thermosets has emerged as an alternative to avoid classical compromises between toughness and thermal stability associated with rubber toughening [3-6]. Some industries, notably the aerospace industry have growing demands for composite material that display both high thermal stability and toughness and as a result alternative toughening agents based on engineering thermoplastic have been used to improve the fracture properties of epoxy resins. The most widely studied systems over the years have been polysulfone, poly(ether imide), poly(ether ketone) etc. [7-9]. Thermoplastic is usually miscible with epoxy monomers, but at a given conversion, depending on composition and reaction temperature, phase separation occurs [10]. Thermoplastic toughening is normally achieved by melt blending at high temperatures or solvent blending before fibre impregnation. High temperature capable prepreg resin can be achieved by using curing agents, usually amines of different functionalities like diamino diphenyl sulfone (DDS). DDS in conjunction with multifunctional epoxies are the basis for high temperature capable prepreg systems. DDS curative is latent, providing long freezer and outlife. It's slow reactivity also allows for moderate temperature applications when it is mixed into the resins.

Glass fiber reinforced systems are responsible for the majority of the fiber reinforced plastic (FRP) / polymer matrix composite (PMC) market, in spite of the advent of higher performance and higher cost, carbon and aramid fibers. Based on an alumina-lime-borosilicate composition, "E" glass produced fibers are considered as predominant reinforcement for polymer matrix composites due to their high electrical insulating properties, low susceptibility to moisture and high mechanical properties. Glass is generally a good impact resistant fiber but weighs more than carbon or aramid. Glass fibers have excellent characteristics, equal to or better than steel in certain forms. Composites made from this material exhibit very good electrical and thermal insulation properties. Glass fiber is one among the high strength and high modulus material used for the preparation of large varieties of composites [11].

In this study, PEI/multifunctional epoxy resin systems were prepared to use as matrix material with 'E' glass fibers. Glass fibers were impregnated with unmodified and PEI modified multifunctional epoxy resins to fabricate composite laminates. Here, thermoplastic poly (ether imide) (PEI) has been added as a modifier to epoxy phenol novolac resin. Epoxy phenol novolac (EPN) resin, cured with diamino diphenyl sulfone (DDS), and it's blends with poly (ether imide) (PEI) at 2.5, 5.0, 7.5, 10.0 'phr', (where phr represents the number of parts of PEI per hundred parts of EPN resin) have been used as a matrix material in various glass fiber reinforced composites.

The objective of the study is to improve the toughness of multifunctional epoxy resin using PEI. The tough thermoplastic like PEI has good thermal stability because of imide group and has the capability to improve toughness. With the thermoplastic modification of epoxy resin and use of modified epoxy resin as the matrix material in GFRP composites, improvement in mechanical properties has been expected. The strength of multifunctional epoxies is comparatively much higher with respect to bifunctional epoxies due to the entanglement of polymer chains. To improve the toughness of multifunctional epoxies, entanglement of polymer chains has to be reduced or the polymer has to be flexibilized by using modifiers. Epoxy-glass fiber composites have a wide area of research, which is expected to continue in future. A lot of attention has been given by *A. Tiwari et.al* [12] on smart and intelligent nanomaterials. They covered latest research and developments in polymer composite nanomaterial including their processing, properties and applications. Other researches can be promoted by using different functional groups in epoxy resin or by changing the functionality of epoxy resin.

Experimental

Materials

The host multifunctional epoxy resin used was epoxy phenol novolac resin (Huntsman Araldite EPN1138) (EEW, 176-181g/eq, functionality 3.6, epoxy value~ 5.50-5.70 eq/kg, purity 98%) and curing agent 4,4'-diamino diphenyl sulfone (DDS) (HT 976) containing 99-100% amine content, which were procured from M/s Ciba Specialty Chemicals Pvt. Ltd., Mumbai, India. DDS was used at a level of addition of 36 parts by weight per hundred parts of resin. The structure of EPN resin has been illustrated in **Fig. 1**. Thermoplastic modifier employed was a commercial grade of poly-etherimide (PEI) (viscosity 20000-50000 cp at 25°C), (Trade name:Ultem 1000) and was kindly supplied by SABIC innovative Plastic India Pvt. Ltd., Mumbai, India with number average molecular

weight ($\overline{M}n$) of PEI was 20,000. The epoxy phenol novolac resin and DDS were used as supplied, while the thermoplastic was dried before use. The glass fiber is woven roving mat "E" type glass fiber based on an alumina-lime-borosilicate composition, provided by S.G.F. Enterprises, Delhi.
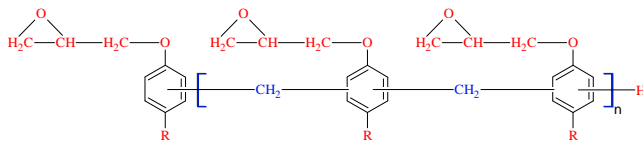

Fig. 1. Epoxy phenol novolac resin.

