Novel E glass composites with polybenzoxazine and insitu generating reactive multi branched titanate for low temperature cure and high thermal resistance applications

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-01-2015-000185.R1
Article Type:	Paper
Date Submitted by the Author:	30-Jan-2015
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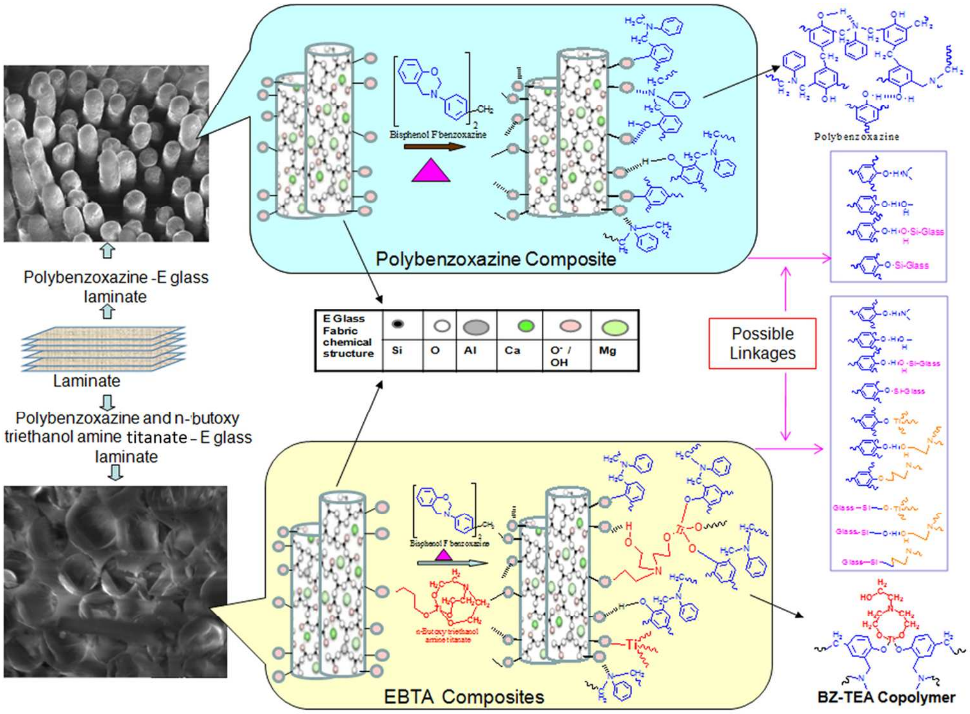

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57x40mm (600 x 600 DPI)

RSC Advances RSC **Publishing**

PAPER

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dCite this: DOI: 10.1039/x0xx00000x

Received..th Janunary, 2014,
Accepted 00th

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Abstract:

A new class of E glass fabric reinforced polybenzoxazine titanate composites (EBTA) were made with bisphenol F benzoxazine (BZ) and insitu generating reactive multi branched n-butoxy triethanol amine titanate (TEA) chelate in various ratio's. Incorporation of TEA into polybenzoxazine matrix could causes uniform dispersion with in the polymer matrix and ring opening of oxazine at lower temperature which results in increase of cross link density, stiffness and hindered network structures responsible for enhancing thermal and water resistance. The hypothetic chemical reaction between BZ & TEA was understood by studying the reaction between model compounds such as phenol, tera isobutoxy titanate and triethanol amine. FTIR and DSC studies were utilized to optimize the curing studies and final cure temperature was established for EBTA composites. DMA analysis carried out on EBTA composites found improved stiffness, crosslink density, service temperatures (Tg) with uniform phase distribution when compared to E glass fabric reinforced polybenzoxazine composite. Thermal stability and char yield with TGA analysis, interfacial adhesion with SEM and hydrolytic stability for EBTA composites up to 23% of TEA were found to be improved when compared to polybenzoxazine composite. Flame retardency of EBTA composites were found to be retained V1 class of polybenzoxazine composite. The EBTA composites have shown low maximum cure temperature, improved service temperature, cross link density, stiffness, water absorption resistance, thermal stability and char yield when compared to E glass fabric polybenzoxazine composite.

