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PAPER

Epoxy benzoxazine based ternary systems of improved thermo-mechanical behavior for structural composite applications

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Abstract: Ternary mixtures of various ratios of bisphenol F benzoxazine as a hardener for bisphenol F novolac epoxy (ER) and diglycidal ether of polyethylene glycol (EL) resins were made in order to study the visco elastic and thermo mechanical properties in compare with homo polymerized polybenzoxazine (F-a). FTIR, DSC were used to characterize the cure characteristic. Dynamic mechanical analyzer and thermo gravimetric analysis were investigated on F-a and ternary samples. An improved TG of curable ternary mixture with 48.1 and 3.1 wt. % of ER and EL respectively with benzoxazine resin was achieved based on trends of ternary diagram. The ternary samples were thermally stable up to 370⁰ C when compared to F-a. Investigation of fracture toughness and SEM images showed improved fracture toughness for the samples having 52% of binary epoxy mixture in the ternary system. The newly developed ternary mixtures showed improved service temperature, thermal stability, cross linking density, processing window and fracture toughness with minimum brittleness when compare to polybenzoxazine. The applicability of the developed ternary mixture was demonstrated by preparing S glass fabric reinforced composite with F-f. It was observed that this S glass fabric composite have improved flexural strength, flexural modulus, ILSS, Shore D hardness & hydrolytic stability when compared with polybenzoxazine composite and found to be very much useful for high performance structural applications.

1.0 Introduction

Polybenzoxazines represent a new class of additional polymerizable phenolic resin having excellent properties such as high thermal stability, high glass transition temperature (Tg), low flammability (high char yield), high modulus, low water uptake and practically no shrinkage upon curing because of which they are considered to be promising matrix materials for composites in aerospace applications. Further more polybenzoxazines possess good electrical insulating properties, excellent mechanical performance, and wide molecular design flexibility that allow the properties of the cured material to be controlled for a wide variety of applications [1–5]. Despite their high performance, benzoxazine based resins shows some disadvantages like high brittleness, low cross linking density, less pot life and voids formation in final product [2]. Alloying, blending or co-curing can be utilized to overcome the disadvantages

of polybenzoxazine with improved mechanical properties or thermal stability of polybenzoxazines. As a result, in recent years other resins, e.g., epoxy resins, phenolic resins, urethane prepolymers etc. were used to cross link with benzoxazine resins to improve their properties [6-9].

Performance of epoxy resin which were used in electronics and aerospace industries strongly depends on the nature of the basic skeleton of epoxy resin i.e. aromatic or aliphatic groups in the main chain and their substituent's and also on type and quantities of curing or cross linking agents and curing conditions. The major cross linking agents with various reactive functional groups includes amine compounds, acid anhydride group, lewis acids, and polyamide group [10-11] have their own advantages and disadvantages [12]. Self polymerizable benzoxazine resins can be used as a cross linker to solve the problems of the currently used cross linking agents [6,

13-16].

The blends of bisphenol A benzoxazine resin (BA-a) with bisphenol A epoxy resin exhibits an increase in cross-linked density and thermo mechanical properties with a minimal loss of brittleness [6]. The epoxy systems for toughness improvement have reported in literature [17-20]. Benzoxazine resin (BA-a) with only flexible aliphatic epoxy showed improved toughness but with a decrease of thermal properties [7]. Benzoxazine (BA-a) with bisphenol A epoxy and diepoxy polyisopropylene glycol improved the shape memory properties with loss of thermal properties [21], epoxy with aromatic chain extenders improved mechanical properties but with loss of thermal properties when compared with BA-a [22]. The aromatic epoxy resins used so far are of bisphenol A type which are of less rigid with low functionality and are not able to get high cross linking required for elevated temperature applications.

Improving fractured properties without sacrificing much of thermal and mechanical properties for benzoxazines with epoxy resins are a critical and challenging task. [23-25] To improve the fracture toughness and thermal properties, there is a need to develop a balanced composition that can improve the Tg and cross link density with low brittleness. Novolac epoxy resins of ternary mixture with its rigid structures i.e. aromatic groups and epoxy groups can enhance the cross linking density and brittleness of the material which results in increase in Tg but at the same time aliphatic epoxy resins improves the segmental mobility, cross linking density and lowers the brittleness of the material which results in lower Tg of polybenzoxazine. Blending of flexible aliphatic epoxy resin to the benzoxazine resin improves fracture toughness, processing window and also helps to overcome the problem of degassing required for benzoxazines to get final void less product.

In this work, bisphenol F novolac epoxy resins (rigid, multifunctional, aromatic epoxy resin) widely used in electronic and flame retardant applications were explored for the first time [26, 27]. Diepoxy polyethylene glycol (flexible, difunctional, aliphatic epoxy resin) is found to be successfully used to increase processing compatibility and fracture toughness [28, 29]. To the best of our knowledge, bisphenol F novolac epoxy resins were not used with bisphenol- F benzoxazine resin and even studies were not carried out for preparing ternary composition using these two resins along with diepoxy polyethylene glycol. This study also attempts to toughen the brittle type bisphenol F polybenzoxazine with enhancement of

glass transition temperature, thermal stability and pot life by cross linking with aromatic and aliphatic epoxy resins in various ratios. The relative effect of incorporation of different ratios of rigid aromatic and flexible aliphatic epoxy resins in comparison with homo polymerized bisphenol F polybenzoxazine resin on visco-elastic properties, thermal stability and processing window has been also investigated under the same conditions. This work also attempted to demonstrate the applicability of developed ternary mixture by preparing S glass fabric reinforced composites and compared with that of polybenzoxazine composite. The chemical structures of the bisphenol F benzoxazine, bisphenol F novolac epoxy and diepoxy polyethylene glycol resins used in this work are represented in Fig-1.

2.0 Experimental

2.1 Raw Materials:

In the ternary mixtures, the letters BZ, ER, and EL stands corresponds to bisphenol F- benzoxazine resin, novolac epoxy resin and aliphatic epoxy resin respectively. The polybenzoxazines precursor such as aniline based bisphenol F benzoxazine type (BZ) with trade name Araldite MT 35700 (softening point of 80-85^o C and has a viscosity at 100^o C is 500 to 2500 cPs) was procured from Huntsman Advanced Materials, Switzerland. Aromatic epoxy resin of multi glycidal ether of bisphenol F novolac (ER) (epoxy eq. wt: 176-181 gm/eq and density: 1.2-1.5 g mL⁻¹) having the trade name Lapox L238 of Atul Ltd., India was used. The aliphatic epoxy resin of diglycidal ether of polyethylene glycol (EL) namely Lapox ARD 61 of Atul, Ltd India having epoxy value and viscosity of 6.0-6.6 eq/Kg and 20-50 cPs respectively was used. The S glass fabric of 0.24 mm thick and release (D200 TFP) fabric were purchased from BGF, USA and De-comp Composite Inc., USA respectively. Both the breather fabric (AB 1060V) and vacuum bagging film (50 micron thick) were obtained from Aerovac, UK. Solvent methyl ethyl ketone (MEK), reagent grade is procured from Merck., India.