Epoxy/ PEI blends and casting procedure

Mutlifunctional epoxy resin systems with different PEI concentrations were cured by melt casting. In case of neat epoxy/ DDS system, molten resin was prepared at 170°C by mixing with a mechanical stirrer and subsequently degassed in a vacuum oven under 50 mm Hg at 175°C. This molder resin was poured onto a preheated chrome steel casting molder (15cm x 15cm) and cured for 2h at 150°C and for 4h at 200°C. Steel molder should be coated with any mold releasing agent (silicone grease) before casting. Absence of voids in the casting is necessary to develop the maximum fracture toughness. For melt casting of PEI modified epoxy phenol novolac resin poly(ether imide) pellets were first placed in hot air oven for one hour at 100°C to remove the moisture present in the PEI [13]. Different weight of PEI (2.5phr, 5phr, 7.5phr & 10phr) was dissolved in an excess of dichloromethane(CH_2Cl_2). Poly (ether-imide) gets dissolved normally in 5-6 hours. This mixture was mechanically stirred into the epoxy resin at 80°C for 2-3 hrs so that the solvent (CH_2Cl_2) gets evaporated and then de-gassed in a vacuum oven set at 80°C, overnight. This mixture was heated up to 130°C and the hardener was dissolved for 20 min to give a homogenous, clear liquid. This procedure can be followed for PEI concentration upto 10 phr. Therefore, the viscosity of the blend becomes too high and a portion of the modifier has to be added as a solution in dichloromethane, after dissolution of the hardener. Five PEI concentrations were selected for this study: 0, 2.5, 5.0, 7.5 and 10.0 phr. The molten epoxy/PEI mixture was mixed thoroughly by a mechanical stirrer and degassed in a vacuum oven at 190°C under 25 mm Hg. The molten mixture were cast and cured for 2h at 180°C and for 4h at 200°C for post curing [14,15]. Cure schedules were optimized with the help of a DSC dynamic scan [16]. Observing the exothermic peaks where cure reactions take place, the curing temperature was fixed. The time duration was fixed by trial and error method. The main purpose of post curing is the blocking of the active site of the crosslinking i.e. to make sure that crosslinking is 100%. Similar procedure has also been adopted by *D.J.P. Turmel* [17].

Preparation of prepreg and laminate processing

Thermoplastic modified resin system was warmed up on heating mantle, attached with temperature controller, until it was mobile and poured uniformly over the fibers. Great care was taken in ensuring that there was no disruption of the fiber alignment. Fibrous layer of the each laminate (24 layers) is coated with the EPN 1138 + PEI + DDS blends at room temperature using dichloromethane as a solvent via hand lay up method. The fabric was cut to 25cm x 25cm size, prior to impregnation; this was done due to the short gel time of 150-170 minutes at 40°C of the resin. First, the lower aluminium plate was covered with teflon film and a thin coat of resin was applied. The first ply was then placed and coated with resin by hand brush. Subsequently, remaining plies were stacked, aligned in the warp direction and impregnated with resin, total of 24 plies are stacked to consolidate the laminate. The uppermost ply was covered with teflon film and upper aluminium plate was placed. The plates were then placed in between platens and heaters put on. The mold temperature was held constant at 80°C for 20 min to ensure gelation. Further the mold was heated upto 120°C which is the desired processing temperature. An impregnation pressure of 40 kg/cm² was applied, and final consolidation carried out for 4 hrs. Excess resin was squeezed out in the final step. The laminates were allowed to cool down to room temperature under pressure, to prevent warping. Various prepared thermoplastic modified multifunctional epoxy resin systems have been used as matrix material for preparation of various GFRP's. The composition of matrix materials for different glass fiber composites are given in **Table1.**

Table 1. Material composition for various epoxy/PEI blends and glass fiber laminates preparation

Blends	Epoxy	PEI (phr)	Weight of epoxy (g)	Weight of PEI (g)	Weight of DDS (g)
EPN1	100	0.0	168.750	0	60.750
EPN2	97.5	2.5	165.703	4.142	59.653
EPN3	95.0	5.0	162.765	8.138	58.595
EPN4	92.5	7.5	159.930	11.994	57.574
EPN5	90.0	10.0	157.191	15.719	56.589

Material characterization

DSC measurements

Glass transition temperature (Tg) of the epoxy/PEI blends was characterized by means of a differential scanning calorimeter (DSC). DSC measurements were conducted using TA instrument 2920 MDSC V 2.6 A, with a microprocessor controller. The method used here is modulated DSC. In all cases, a sample of approximately 10 mg was used at a heating rate of 10°C min-1 over a temperature range of 30°C-350°C. In these experiments, the sample was cured during the first temperature scan, allowing evaluation of the heat of reaction. The sample was then cooled slowly to room temperature and a second scan was run to determine the final Tg.