1. Introduction

Phenolic resin composites though preferred for wide range of applications but limited due to low shelf life of the resin, release of volatiles during cure and brittleness of the final composites [1-4]. Polybenzoxazines are of novel type of additional curable phenolic resin which overcome the shortcomings of conventional novolac and resole type phenolic resins. They possesses the attractive properties of the traditional phenolic resins and also have additional unique characteristics that are not found in the traditional phenolic resins, such as inexpensive raw materials for preparation, good molecular design flexibility to achieve required specific properties of cured product, no by-products release upon curing for void less products and low moisture absorption for improved storage life [5-11]. However, polybenzoxazine also associated with certain shortcomings such as low thermal resistance due to low cross link density and high curing temperature like 200^0 C or in some cases up to 250^0 C that cannot meet the requirements of some high performance advanced composites [12-15].

To improve the performance of polybenzoxazine, two approaches have been reported. The first one is molecular structure modification by designing new benzoxazine monomers with reactive, additional functional group such as ethenyl, phenyl ethenyl, allyl, propagyrl, maleimide and epoxy [16-20]. This is a highly laborious process which involves utilization of expensive raw materials. The other approach is the formation of composites or blends with organic polymers or inorganic fillers for the preparation of hybrid materials with perfectly defined structures. Organic polymers such as epoxy, phenolic and polyimide resins [14, 21-23] and inorganic fillers such as clay [24], metal particles [25], metal oxide [26], silica nanotubes [27] and layered silicates [28, 29] have been blended with benzoxazine resins to lower the curing reaction temperature or improve thermal resistance of benzoxazine resins. Introduction of organo-inorganic polymers with highly branched molecular structures with reactive end groups [30-33] which provides compatibility and homogenous distribution with polybenzoxazine will also improves the performance of polybenzoxazines. Reactive, multi branched polymers such as allyl-functionalized hyper branched polyimide [34], dendrite based polymers, [35, 36], boron containing rigid, multi branched reactive structures [37–40], diglycidyl ether of (2, 5-dihydroxy phenyl) diphenyl phosphine oxide (Gly-P) [41] and diglycidyloxy methyl phenyl silane (Gly-Si) [42] with various resins were used.

Unfortunately these methods improve mechanical properties and thermal resistance but not effective in lowering the final cure temperature. Lowering of the maximum cure temperature without sacrificing the thermal resistance is a challenging task to explore new methods in order to improve the overall properties of benzoxazine resins. n-butoxy triethanol amine titanate is a unique organo inorganic chelating complex with titanium as the central atom in the complex acts as lewis acid which readily abstracts electron pair of electron donor atom like amine or alcohol or carboxylic acid and lowers the reaction temperature required for cross link reaction [43-48]. Reaction of titanium with oxazine ring will results in tightening in the network that increase the service temperature, cross link density and thermal stability. Organic groups present in the complex generates insitu reactive polar functional groups helps in uniform dispersion and overcomes the disadvantages of incompatibility faced by most of the inorganic fillers and also helps in providing effective bonding with glass fabric reinforcement.

To the best of our knowledge, blending of bisphenol F benzoxazine with n-butoxy triethanol amine titanate (TEA) chelate complex has not been reported. Direct blending of TEA with benzoxazine instead of sol-gel process can overcomes the usage of water and this prevents hydrolysis, improper cure or voids formation with non stoichiometric excess of water [49-54]. Hence, in the present work, the n-butoxy triethanol amine titante (TEA) is directly blended with bisphenol F benzoxazine resin (BZ) to achieve improved performance. In order to demonstrate and establish the reaction between BZ and TEA, reactivity is studied between model compounds such as phenol, tera isobutoxy titanate, and triethanol amine. In this study, E glass reinforced composites of benzoxazine and various benzoxazine-TEA blends were prepared and investigated their curing characteristic, stiffness, service temperature, cross link density, phase distribution, thermal stability, hydrolytic stability and flame retardant properties when compared to benzoxazine composite.

2.0 Experimental

2.1 Raw Materials:

The polybenzoxazine precursor, aniline based bisphenol F benzoxazine (BZ) type with trade name Araldite MT 35700 having softening point of 80-85^0 C and viscosity at 100^0 C is 500 to 2500 cPs was procured from Huntsman Advanced Materials, Switzerland. n- Butoxy triethanol amine titanate (TEA) with trade name of Fine Hard 1954 (Ti from TiO_2 is 20.75 wt. % and relative viscosity at 50^0 C is 136 sec.) was purchased from Fine Finish Organics Limited, Mumbai, India. Tetra isobutoxy titanate with trade name PBT having density 1.02 g/cc was procured from Synthochem, Indore India. Triethanol amine (TE) having density: 1.12 g/cc and refractive index:1.484 was purchased from Merck, India. Phenol (PhOH) having freezing point 39.5^0 C was procured from Qualigen, India. The E glass fabric of Hindustan fabrics, Mumbai, India and release (D200 TFP) fabric from De-comp Composite Inc., USA respectively were used. Both the vacuum bagging film (50 micron thick) and breather fabric (AB 1060V) were obtained from Aerovac, UK. Solvent methyl ethyl ketone (MEK) of reagent grade is procured from Merck, India.