2.2 Preparation of epoxy-benzoxazine ternary mixtures:

Both BZ and ER resins of desired quantities are taken in separate beakers and heated at 80^o C to reduce its viscosity. ER of low viscous resin is cooled to 50^o C and added EL resin and mixed well with mechanical stirring for 10 minutes. This resin mixture (ER+EL) was added to BZ at 80^oC and stirred well mechanically. The blended resin was poured in open mould and material is cured as per cure cycle depicted in Fig-2 to obtain epoxy-benzoxazine ternary mixture. Table-1 represents sample code of the formulations, different mass ratios of BZ, ER and EL taken for the experiments with the

corresponding weight percentage (wt %). The cured samples are transparent with light yellow to dark red in colour depending on the composition of the mixture and no sign of phase separation was observed on the ternary systems.

2.3. Preparation of S glass reinforced polybenzoxazine (SGF-a) composite:

Prior to the preparation of glass–benzoxazine preregs, BZ (240 gms) was taken into a vessel, MEK solvent (72 gms) was added and the mixture is heated at 70°C to obtain a clear solution of benzoxazine resin. The prepared benzoxazine resin solution was uniformly spread on the glass fabric with brush and the preregs are allowed for drying at room temperature till it gets tackiness. Preregs were cut in to 15 no. of plies of 300 x 300 mm size and all plies were placed on a release agent coated metallic mould by laying and rolling each ply with roller manually and a releasing film and metallic caul plate was placed over the layers. The set up is enclosed in breather cloth and vacuum bag, curing was carried out in the oven under vacuum of 400 mm Hg as per the cure cycle represented in Fig- 2 to obtain SGF-a composite. This material will be used as a reference material for comparison with epoxy-benzoxazine ternary mixture composites (SGF-f).

2.4. Preparation of S glass reinforced ternary mixture (SGF-f) composites:

Prior to the preparation of S glass ternary mixture preregs, both ER resin of 115.2 gm and BZ resin of 115.5 gms are mixed in MEK (59 gm and 90 gms respectively) separately in beakers and dissolved at 80°C till the low viscous resin obtained. ER resin solution was cooled to 50°C and then EL resin of 9.2 gm was added and mixed well with mechanical stirring for 10 minutes. To this resin mixture prepared benzoxazine resin was added and again mixed well with mechanical stirrer. From the prepared epoxy-benzoxazine resin, 240 gms have been taken and uniformly spread with brush on the glass fabric of 1.5 meter. The preregs are allowed for drying at room temperature till it gets tackiness. For making the SGF-f composite, similar procedure and cure cycle of SGF-a was followed except using epoxy benzoxazine preregs instead of polybenzoxazine preregs.

2.3. Instrumentation

ATR-FTIR spectra were recorded using an Agilent 640 series FTIR equipped with the Ge-ATR accessory. All samples were examined with a spectral resolution of 4 cm⁻¹ and scanned from 600 to 4000 cm⁻¹ in the transmission mode.

Differential scanning calorimeter (DSC) thermo grams were recorded with a TA Instruments (USA) DSC 2920 module at a heating rate of 10⁰ C per min. under flow rate of 60 ml min⁻¹ of nitrogen atmosphere. Sample taken for test is 10-20 mg in hermitically sealed aluminium pan.

The visco elastic properties and transition temperatures of cured samples were studied using DMA with a TA instrument, USA model Q 800 under dynamic condition with heating rate of 5⁰ C min⁻¹. Visco elastic studies of cured samples were done on rectangular bars with specimen dimension of 60 × 10 × 3 mm in flexural mode at 1 Hz frequency with a heating rate of 5⁰ C min⁻¹. The evolution of the loss modulus (E) and energy dissipation (Tan δ) with temperature were measured.

TGA of TA instrument model SDT 2960 was used to study the thermal decomposition of the blends in platinum crucible under air atmosphere for sample size: 10 to 30 mg as per ASTM E2550. Cured samples were weighed in the sample pan and then heated in a TGA furnace at a rate of 10⁰C min⁻¹ under atmosphere between 30 and 600°C.

Melt viscosity and gelation behaviours of each resin mixture were investigated using a rheometer (Anton Paar, Germany, Model no MTR301) equipped with disposable parallel plate geometry. The measuring gap was set at 1 mm. The processing window for isothermal condition i.e. 170⁰ C was performed under oscillatory shear mode at a frequency of 1 rad/s (0.159 Hz). Melt viscosity was determined from complex viscosity as a function of time in minutes. Gel time was determined at isothermal condition at intersection point of storage modulus and loss modulus as a function of time.

Fracture toughness (K_{IC}) and flexural properties were studied on a universal testing machine of United 50 KN. Fracture toughness (K_{IC}) was studied by collecting five samples having 50 mm x 8mm x 4 mm dimensions from each of the ternary sample at a cross head speed of 10 mm/min. A notch was made at the centre of the specimen and tested as per ASTM D 5045-07. Flexural properties were measured at a cross head speed of 2 mm/min as per ASTM D 790. Five samples with dimensions of 80 × 13 x 3.2 mm were tested for each composite type. Samples were flexed until breakage in three-point loading with a 50mm support span.

Fractured surfaces of fracture toughness tested samples of F-a & ternary samples were analyzed with scanning electron microscope (SEM, JEOL JSM 5800 Digital).

Water absorption was estimated as per JIS K7209. The sample of dimensions 20 x 20 x 3 mm was weighed to the nearest 0.1 mg and the mass was taken as M 1. The test samples, than placed in a container containing boiling water and boiled for 2 hours. The tested samples were taken out of the boiling water and kept for 15 min in ambient temperature water. After removing from the water, the tested samples were weighed to the nearest 0.1 mg, and the mass was taken as M 2. Water absorption was calculated by the following equation.

$$\text{Water absorption (\%)} = [(M 2 - M 1) / M 1] \times 100$$

Shore D Hardness was measured as per ASTM D 2240 using Bareiss hardness tester, Germany, at room temperature. The Shore D hardness is a measure on the scale from 0 to 100 value for the resistance of a material to the penetration of a needle under a defined spring force. The measurement was carried out for five times at different positions of each type of sample and the average hardness value of the sample was obtained.