Mechanical property determination of epoxy/PEI blends and glass fiber composites

A range of mechanical properties was used here to evaluate the composite material using Tinius Olsen universal testing machine (UTM). Flexural tests were performed by a three point bending test. Samples of dimensions (100x13x4.8) mm were prepared according to ASTM D 790-84. The load

range of epoxy-PEI blend was 0-60 kg and support span was 60 mm, whereas for glass fiber reinforced composites, load range used was (0-250) kg and span was 70 mm.

Tensile properties are important for a material that is going to be stretched or under tension. Tensile strength has been determined by static tension tests in accordance with ASTM D 638 for epoxy-PEI blends and ASTM D 3039-76 for glass fiber reinforced composites. Used load range of blends and composites was (0-500) kg and (0-10,000) kg respectively with 50 mm supporting span. Sample size is (180x13x4.8) mm.

Inter laminar shear strength (ILSS) test was conducted on the unidirectional laminates. An Instron 4505 screw-testing frame controlled by the Instron Series IX software was used in the experiments. The interlaminar shear strength test was performed in accordance with ASTM D 2344-84 [18]. Samples of dimensions (40x13x4.8) mm have been cut. The load range used was (0-500) kg and loading span was 25 mm.

Impact strength is an important mechanical property which measures the ability of a material to withstand an impact blow, i.e. to absorb energy. Instrumented Tinius Olsen impact universal testing machine is used for the charpy impact test. The sample size (78x13x4.8) mm was cut in accordance with ASTM D 256. Five samples from each set were tested for various mechanical studies.

Dynamic mechanical analysis (DMA)

The viscoelastic properties of neat epoxy resin, blends and composites were measured using TA instruments 2980 DMA V1.7B, dynamic mechanical analyzer in a 3-point bend loading configuration by ramping the temperature at 5°C/min from 35°C to 300°C with a liquid nitrogen cooling accessory. The specimens were loaded within the linear range of the stress-strain response in flexure and loading frequency was 1Hz. Rectangular specimens of 50 x 15 x 5 mm^3 were used for the analysis.

Scanning electron microscopy (SEM) analysis

A Carl ziess EVO 50 low vacuum scanning electron microscope (SEM) was used to examine the fracture surfaces of the neat epoxy and PEI toughened epoxy-glass fiber composite samples. A thin section of the fracture surface was cut out and mounted on an aluminium stub using a conductive (silver) paint and was sputter coated with gold prior to fractographic examination. SEM photomicrographs were obtained under conventional secondary electron imaging conditions and with an accelerating voltage of 3 KV.

Results and Discussion

Thermal behavior

Thermal properties of the unmodified and thermoplastic modified systems were measured by means of DSC. In the first series of experiments the sample was cured during the first temperature scan to determine the magnitude of the curing exotherm, while the second scan was used to evaluate the final glass transition temperature of the cured material. **Table 2** indicates the minimal effect of the modifier content on the glass transition temperature, Tg achieved in the unmodified and PEI modified epoxy resin.

Table 2. Glass transition temperature (T$_g$) and Heat of reaction of unmodified and thermoplastic modified epoxy resin.

Blends	Glass Transition Temperature T$_g$ (ºC)	Heat of reaction ΔH (J/g)
EPN1	179.54	191.2
EPN2	180.21	192.8
EPN3	180.67	192.6
EPN4	182.38	193.4
EPN5	183.61	194.6