2.2. Preparation of model compounds:

8.5 g of PBT is taken in a round bottom flask and added 10.84 g of PhOH and mixed well to obtain uniform mixture PhOH: PBT. 10 g of BZ is taken in a round bottom flask and heated to 80^0 C to get a low viscous solution. 3 g of PBT is added to this solution and stirred well to get uniform mixture BZ: PBT. For preparation of BZ:TE mixture, similar procedure of preparation of BZ:PBT is followed by adding TE instead of PBT. Curing of all samples are carried out as per Fig-1a.

2.3. Preparation of E glass fabric reinforced polybenzoxazine (EBTA0) composite:

Prior to the preparation of glass–benzoxazine prepregs, BZ (240 g) was taken into a vessel, MEK solvent (72 g) was added and the mixture were heated at 70°C to obtain a clear solution of benzoxazine resin. The prepared benzoxazine resin solution was cooled to room temperature and uniformly spread on the E-glass fabric with brush. The prepared BZ prepregs were allowed for drying at room temperature till it gets tackiness. The prepregs were cut in to 7 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. A releasing film and metallic caul plate was placed over the layers. The set up was enclosed in breather cloth and vacuum bag and the curing was carried out in the oven under vacuum of 400 mm Hg as per the cure cycle represented in Fig-1a to obtain EBTA0 composite. This composite was used as a reference material for comparison with E glass fabric reinforced polybenzoxazine titanate (EBTA) composites

2.4. Preparation of E glass reinforced polybenzoxazine titanate composites (EBTA):

To the prepared benzoxazine solution (as per procedure given in 2.3) TEA was added and stirred well at room temperature (gently). Table-1 represents sample code of the formulations, different weight of BZ and TEA and their wt% taken for the experiments. From the prepared BZ-TEA mixture, 200 g have been taken and uniformly spread with brush on the E glass fabric. The prepared BZ-TEA prepregs were allowed for drying at room temperature till it gets tackiness. For preparing EBTA composites, similar procedure given in section 2.3 and cure cycle as per Fig-1b were followed.

2.5. Determination of density, fiber and volume fractions:

Density of cured resins, fiber and composites were determined separately by liquid displacement method . In this test, the sample is weighed in both air and water separately and calculated using equation 1.

$$\rho_s = [W_a/(W_a - W_w)] \times \rho_w \qquad \text{(Eq. 1)}$$

Where ρ_s : Density of sample, W_a: Wt. of sample in air, W_w: Wt of sample in water and ρ_w : Density of water

Fiber volume fraction (V_f) and void volume fraction (V_v) were obtained by determining resin content using ignition loss method. The composite sample is heated at 650^0 C in air till constant weight is obtained. V_f and V_v are theoretically calculated with equations 2 and 3 respectively.

$$V_f = (W_f / \rho_f) / (W_c / \rho_c) \qquad \text{(Eq. 2)}$$

$$V_v = 100 - \rho_c [(r / \rho_r) + f / \rho_f)] \qquad \text{(Eq. 3)}$$

Where $W_{c,\,f}$: Wt. of composite, and fiber respectively , V_v : Volume fraction of void, $\rho_{c,\,r,\,f}$: Density of composite, resin and fiber respectively, r: Resin content (%), f: Fiber content (%)

2.6. Water absorption resistance test for EBTA0 and EBTA composites:

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 was then 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 at 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 using equation 4

$$\text{Water absorption (\%)} = [(M_2 - M_1)/M_1] \times 100 \qquad \text{(Eq.4)}$$

2.7. Flame retardant test for EBTA0 and EBTA composites:

Four specimens of 4 mm thick, 125 mm long and 13 mm wide were used for the testing. The specimens were vertically hanged and n-butane gas burner with blue flame was burned for 10 seconds (first ignition) at the bottom. After first ignition, the burner was removed to observe self-extinguishing time and the dripping characteristics. The second ignition was carried out for 10 seconds on the same (first ignited) sample and the self- extinguishing time/dripping characteristics were recorded.