3.0 Results & Discussion

Various epoxy-benzoxazine ternary mixtures prepared by using variable weight percentages of BZ, ER and EL as shown in the Table-1 were used in this study. These epoxy-benzoxazine ternary mixtures prepared were inspected with reference to pure polybenzoxazine in terms of T_g , processing window, viscosity, fracture toughness and morphological properties. The formulations includes weight ratios of pure benzoxazine F-a (BZ/ER/EL : 1/0/0), epoxy-benzoxazine ternary mixtures F-b (BZ/ER/EL : 1/0.25/0.05) F-c (BZ/ER/EL : 1/0.75/0.05), F-d (BZ/ER/EL : 1/1.5/0.1) and F-e (BZ/ER/EL : 1/3/0.3). Functional group changes and curing characteristics were studied for all the five blends before and after curing with FTIR and DSC.

3.1 Curing studies

The FTIR spectra of BZ, ER, and EL are shown in Fig-3. The characteristic infrared absorption peaks of BZ were found at 942, 1027, 1232 and 1490 cm^{-1} are due to the oxazine ring and the presence of tri-substituted benzene of the oxazine ring. The characteristic peaks of ER and EL are 913 cm^{-1} and 864 cm^{-1} are due to epoxide rings. ER epoxy resin shows additional peaks at 1608, 1582 & multiple peaks below 800 cm^{-1} due to the presence of aromatic groups. During curing, initially at elevated temperatures ring-opening homo polymerization of the benzoxazine ring produces phenolic hydroxyl group structures, which further can react with

both the epoxy resins at elevated temperatures [30], as shown in Fig-4. Ring opening homo polymerization results in the disappearance of peak at 1498 cm^{-1} and appearance of peak at 1477 cm^{-1} due to formation of tetra-substituted benzene structures and disappearance of peaks at 913 cm^{-1} and 864 cm^{-1} and appearance of peak at 3400 cm^{-1} due to copolymerization of phenolic hydroxyl group with both epoxy resins. Fig-5 represents FTIR of cured samples for F-a and epoxy-benzoxazine ternary mixtures. The disappearance of peaks 1498 cm^{-1} , 913 cm^{-1} and 864 cm^{-1} in F-b & F-c indicates that curing was completed. The presence of absorption peaks at 913 cm^{-1} and 864 cm^{-1} shows that curing has been not completed for F-d & F-e due to left over un reacted epoxy group. This is due to non stoichiometric ratio of epoxy prepolymers in compare to benzoxazine prepolymer for the reaction between the oxazine and epoxy. Thus, it was evident that in all formulations the epoxy appears to be reacting with the phenolic hydroxyl groups of homo polymerized benzoxazine without external catalyst.

DSC analysis has been carried out to determine the curing characteristics of before cure samples of F-a, BZ/ER (1:0.75 wt. ratio), BZ/EL (1:0.1wt. ratio) and F-c (BZ/ER/EL: 1:0.75:0.1). Fig-6a represents DSC thermogram of neat resin of BZ (before cure) shows a single, well defined exotherm with the onset temperature of cure at 176°C and the peak exotherm at 227.85°C corresponding to the characteristic cure temperature for the ring opening self polymerization of benzoxazine resin [31]. The neat epoxy prepolymers will not show curing reaction without initiators or catalysts and shows endothermic thermal events like evaporation process 250°C [7]. DSC scan carried out for BZ/ER (1:0.75 wt. ratio) and BZ/EL (1:0.1wt. ratio) were shown in Fig-6b and Fig-6c respectively. Fig-6b shows slight splitting characteristic exothermic peaks at 248° C and 274° C respectively due to ring opening self polymerization of benzoxazine prepolymer and the reaction between the epoxide group on the epoxy with the phenolic hydroxyl groups of polybenzoxazine [7, 22, 32, and 33]. Fig-6c shows a single exothermic peak at 237° C instated of two peaks when compared to BZ/ER due to low concentration of EL [22]. In both BZ/ER and BZ/EL, there is a shift of exothermic peak towards high temperature and decrease in area of benzoxazine peak in the binary mixtures indicating retardation of reaction when compared to the self-polymerization of neat benzoxazine resin due to dilution effect [13,14]. DSC of Fig-6d represents the ternary mixture of F-c showing slight splitting characteristic exothermic peaks at 253° C and 274° C and shift of exothermic peak towards high temperature

and decrease in area of benzoxazine peak in the ternary mixtures when compared to BZ, BZ/ER and BZ/EL due to combined effects of BZ/ER and BZ/EL. Fig-7 represents the DSC scan of F-a and epoxy-benzoxazine ternary mixtures after curing. The disappearance of second exothermic peak in F-d and F-e is not total which indicates that the epoxy-benzoxazine ternary mixtures were not cured due to the left over un reacted epoxy resin. DSC scan of epoxy-benzoxazine ternary mixtures F-b and F-c shows that the exothermic heat of reaction was completely disappeared which corresponds to the fully cured stage of the ternary mixture with 100% conversion. This shows that the epoxy-benzoxazine ternary mixtures were self-polymerizable upon heating and need of catalyst or curing agent is not required for the polymerization to takes place. All these results are in good agreement with our FTIR studies.

3.2 Optimizing the formulation:

It is now evident that among all the formulations, epoxy-benzoxazine ternary mixtures F-d & F-e were not completely cured. In order to optimize the formulation and also to study their stiffness and cross link density with storage modulus, glass transition temperatures (T_g) with loss modulus and $\tan\delta$, all the formulations were subjected to DMA studies. Storage modulus (E') and loss modulus (E'') scan for F-a and other epoxy-benzoxazine ternary mixtures were shown in Fig-8a-b. Fig-8a and table-2 shows storage modulus of glassy plates at 35^o C that corresponds to stiffness of F-a and other ternary mixtures. The stiffness of F-a is more when compared to ternary mixtures due to the presence of strong hydrogen bondings. The less stiffness of ternary mixtures when compared to benzoxazine is may be due to presence of flexible epoxy groups in the epoxy mixture. Storage modulus of rubbery plateau regions i.e., above glass transition temperature were used to calculate the cross link density qualitatively from the equation given below [34].

$$C = E'_R / 3RT$$

Where, C is the crosslink density, R is the gas constant, and T is the absolute temperature (i.e. at $T_g + 40^\circ\text{C}$) and E'_R is the rubbery modulus at T. Table-2 shows that cross link densities calculated for F-a is less when compared to all other ternary mixtures. These results indicate that crosslink density of polybenzoxazine increases gradually with the increase of binary epoxy mixtures up to 52% (i.e. for samples F-b and F-c). Further increase in the epoxy mixture decreases crosslink density (i.e. for samples F-d and F-e) is may be

due to left over un reacted epoxy mixture which acts as plasticizer. These results are in good agreement with FTIR and DSC studies.