A single Tg (ranges between 179°C to 183°C) was observed in all blends due to the close proximity of the Tg's of all the individual components **Fig. 2**. This is because the glass transition temperature of the thermoplastic PEI is itself 220°C. However, the Tg depends significantly on the percentage of the thermoplastic in the blend, indicating an increase of the crosslink density as the content of the reactive thermoplastic is increased. DSC scans of the cured material did not show any further exotherms indicating that the curing process is complete. It was observed that the heat of reaction oscillating at the 191.2 J/g is shown with very less amplitude. The values of the heat of reaction for all PEI/epoxy blends are slightly higher than the values for the neat systems. Change in heat of reaction is in accordance with the result of *L. Barral et al* [19, 20].
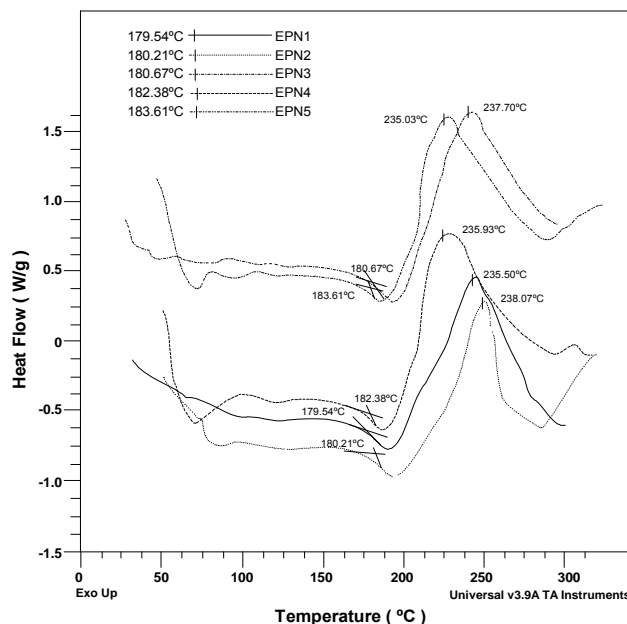

Fig. 2. Glass transition temperatures for neat epoxy and various epoxy-PEI blends

Mechanical properties of epoxy/PEI blends and glass fiber composites

Unmodified and thermoplastic modified epoxy phenol novolac resin and its glass fiber reinforced composites have been subjected to various mechanical tests. Results obtained for different GFRP composite systems have been reported in **Table 3.**

Table 3. Mechanical properties of PEI modified epoxy phenol novolac resin and its GFRP laminates

Blends	Thermoplastic modified epoxy resin			Glass fiber composites		
	Flexural Strength (MPa)	Flexural Modulus (GPa)	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Tensile Strength (MPa)
EPN1	105	2.98	31	1215	185	7134
EPN2	109	2.76	33	1613	177	8364
EPN3	110	2.76	34	1822	174	10190
EPN4	113	2.75	37	2139	137	13127
EPN5	115	2.73	38	2482	130	14364

Data shows that the presence of the poly (ether) imide modifies the mechanical behavior of the epoxy phenol novolac resin. Flexural moduli of PEI modified epoxies were reduced slightly. An increase in the amount of modifier leads to a minor decrease in flexural modulus (E) of the blends because of the addition of poly (ether imide), having an inferior modulus in comparison to neat epoxy. Flexural strengths of the PEI modified epoxy show a little increment than neat epoxy resin. For glass fiber composites, flexural strength values increases with the addition of PEI upto 10 phr. This may be due to the superior toughness of the thermoplastic material which results in an increase in flexural strength of the modified epoxy-glass fiber composites than the neat epoxy resin toughened glass fiber reinforced composites (GFRP). Very slight decrease in flexural modulus values was observed. These changes were very small when compared with the variations in other mechanical tests performed. The modulus was relatively unaffected because of the small concentration of the modifier used. The particle made up a very small fraction of the matrix, causing little changes in its modulus. These results can be explained by PEI effectively reducing the entanglement of polymer chains which results in increasing the molecular mobility and improving the toughness of cured epoxy resin without lowering the strength **[21]**. As expected, tensile strength of the multifunctional epoxy resin increases significantly with the incorporation of thermoplastic. This is due to the effect of blending of thermoplastic material (PEI) which has superior toughness in comparison to the unmodified epoxy resin. The epoxy makes miscible blends with PEI till 5 phr of PEI, after that increase in PEI content in epoxy i.e. 7.5:92.5 and 10.0:90.0 blends, the phase separates out which results in the increase in the mechanical properties. The tensile strength of the laminates varies with the change in the modifier concentration and increases up to 10 phr PEI concentration in matrix material. Still increasing the concentration of PEI in matrix material, the composition becomes uncompatiblized due to stoichiometric disbalance and PEI is phase separated out via crystallization leading to the deterioration in the mechanical properties.

ILSS refers to the interlaminar shear strength that depends primarily on the matrix properties and fiber-matrix interface shear strength. In the ILSS test, the load was applied with the loading nose perpendicular to the fibers. **Table 4** represents the variation in ILSS of the laminates as the concentration of the modifier in the matrix was varied. A small increase in the ILSS was observed at 2.5 phr PEI.