2.8. 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 650 to 4000 cm^{-1} in the transmission mode.

Differential scanning calorimeter (DSC) thermo grams were recorded with a TA Instruments (USA) DSC 2920 model at a heating rate of 10 ^{0} 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. 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 5 ^{0} 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 10^{0}C min^{-1} under atmosphere between 30 and 600^{o}C.

Density of cured resin, fiber and composite were determined separately as per ASTM D 792. Fiber volume fraction (V_f) and void volume fraction (V_v) were determined as per ASTM D 2734-09. Water absorption was estimated as per JIS K7209.

Flame resistance was conducted and estimated as per UL-94V flammability vertical test. Fractured surfaces of flexural tested samples of polybenzoxazine and EBTA composites were analyzed with scanning electron microscope (SEM, JEOL JSM 5800 Digital).

3.0 Results & Discussion

Chemical structures of benzoxazine (BZ), n- butoxy triethanol amine titanate (TEA) and model compounds such as phenol (PhOH), triethanol amine (TE) and tetra isobutoxy titanate (PBT) used in our work are represented in Fig-2. It is believed that the addition of TEA to E glass fabric reinforced bisphenol F polybenzoxazine composites shows three fold advantages. The acidic nature of titanium lowers maximum cure temperature that causes tight network of rigid phenoxy titanate structures and enhances the cross link density, service temperature, thermal stability and brittleness of the material [46, 55-58]. The second advantage is that the aliphatic, reactive multi branches of TEA lowers the brittleness with uniform dispersion which prevents phase separation and also helps in increasing cross link density and providing effective interfacial adhesion between E glass fabric and BZ-TEA copolymer is the third advantage [43-47]. Various E glass fabric reinforced benzoxazine – TEA composites were prepared by using variable weight percentages of BZ and TEA as shown in the Table-1. Different weight ratios of E glass fabric reinforced benzoxazine-TEA were represented as EBTA0 (BZ/TEA: 1/0); benzoxazine-TEA mixtures EBTA4 (BZ/TEA: 1/0.2); EBTA6 (BZ/TEA: 1/0.3), EBTA8 (BZ/TEA: 1/0.4), and EBTA10 (BZ/TEA: 1/0.5). These polybenzoxazine titanate composites prepared were inspected with reference to E glass fabric reinforced pure polybenzoxazine (EBTA0) composite in terms of service temperature (Tg), cross link density, thermal stability, hydrolytic stability, morphological properties and flame retardant properties.

It is difficult to investigate the curing reaction between BZ and TEA as it forms complex multifunctional network structures. Hence, in order to demonstrate and establish the chemical reaction between BZ and TEA, model compounds such as phenol , tera isobutoxy titanate, triethanol amine and their mixtures with weight ratio's PhOH:PBT (1.2/1), BZ:PBT (1/0.3) and BZ:TE (1:0.3) have been chosen. Functional group changes and curing characteristics were also studied with model compounds.

3.1. Model study for understanding the reactivity between BZ & TEA:

Hypothetic reaction between BZ and TEA can be predicted by evaluating DSC and FTIR for BZ and model compounds such as PBT, TE, PhOH and their mixtures.

DSC scan carried out for BZ, PBT and TE were shown in Fig-3a. BZ shows a single, well defined, sharp exotherm with the onset temperature of cure at 176^{o}C and the peak exotherm at 240 ^{0}C with heat flow area of 318 J/g which corresponds to the characteristic cure temperature for the ring opening self polymerization of benzoxazine resin [59-61]. DSC curve of PBT and TE does not show any curing reaction without any initiator (catalyst or active hydrogen containing compound) and shows endothermic events at above 200^{0}C which is may be due to boiling and decomposition [46,55]. Further, DSC scan carried out for different mixtures of precured samples of PhOH:PBT (1.2:1 wt%), BZ:PBT (1:0.3 wt%), and BZ:TE (1:0.3 wt%) were shown in Fig-3b. DSC of PhOH:PBT mixture shows an endothermic peak around 107 ^{0}C due to evolution of butyl alcohol with replacement of phenoxy group on titanium and resulting in the formation tetra phenoxy titanate [46,55-58] . DSC of BZ:PBT showed an endothermic peak around 107 ^{0} C and exothermic peak around 185 ^{0}C. This shift of exothermic peak towards lower temperature in comparison with BZ indicates acceleration of reaction due to acidic catalysis of titanium group with the evolution of butyl alcohol[62,63]. DSC of BZ:TE showed exothermic peaks at 214^0 C with a shift towards lower temperature in comparison with BZ due to acceleration of polymerization reaction caused by alcoholic groups of TE [64-65]. These model reactions indicates that titanium accelerate the ring opening of benzoxazine at lower temperatures due to the replacement of alkoxy groups present on titanium with phenoxy groups of BZ. Hydroxyl groups of alkyl amine (TE) also participate in the polymerization reaction with oxazine .