Loss modulus (E'') scan for F-a and other epoxy-benzoxazine ternary mixtures were shown in Fig-8b and summarized in Table-2. From the figure, the T_g 's of the F-a and epoxy-benzoxazine ternary mixtures F-b, F-c, F-d and F-e were found to be 173, 181, 182, 94 and 63^o C respectively. The ternary diagram Fig-9 represents the relationship between monomer composition of the three resins i.e., benzoxazine monomers / aromatic novolac epoxy resin / aliphatic epoxy resin and their effect on T_g . Polybenzoxazine always possesses a relatively low cross linked density compared with the other resins such as epoxy because of its multi functionality and its prevalent inter and intra molecular hydrogen bonding. Initially the incorporation of binary epoxy mixture in the benzoxazine matrix causes additional cross links of epoxy in the benzoxazine matrix and effects on increasing the glass transition temperature of the ternary mixture over the pure polybenzoxazine.

From the Fig-9 (ternary diagram), It is observed that T_g of F-a is 173^o C and the ternary mixtures F-b, F-c with binary epoxy mixture of about 24.1 & 44.5 by wt.% showed T_g 's 181 and 182 ^oC respectively which are higher than the F-a. The T_g s of the samples F-d and F-e were observed to be 94 and 63^o C with binary epoxy mixture of about 61.7 & 76 by wt.% respectively lower than the F-a. This decrease in T_g of F-d and F-e samples in comparison to F-a are due to excess unreacted epoxy resin mixture in the cured ternary sample which acts as a plasticizer. This is in good accordance with our assumptions made with FTIR and DSC studies. Hence, the enhancement of T_g depends up on the choice of the ternary mixture composition used. Novolac epoxy resin of ternary mixture with its rigid structures enhances the cross linking density and brittleness of the material and results in increase in T_g of polybenzoxazine where as aliphatic epoxy resin lowers the brittleness, which results in lower T_g . Hence, a balanced composition is very much required that can improve the T_g , cross link density with low brittleness. Based on the trends of improvement of T_g with respective to the monomer composition in the ternary diagram in Fig-9, a new balanced formulation of epoxy-benzoxazine ternary mixture F-f (BZ/ER/EL: 1/1/0.08 wt ratios) was chosen. FTIR, DSC and DMA studies on newly developed epoxy-benzoxazine F-f shown in Fig-10a to 10c reveals fully cured sample with significant improvement of T_g i.e., 191^oC. This is in good agreement with the prediction made in Fig-9 and conforms that the

new formulation has even higher glass transition temperature than epoxy-benzoxazine ternary mixture F-c.

Tan δ scan carried out as a function of temperature on F-a and other epoxy-benzoxazine ternary mixtures F-b to F-f were given in Fig-11. Appearance of a single Tan δ peak for each composition for all the formulations shows that the monomeric materials had copolymerized without any detectable phase separation. The Tan δ peak height and width at half height for each ternary composition is summarized in Table-2. From Fig-11, it was observed that the height of the Tan δ peak for F-a to F-c and F-f decreases which indicates the increase of cross link density as the binary epoxy resin mixture of ternary mixture increases up to 52 wt.%. The decreasing height is associated with the lower segmental mobility and fewer relaxing species, and thus is indicative of a higher degree of cross linking for the epoxy rich samples [6]. However, uncured ternary mixtures F-d and F-e containing more than 52 wt.% of binary epoxy mixture causes the increase in the peak height due to non stoichiometric unreacted epoxy left in the composition results in low cross linking density with more segmental mobility. The peak width at half-height broadens as the addition of epoxy increases the number of modes of branching as a result of more cross linking sites in the ternary mixture. The observed width at half height was found to be increase up to 52 wt.% of binary epoxy mixture due to stoichiometric ratio of epoxy mixture to the polybenzoxazine which results in more cross linking reaction sites in the network and hence, wider distribution of peaks. Samples containing excess of binary epoxy mixture more than 52 wt. %, peak width at half height decreases and sharpness of the peak increases due to less cross linked reactive sites in the network and results less complex in network branching.

3.3 Melt viscosity and Gel time studies:

Thermodynamic stability of before cured samples of F-a and epoxy-benzoxazine ternary mixtures F-b, F-c and F-f for processing has determined in the vicinity of the melt viscosity and gel point at 170°C by isothermal melt viscosity method using rheometer. Melt viscosity during fabrication processing will be useful for escaping any volatiles present in the components and produces void less desirable product and also helps in reduction of cost in production by preventing purification or degassing of precursors used [35]. Fig-12a shows that the isothermal melt viscosity at 170°C of epoxy-benzoxazine ternary mixtures F-f, F-b and F-c is quite low i.e. below 0.8 pas for long duration i.e. 52.1,

74.5 and 113 min. respectively when compared with F-a which is 40.5 min. This long duration of melt viscosity in the ternary mixtures is due to existence of two types of reactions shown in our DSC results. Therefore, ternary mixture with less than 48.1 and 3.8 by wt. % of aromatic and aliphatic epoxy resin respectively with benzoxazine is recommended to retain its low viscosity with sufficient period.

Fig-12b shows the plots of storage modulus and loss modulus as a function of time in seconds at 170°C exhibits processing window useful for polymer compounding and processing of before cure samples of F-a and ternary mixtures F-b, F-c and F-f. The gel point of ternary mixtures F-f, F-b and F-c are shifted to higher time in compare to F-a i.e., from 32 minutes to 61, 79 & 115 minutes respectively. Here the gel point, as understood from DSC studies was controlled mainly by the ring-opening polymerization of the oxazine ring which occurs above 160°C [10]. The processing window of each benzoxazine resin can be controlled by adding appropriate amounts i.e., 48.1 and 3.8 by wt. % of aromatic and aliphatic epoxy in ternary mixture respectively. The ternary mixtures F-b, F-c and F-f were showing sufficient processing window with enhanced gel time, which is really advantageous for various fabrication processes.

3.4 Thermo gravimetric analysis

The developed epoxy-benzoxazine ternary mixtures showing high Tg and sufficient processing window when compared to pure benzoxazine were subjected to thermo gravimetric analysis. Fig-13 shows the TGA thermo grams of F-a and ternary mixtures F-b to F-f. Thermal degradation of polybenzoxazine shows initial decomposition below 300°C due to pyrolytic evolution of aniline derivative of mannich bridge, intermediate degradation between 300°C and 400°C due to the evolution of substituted phenolic derivative and the final degradation above 400°C due to the evolution of phenol. The general thermal degradation pattern of cured samples of aromatic and aliphatic epoxy resin of ternary mixture exhibits in two steps. In the epoxy resins, initial weight loss at about 280–320°C is due to the formation of olefin by loss of secondary hydroxyl group of the propyl chain in epoxy resin and the second step degradation of bisphenol group occurs at 350–380°C [36]. The temperatures at 2 % wt loss, 5% wt loss and the char yield at 600°C are given in Table-2. All ternary mixtures showed improved thermal stability with relatively high

decomposition temperature at 2%, 5% weight loss when compared with F-a due to increase of crosslink density. The char yield for the ternary mixture F-f which increase significantly due to increase of cross linked with more aromatic structures in compared with the F-a. F-f showed relatively high decomposition temperature at 2%, 5% weight loss i.e. up to 330°C, 364°C and char yield of 46.28%. The other samples F-b, F-c shows less char yield than F-a and F-f due to decrease of aromatic structures and low cross linking density. The ternary samples F-d and F-e showed less char yield in comparison to F-a and other ternary mixtures due to plasticity of non-stoichiometric epoxy structures.