This was most likely due to the reinforcement of the matrix by thermoplastic. With the use of PEI, the adhesion property of the resin considerably increases due to intermolecular attraction and effectively packed cross-linking within the system. The largest increase in ILSS was seen at PEI 7.5 phr. This increase may have resulted from the thermoplastic particles reinforcing the interlayer region. When 10 phr PEI was used, the ILSS decreased slightly. It is possible that the more ordered thermoplastic particles in this sample acted as flaws or crack initiators instead of reinforcements.

The impact response of GFRP is a complex and important issue. The results from the impact strength of epoxy-GFRP's given in **Table 4** represents that impact strength of the laminates increases with PEI concentration in the blend up to 7.5 phr which may be attributed to the formation of semi IPN structure within the laminate. Impact strength also increases due to increase in molecular weight of matrix material, upon addition of PEI. The small decrease in impact strength at 10 phr PEI concentration is probably due to the stoichiometric disbalance because at 10 phr PEI concentration, phase separation occurs which results in decrease in impact strength at the given concentration. The phenomenon of phase separation in thermoplastic/ thermoset blends is controlled by the concentration of thermoplastic with respect to the critical composition, which is clearly supported by the morphological analysis (**Fig. 5a-5e** and **6a-6e)**.

Table 4. ILSS and Impact Strength of EPN-PEI blends / GFRP laminates.

Blends	ILSS (MPa)	Impact Strength (KJ/M^2)
EPN1	435	8
EPN2	529	12
EPN3	653	17
EPN4	861	22
EPN5	798	19

Dynamic mechanical behavior of modified epoxy-glass fiber composites

Dynamic analysis, **Table 5** gives a clear idea about the viscoelastic properties as well as the phase structures of the blends and composites. **Fig. 3a-3c** and **4a-4c** exhibit the comparison of dynamic mechanical properties of neat epoxy, various epoxy-PEI blends and subsequent glass fiber composites with respect to the thermoplastic concentration.

Table 5. DMA data for EPN-PEI blends / GFRP laminates

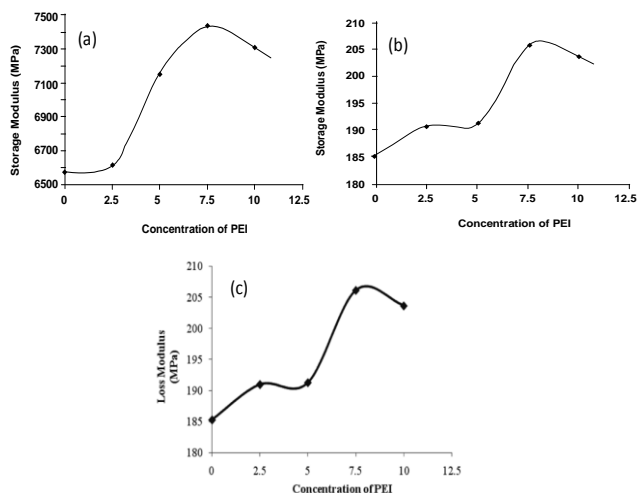| Blends	Thermoplastic modified epoxy resin			Glass fiber composites		
	Storage Modulus (MPa)	Loss Modulus (MPa)	Loss Factor tan δ	Storage Modulus (MPa)	Loss Modulus (MPa)	Loss Factor tan δ
EPN1	6581	185	0.0281	29191	537	0.0183
EPN2	6617	191	0.0288	31268	586	0.0187
EPN3	7158	191	0.0267	34743	624	0.0179
EPN4	7442	206	0.0277	36192	689	0.0190
EPN5	7316	204	0.0278	36032	646	0.0179

Fig. 3. (a) Variation in storage modulus of various epoxy-PEI blend (b) Variation in loss modulus of various epoxy-PEI blends (c) Variation in tan δ various epoxy-PEI blends.

Storage modulus (E') is the most important property to assess the load bearing capacity of any material. Storage modulus E' is recorded at room temperature (35°C). In general all the modified systems have more value of storage modulus at room temperature than the neat one. Storage modulus for epoxy/PEI (92.5:7.5) blend was found maximum at room temperature. It means this composition has more resistance towards deformation by an applied force, thus posses high stiffness. There is a considerable increase in the modulus of the matrix with the incorporation of different concentration of PEI in the epoxy matrix material. The E' value was found higher than neat epoxy resin and it was observed maximum at 7.5 phr PEI. At 10 phr PEI, there is a small decrease in E' value. The increase in E' may be attributed to the increase in the stiffness of the matrix with the introduction of thermoplastic. E' decreases with the increase in temperature and there is a sharp decline in the E' value at glass transition region. This behavior can be attributed to the increase in the molecular mobility of the polymer chains above Tg. Above T_g, molecular mobility of the polymer chains increases causing the decline in E' value. Studies done by Zhang et. al. [22] also supports the improvement in the modulus of epoxy resin composites with the addition of PEI.