3.5 Fractured Toughness

Fractured mechanical properties K_{IC} carried out for cured ternary mixture samples were given in Table-2. Fracture toughness of ternary mixtures has improved significantly with addition of aromatic and aliphatic epoxy resin mixture up to 48.1 and 3.8 by wt. % respectively, but the improvement trend was not clearly understood. From the Table-2, it was observed that fracture toughness of samples F-f, F-b and F-c were found to be improved from 0.7 Mpa.m^{1/2} of F-a to 1.42, 1.37, and 0.80 Mpa.m^{1/2} respectively. The improvements of fracture toughness of ternary mixtures when compared to polybenzoxazine were due to the addition of the aliphatic epoxy resin in the ternary mixture. This aliphatic epoxy resin enhances the flexible segments to the polybenzoxazine matrix and contributes for the increase of fractured toughness of the ternary mixtures. This phenomenon was due to the basic principle that the addition of the more flexible or less stiff epoxy into the more rigid polybenzoxazine can cause the toughening of the resulting polymer composition [6]. For uncured ternary mixture F-d and F-e fracture toughness decreases from 0.7 MPa of F-a to 0.67 Mpa, 0.53 MPa respectively. This is due to the presence of large content of rigid aromatic epoxy resin system when compared to aliphatic epoxy, which acts as anti plasticizer by changing the network and results in decreasing Tg and toughness properties. This is in good accordance with our assumptions made during DMA studies.

3.6 Morphology studies:

SEM pictures obtained from the fracture surfaces of F-a and other ternary mixtures were shown in Fig-14. The appearance of the fracture surface of all the formulations suggests that polybenzoxazine is well incorporated and uniformly distributed in the epoxy mixture network of ternary samples. The presence of characteristic river like patterns with higher roughness of the plastic

zone indicates the higher fracture toughness of the sample [25]. From Fig-14a it was observed that F-a exhibits a smooth fractured surface without any crack growth which represents brittle failure of the material. This indicates that polybenzoxazine has low toughness due to constrain segmental mobility. Fig-14b-d of samples F-b, F-c and F-f showed that there is sharp contrast in the fracture surfaces of the samples with formation of river marks running in the parallel directions indicating significant crack deflections. It was observed that formation of rough surface increases with increase of aromatic and aliphatic epoxy resin wt. % from 0 to 48.1 and 0 to 3.8 wt. % respectively. As a result of non constrainable segmental mobility in the ternary mixture causes the initiation and propagation of secondary cracks with decreases of stress concentration at the crack tip. This consumes extra energy for creating more fracture surface area and thus contributes to more toughness. Hence, the toughness of these compositions was observed to be more when compared to polybenzoxazine. Fig-14e & 14f represents the uncured ternary mixtures F-d and F-e showing typical wavy form of brittle nature without any crack deflections and glassy surface respectively, which indicates that material has less toughness. These observations are in good accordance with fracture toughness results.

3.7. Properties of S glass fabric reinforced ternary mixture composites:

The high performance of structural composites depends upon high interfacial strength and thermo mechanical properties of polymer matrix reinforced with glass fabric. Table-2 and Fig-15 represents the mechanical properties, hardness and hydrolytic stability of F-f and polybenzoxazine S glass reinforced composites. It was observed that flexural strength, flexural modulus, ILSS, shore D hardness and water absorption of F-f were found to be improved from 525 Mpa, 24.4 Gpa, 34 Mpa, 62.84, 72 and 5.96 % of F-a composite to 689 Mpa, 31.42 Gpa, 35.5 Mpa, 72 and 0.74 % respectively. This improvement is due to increase in the cross linking density, Tg and interfacial strength of binary epoxy mixture in the ternary mixture composite when compared to polybenzoxazine composites [37]. This shows that the developed ternary mixtures with improved mechanical, thermal and hydrolytic properties are best suit for high performance structural composites in comparison to polybenzoxazines.

4. Conclusion:

The purpose of this study is to decrease the brittleness and improve the thermal stability, cross linking density, processing window and fracture toughness of bisphenol F polybenzoxazine. In this study, we have investigated various formulations by blending bisphenol F- benzoxazine resin with bisphenol F novolac epoxy and flexible diepoxy resin as a ternary mixture with out use of an external catalyst. It is believed that the copolymerization reaction occurs by the two consecutive reactions i.e., initially, ring opening homo polymerization of benzoxazine precursor followed by epoxy ring opening reaction with phenolic groups of homo polymerized polybenzoxazine with rigid and flexible epoxy resins. Investigation with FTIR and DSC showed that ternary samples with binary epoxy mixture up to 52 wt. % were completely cured. DMA studies were carried out to find the service temperature, cross linking density and network structure for all the ternary mixtures and found to be improved when compared to the homo polymerized polybenzoxazine (F-a). The Tg of F-b and F-c are found to be greater than F-a.

Based on the trends of improvement of Tg with respective to the monomer composition in the ternary diagram, a new balanced formulation of epoxy-benzoxazine ternary mixture F-f was chosen. Melt viscosity and gel time for ternary mixtures were determined and found that F-b, F-c and F-f were having low viscous with latent curing and hence possess improved processing window when compared with F-a. TGA of all ternary mixture samples showed improved thermal stability up to 370^o C in comparison to F-a. Fracture toughness for F-b, F-c and F-d ternary mixtures were improved in compare to F-a and was confirmed with SEM. Hence, the newly developed ternary mixtures F-b, F-c and F-f achieved maximum improved service temperature, thermal stability, cross linking density, processing window and fracture toughness with minimum brittleness when compared to polybenzoxazine. The applicability of the ternary mixture was demonstrated by preparing S glass fabric reinforced composite with F-f. These composites showed improved mechanical properties, hardness and hydrolytic stability when compared to polybenzoxazine composite. Hence this work has proved that the developed ternary mixture will be having more advantage in high performance structural applications than F-a. These new materials overcome many of the traditional shortcomings associated with conventional resins, while demonstrating excellent visco-elastic and thermo mechanical characteristics.

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Notes and references

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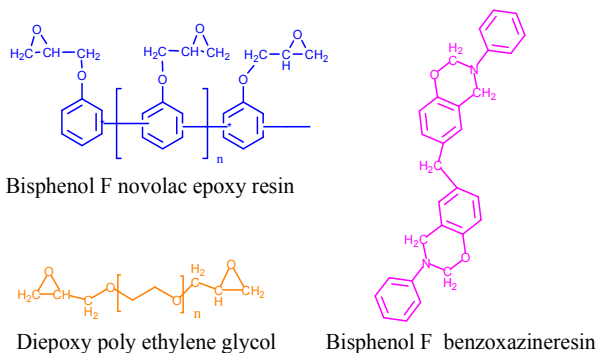


Fig-1: Chemical structures of the Bisphenol F benzoxazine (BZ), Bisphenol F novolac epoxy resin (ER) and Diepoxy polyethylene glycol (EL)

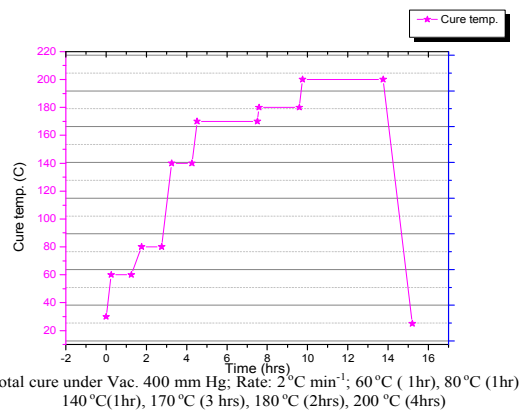


Fig-2: Cure Cycle for curing ternary mixtures

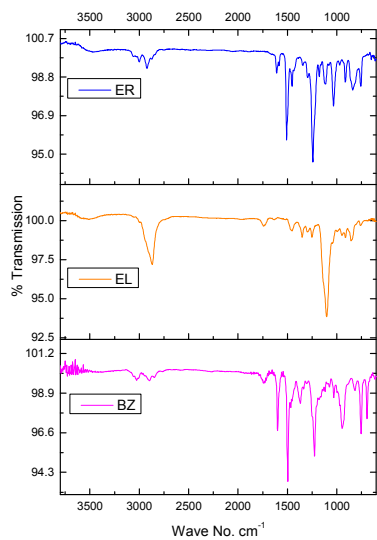


Fig-3: FTIR spectra of BZ, ER, and EL resins

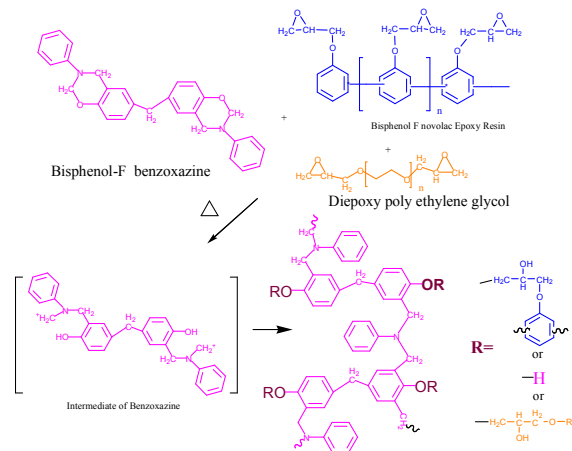


Fig-4: Schematic representation of curing reaction of ternary mixtures

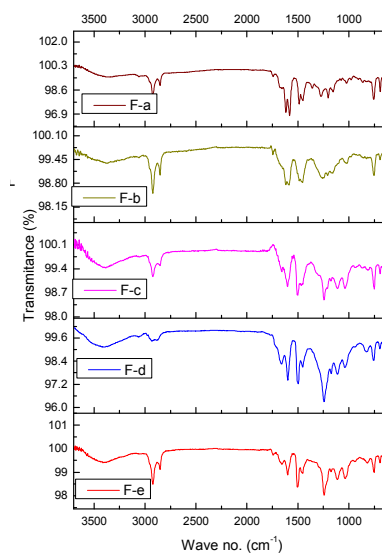


Fig-5: FTIR of cured samples of F-a and epoxy benzoxazine ternary mixtures

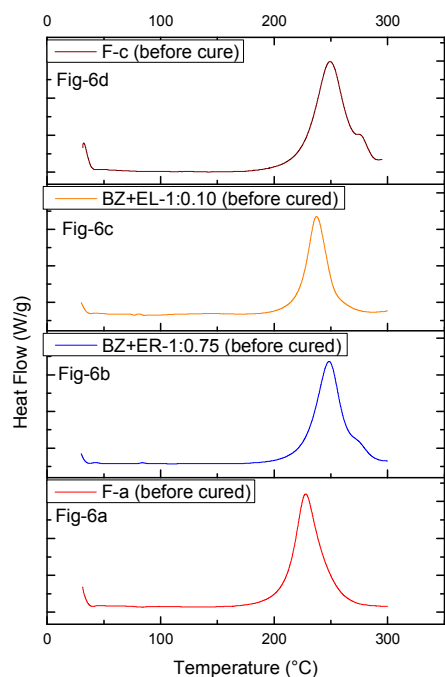


Fig-6a-d: DSC scan of before cure formulation , 5a: F-a, 5b: BZ+ER, 5c: BZ +EL and 5d: F-c