Loss modulus (E") is the measure of the energy dissipated as heat per cycle under deformation or, it is the viscous response of the material. **Fig. (3b)** shows that there is a gradual increment in the values of loss modulus. At a very small content of thermoplastic modifier, some of the epoxy remains uncrosslinked because at such small PEI concentration (2.5 phr), the modifier PEI forms a dispersed phase and acted as a solute in epoxy resin continuous phase. As the content of PEI in the blend increases, it forms saturated solution and still increasing the PEI concentration, phase separation occurs. Increase in the value of the loss modulus for epoxy/PEI. 92.5:7.5 composition shows that this blend can be used upto 190.43°C without complete loss of modulus and with the constant dissipation of energy as heat. **Fig. (4b)** shows the trends of variation of the loss modulus (E") for different composite systems, with variation of temperature. The loss modulus value in the transition region is much higher for

GFRP composites with modified epoxy matrix than for composite with neat epoxy resin matrix material. The higher modulus at this temperature is due to the increase in internal friction that enhances the dissipation of energy. Additionally, the presence of high modulus glass fibers reduces the flexibility of the material by introducing constraints on the segmental mobility of the polymeric molecules in the relaxation process [23].

The ratio of the loss modulus to the storage modulus is measured as the mechanical loss factor or tan δ. The damping properties of the material give the balance between the elastic phase and viscous phase in a polymeric structure. The values of mechanical damping **Fig. 3c** tan δ became less than the neat value, which signifies that the modified system becomes much elastic in nature in comparison to the neat epoxy, and its value comes considerably same for all the modified samples. So, high value of tan δ, material will be less elastic in nature. In composites, damping is influenced by the incorporation of fibers [24]. It is observed that as temperature increases, damping goes through a maximum in the transition region and then decreases in the rubbery region shown in **Fig. 4c**. The lowering of peak height also indicates good interfacial adhesion. The width of tan δ peak also becomes broader than the matrix. The position and height of the loss tangent peak in the relaxation spectra of a polymer are indicative of the structure and extent to which the polymer is crosslinked. In the glass transition region, the storage modulus falls during heating to a level of one-thousandth to one ten-thousandths of its original value. As the loss factor is the ratio of the loss modulus to storage modulus, drop in storage modulus suppresses the rise in the loss factor initially. The temperature at which the loss factor is a maximum is therefore higher than the temperature corresponding to maximum loss modulus.
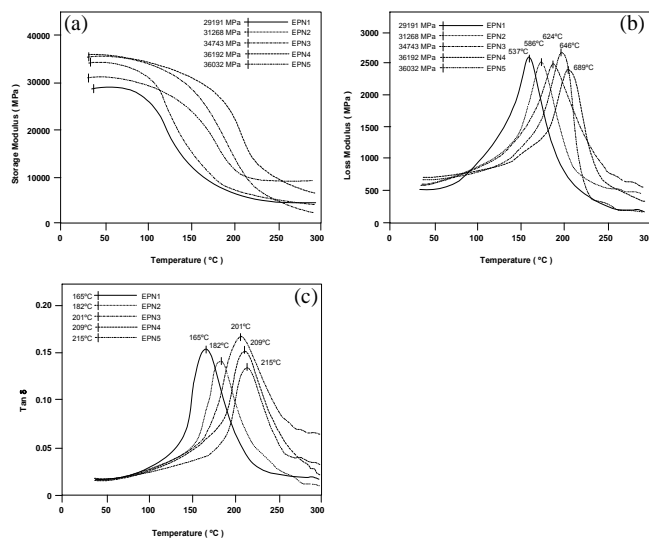

Fig. 4. Storage modulus Vs temperature plot for epoxy resin-PEI/GFRP composites (b) Loss modulus Vs temperature plot for epoxy resin-PEI/GFRP composites (c) Tan δ Vs temperature plot for epoxy resin-PEI/GFRP composites.

Scanning electron microscopic (SEM) analysis

The fracture surfaces of epoxy/PEI blends and corresponding GFRP composites were analyzed by SEM.