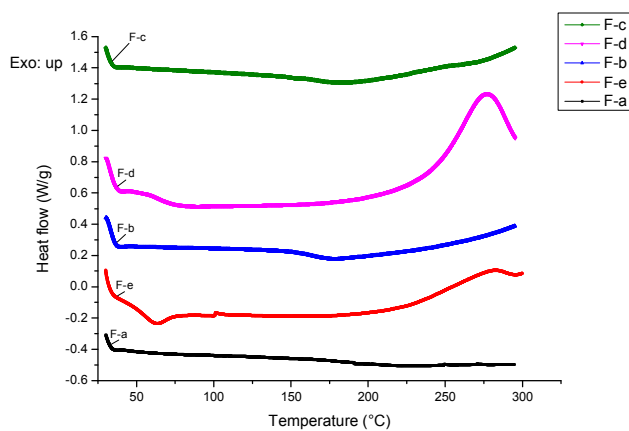


Fig-7: DSC scan of cured samples of F-a and epoxy benzoxazine ternary mixtures

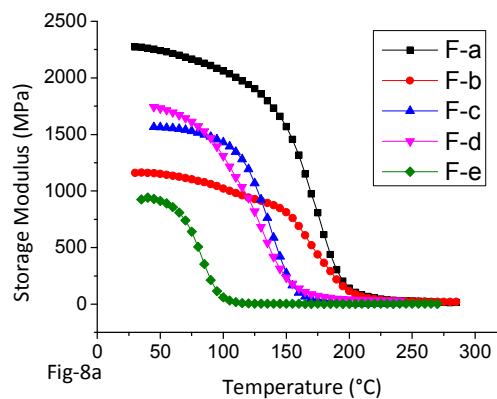


Fig-8a

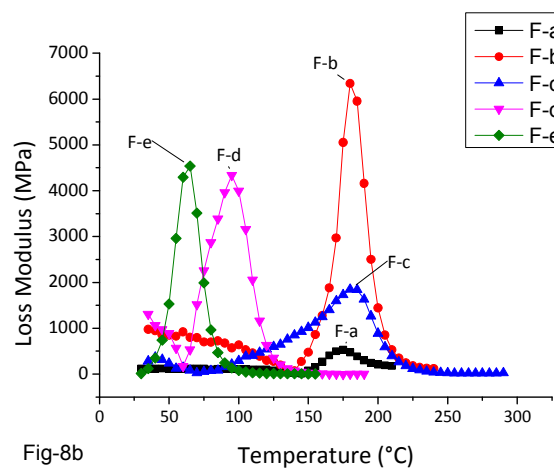


Fig-8b

Fig-8a, b: DMA scan for F-a and other epoxy benzoxazine ternary mixtures, Fig-8a: Storage Modulus scan, Fig-8b Loss modulus scan

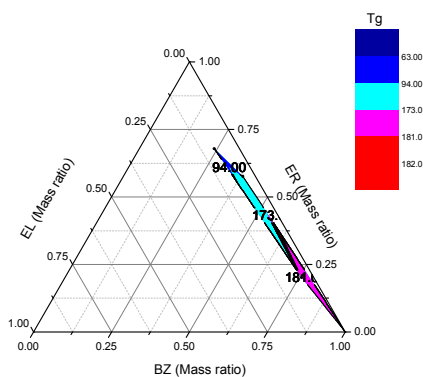


Fig-9: Ternary diagram of ternary mixtures

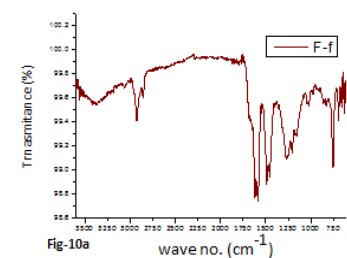


Fig-10a

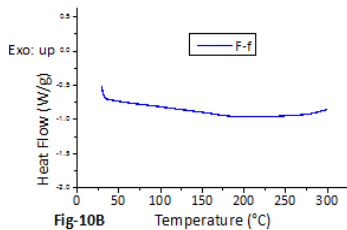


Fig-10B

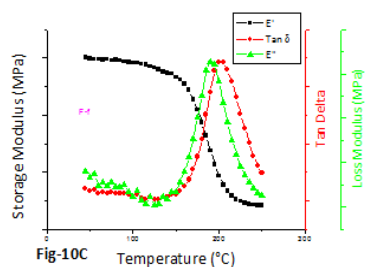


Fig-10C

Fig-10a – 10c : Characterization results of F-f ternary mixture:

10a: FTIR, 10b: DSC and 10c: DMA scans

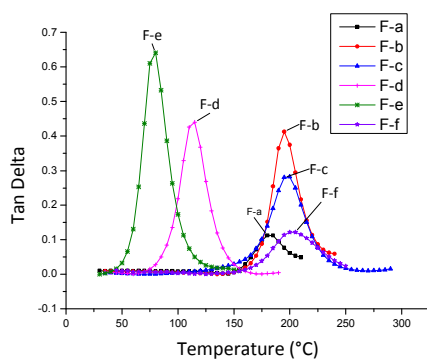
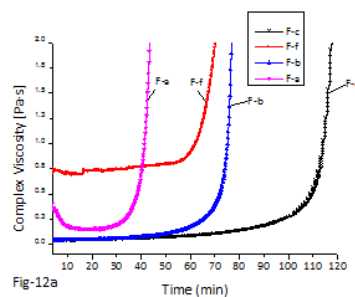
Fig-11: Tan δ scan of F-a and all epoxy benzoxazine ternary mixtures

Fig-12a

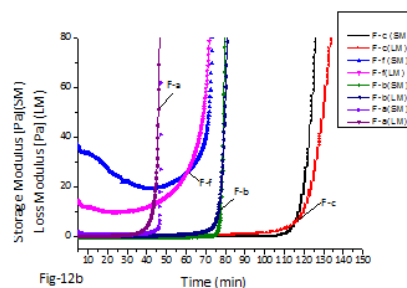


Fig-12b

Fig-12a, b: Isothermal rheological behaviour of before cure samples F-a and ternary mixtures (F-b, F-c & F-d), 12a: Viscosity curve, 12b: Processing window

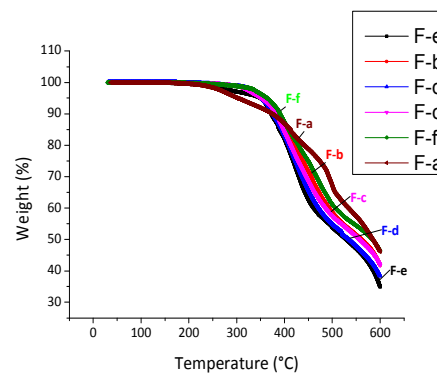


Fig-13: TGA thermogram of F-a and all ternary mixtures

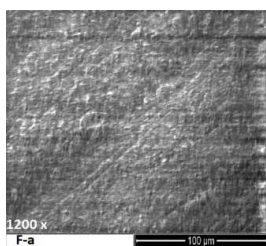


Fig-14a:

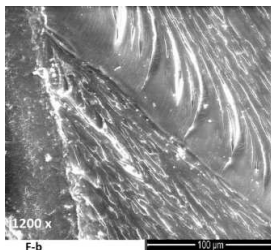


Fig-14b

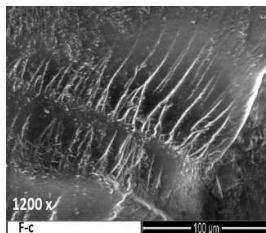


Fig-14c

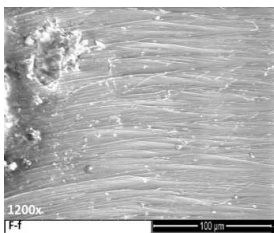


Fig-14d

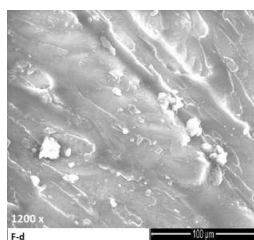


Fig-14e

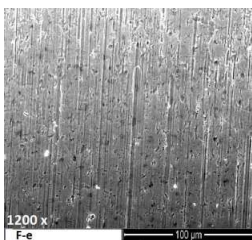


Fig-14f

Fig-14a-f: SEM images for fracture toughness tested samples, 14a: SEM of F-a, 14b-d: SEM images of F-b, F-c and F-f, 14e & 14f SEM of F-d and F-e samples

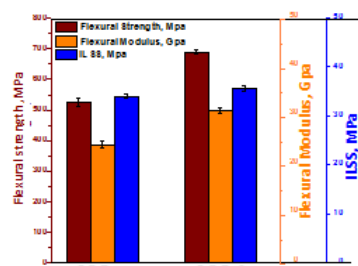


Fig-15a

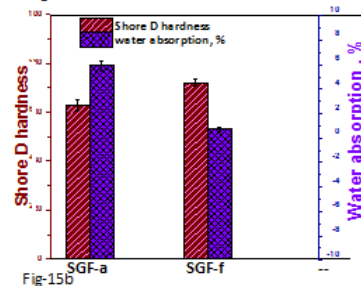


Fig-15b

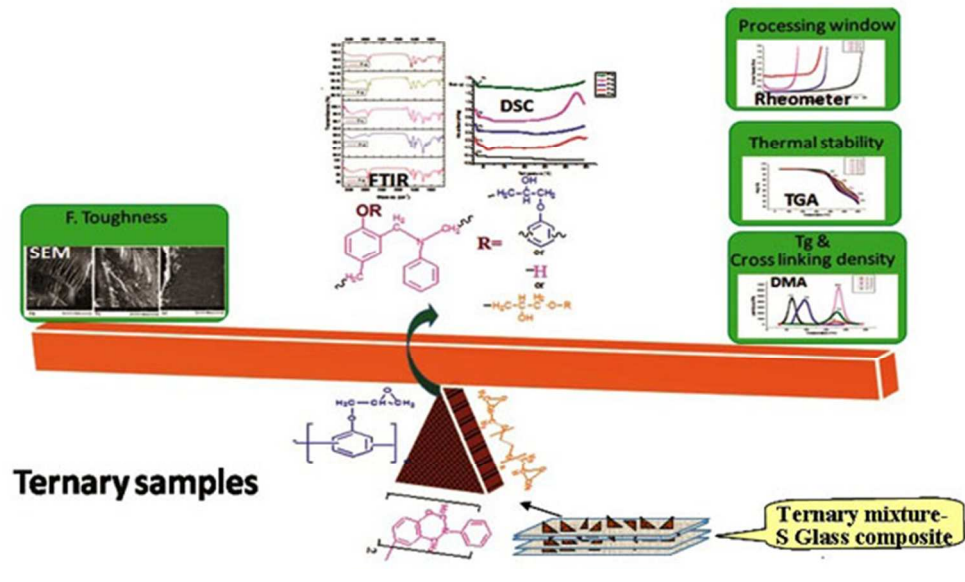
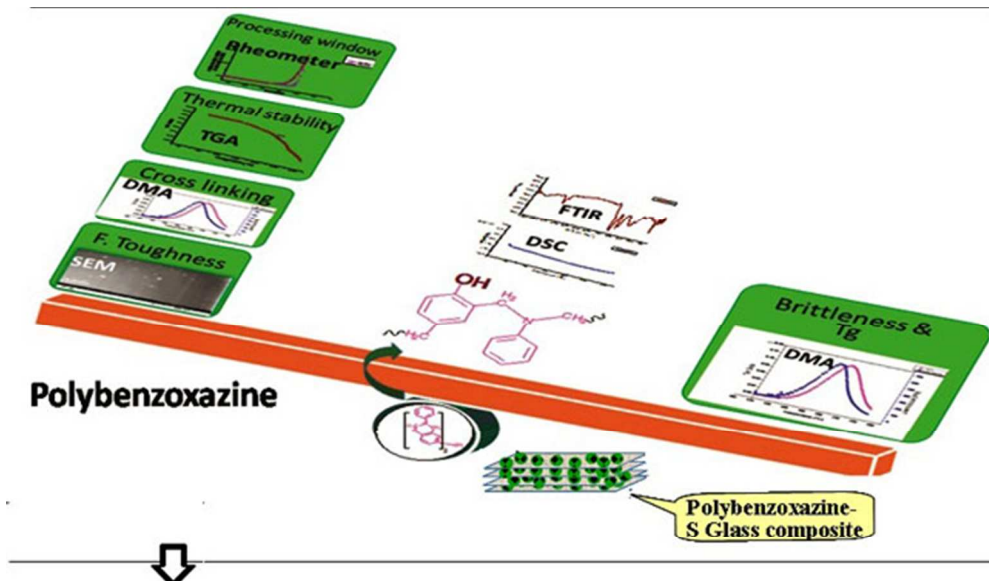
Fig-15a, b: Properties of SGF-a and SGF-f, Fig-15a: Mechanical properties Fig-15b: water absorption and shore D hardness properties

Table-1: Sample codes and weight percentages of ternary mixtures

Sample codes	Benzoxazine resin (BZ), wt %	Novolac epoxy resin (ER), wt %	Diepoxy polyethylene glycol (EL), wt %	Weight ratio's BZ/ER/EL
F-a	100	0	0	1/0/0
F-b	75.83	20.22	3.94	1/0.26/0.05
F-c	55.55	41.58	2.91	1/0.75/0.05
F-d	38.32	57.63	4.03	1/1.5/0.10
F-e	23.98	67.93	8.08	1/3/0.3
F-f	48.01	48.13	3.8	1/1/0.08

Table-2: Thermal and mechanical properties of ternary mixtures

Sample codes	E'			E''	Tanδ		TGA			Fracture Toughness
	RT, Mpa	Tg +40 ⁰ C, Mpa	Cross link density, gm mole ⁻¹	Tg, °C	Height	Width at half height, °C	2% wt. loss, °C	5% wt.loss, °C	Char yield 600 ⁰ C (air), wt %	K _{IC} , Mpa.m ^{1/2}
F-a	2269	58.65	3.50	173	0.18	25.25	256.02	300.74	46.11	0.7
F-b	1163	42.34	5.32	181	0.37	25.53	318.92	358.36	41.81	1.37
F-c	1565	47.93	5.80	182	0.26	33.69	317.93	351.94	40.84	0.8
F-d	1749	34.36	3.86	94	0.43	26.7	326.71	351.75	38.35	0.67
F-e	941.6	10.61	3.72	63	0.64	24.97	268.79	350.35	34.9	0.532
F-f	1691	35.85	6.04	191	0.10	42.16	330.64	363.88	46.28	1.42



110x127mm (150 x 150 DPI)