The SEM micrographs of the corresponding fracture surfaces taken near the initial crack tip have been shown in **Fig. 5 (a-e).**
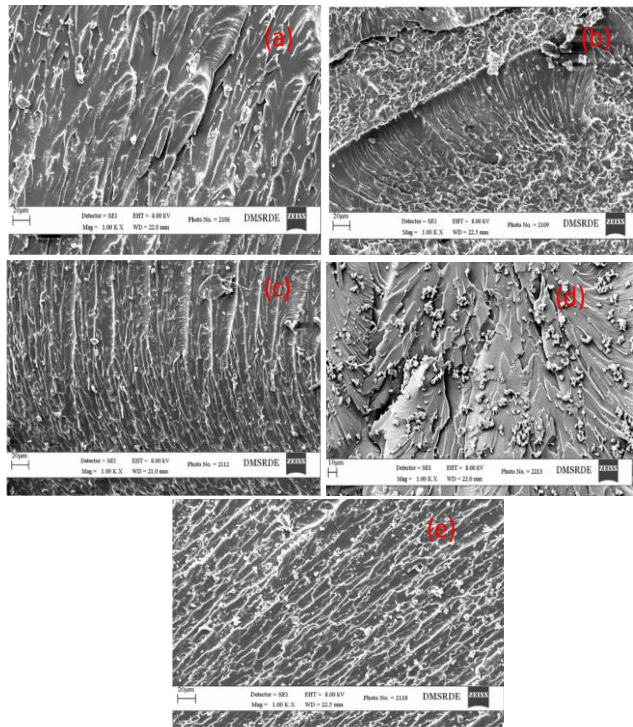

Fig. 5. Scanning electron micrograph of (a) neat Epoxy resin casting, (b) Epoxy/PEI(2.5phr) blends, (c) Epoxy/PEI(5phr) blends, (d) Epoxy/PEI(7.5phr) blends, (e) Epoxy/PEI(10phr) blends.

The neat resin sample **Fig. 5(a)** exhibited a smooth and featureless surface representing brittle failure of a homogenous material. For PEI modified epoxy specimen (2.5 phr PEI) many river markings have been appearing **Fig. 5(b)**. The river markings became more extensive and deeper at 5 phr PEI concentration **Fig. 5(c)**. The initial miscibility of epoxy / thermoplastic blends was attributed to the low molecular weight of the epoxy polymer. During curing, molecular weight of the resin increased resulting in two phase morphology. In system EPN 4 and EPN 5, an increase in the PEI content leads to the formation of a heterogeneous morphology, classically observed in thermoplastic/ thermoset blends **Fig. 5(d)** and **5(e)**. The heterogeneous morphology was developed because of the reaction induced phase separation (RIPS). Phase separation is due to the high viscosity of the systems which is in accordance to the results of M.Naffakh et.al. & B.S.Kim et.al. **[25, 26].** Due to RIPS, different morphologies can be achieved in polymer blends. Usually the mechanism of phase separation was found to be dependent on the composition of the blends, nature of the curing agent and the temperature **[27].** When the composition of the blend was near critical composition, phase separation occurred by spinodal decomposition. Composition located close to the critical point produce bicontinuous morphologies, which as usually desired to obtain a significant increase in toughness. Below the critical composition, at low thermoplastic concentrations, the homogeneous solution tends to form

thermoplastic rich particles in continuous epoxy rich phase, also provide a certain toughening.

Scanning electron micrographs of the fracture surfaces created by mechanical fracturing of neat epoxy composite and PEI modified composite were obtained as shown in **Fig. 6(a-e)**.
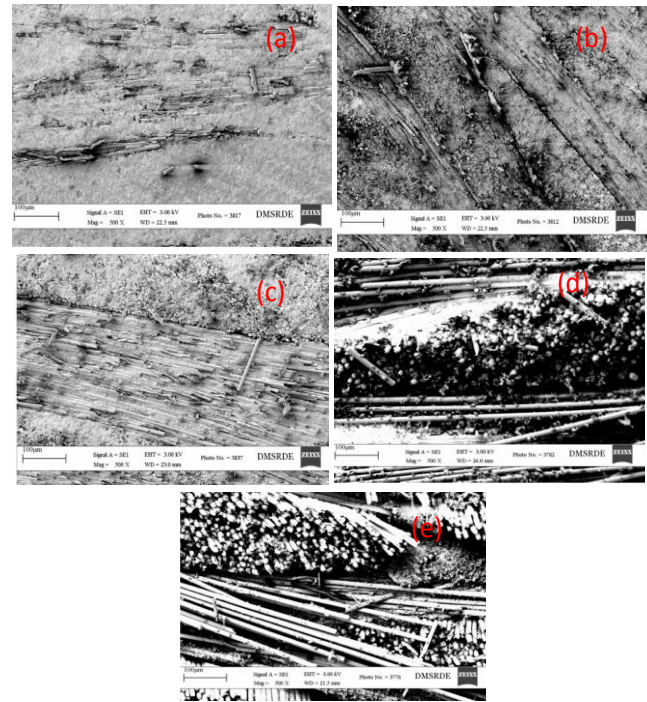

Fig. 6. Scanning electron micrograph of (a) neat Epoxy and glass fibre composite, (b) Epoxy/PEI(2.5phr)/ glass fibre composite, (c) Epoxy/PEI(5.0phr)/glass fibre composite, (d) Epoxy/PEI(7.5phr)/glass fibre composite, (e) Epoxy/PEI(10.0phr)/glass fibre composite.

Fiber bonding and adhesion between the fiber and the matrix are clearly figured out from morphological studies. The interaction between matrix and glass fibers is clear from scanning electron micrographs. In order to achieve good toughening in a thermoplastic modified epoxy composite system, adequate interfacial adhesion is necessary. From the electron micrographs, all samples look similar and exhibited phase separated morphology. Neat epoxy resin composite scanning electron micrograph, **Fig. 6(a)** showed a smooth surface indicating the brittle behavior of EPN resin, and the strongly bonded fiber-matrix interface. The PEI modified GFRP composite systems exhibited rougher matrix surface than those with neat epoxy resin. At low PEI concentrations (at 2.5 phr and 5.0 phr), thermoplastic is homogeneously distributed in epoxy matrix material, whereas, at high PEI concentrations (7.5 phr and 10.0 phr), phase separation of thermoplastic is observed, which may be attributed to the low solubility of the thermoplastic in epoxy resin. This morphological feature can be presumably considered responsible for the observed slight depression in the above stated mechanical properties at 10 phr PEI concentration. In **Fig. (6b-e)**, the surface of the fibers is much rougher. The matrix traces found stuck to the surface of fibers which clearly reveals strong adhesion and good interface attraction between glass fibers and matrix material. The glass fibers are embedded within the matrix for 2.5 phr and 5.0 phr PEI concentration

Fig. 6(b) and **6(c)**. **Fig. 6(d)** shows that some fibers are pulled out of the matrix as a result of mechanical fracturing done in sample preparation.

In **Fig. 6(e)**, some glass fiber experience fiber pull out and lay adjacent to the micron – sized glass filaments. Fiber pull out and delamination are the key features that are associated with the composites but very little fiber pull out was observed in the case of the thermoplastic modified epoxy matrix and GFRP composites, which reveals the efficiency of the modified matrix to hold the fibers. In the micrographs, the glass fibers protruding from the composite indicates the degree of fiber pull out and crack deflection. The fiber surfaces that protrude are not clean, with some adhering matrix material. Strong interaction between thermoplastic and epoxy resin in matrix material leads to efficient stress transfer from the matrix to reinforcing glass fibers that reduce the crack growth rate, leading to good mechanical strength of the composites **[28].**

Conclusion

Effect of PEI modification on the mechanical, dynamic mechanical and morphological properties of E- glass fiber reinforced epoxy phenol novolac resin has been studied in detail. The properties of the material between fiber reinforcement and polymer matrix have a significant influence on the mechanical properties of GFRP's. If the polymer matrix is fairly brittle (unmodified epoxy), there may be a corresponding reduction in mechanical properties. In this study, the mechanical properties viz. tensile strength, flexural strength, flexural modulus, inter laminar shear strength and impact strength of GFRP's were found to be increasing, when a poly(ether imide) thermoplastic modifier was incorporated into the multifunctional epoxy phenol novolac resin matrix. The highest tensile strength and flexural strength were obtained with 10 phr PEI concentration. Similarly, ILSS and charpy impact tests showed the highest increase in mechanical properties at 7.5 phr PEI concentration. Considerable improvements in the above stated properties are observed which are associated with a small decrease in the flexural modulus as compared with the neat epoxy resin-glass fiber composite. A significant increase in storage modulus also corresponds to improvement in mechanical properties. Mechanical properties of glass fiber composites are also affected by the fiber / matrix interface which is clearly evidenced by scanning electron microscopy. SEM analysis of multifunctional epoxy / PEI / glass fiber composite shows better exfoliation of the PEI layers that results in improved mechanical property. Use of different mixing orders of the concentrations of PEI enhanced the mechanical properties of the matrix material, and so as of the composite structures. The work can be used for defense applications where high temperature susceptible and lightweight structures are required. This thermoset-thermoplastic blend has been used as matrix material for manufacturing of light weight military shoes and bullet proof jackets. Researchers may study the variation in mechanical strength and thermal stability of the system by replacing the functional group of epoxy resin. Incorporation of nano particles may be useful to enhance the strength, and hence the end use of the material **[29].**

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