The FTIR spectra of precured samples of pure BZ, PBT, and TE, are shown in Fig-4a. The characteristic infrared absorption peaks of BZ observed at 945, 1029, 1225 and 1495 cm^{-1} are due to the presence of oxazine ring and tri substituted benzene of the benzoxazine. The characteristic peaks of PBT are at 1123, 1094 and 1037 cm^{-1} corresponds to alkoxy groups attached to titanium and TE showed 3339, 1068 and 1038 cm^{-1} due to hydroxyl groups of tertiary alkyl amine groups. FTIR spectrums carried out for cured mixtures of PhOH:PBT (1.2:1 wt%) and BZ:TE (1:0.3 wt%) are shown in Fig-4b. The disappearance of characteristic peaks of alkoxy groups of PBT i.e. 1123, 1094 and 1037 cm^{-1} and appearance of new peaks at 1270 cm^{-1} in PhOH:PBT mixtures corresponds to the formation of phenoxy titanate structures[46, 55-58]. Cured BZ:TE mixture shows the disappearance of characteristic peaks of oxazine ring of BZ and hydroxyl group at 3339 cm^{-1} of TE which indicates the ring opening reaction of benzoxazine structures with hydroxyl groups of TE [64,65].

Hence, it was observed from the model compounds that three possible chemical steps were involved during polymerization reactions of PhOH:PBT , BZ:PBT and BZ:TE mixtures which are shown in Scheme-1. The first step is the ring-opening step in which titanium of PBT present in the first two blends i.e. PhOH:PBT and BZ:PBT initiate the reaction by abstracting the electron pair of oxygen present in the phenol of PhOH:PBT mixture and oxazine ring of BZ:PBT mixture which results in the ring opening [46, 55-58] and the second step is the electrophilic substitution of the resulted iminium ion with the free ortho positions of other oxazines which results in polymerization [66, 67]. Further, this substituted titanate group reacts with other benzoxazine or phenolic groups of reacted mixture with replacement of alkoxy groups and results in di or tri or tetra substituted phenoxy titanates based on the less steric hindrances [68]. The reaction between BZ and TE indicates that hydroxyl groups of TE can also take part in the polymerization with benzoxazine and results in complex network structures. [64,65]

3.2. Curing studies

3.2.1. FTIR analysis for EBTA composites:

Based on the model compounds study, hypothetically proposed chemical reaction between BZ and TEA of EBTA composites are shown in Scheme-2. EBTA6 is selected as a representative example for carrying out curing studies of EBTA composites. The FTIR spectra of precured samples of TEA and EBTA6 are shown in Fig-5a. The characteristic peaks 1073 and 1030 cm^{-1} of TEA are due to the presence of alkoxy groups of titanate. EBTA6 sample showed all characteristic peaks of BZ and TEA. The progress of the curing reaction of EBTA6 is monitored at isothermally for different intervals at temperatures 30°C, 80°C (1hr), 150 °C (1hr), 180 °C (2hr) in oven. FTIR spectra carried at room temperature of EBTA6 at various cured stages represented in Fig-5b showed the gradual progress of the ring opening and polymerization reactions with increase of time and temperature. The curing has been completed at 180 ^{0} C (2hr). The observed disappearance of characteristic peaks corresponds to absence of oxazine and tri substituted benzene rings of BZ and appearance of peak at 1457 cm^{-1} is due to the formation of tetra- substituted benzene structures. The disappearance of characteristic peaks corresponds to the absence of alkoxy titanate groups of TEA and appearance of peaks at 1017 and 1270 cm^{-1} is due to the formation of phenoxy titanate and aromatic ether linkages. These changes suggest the completion of the ring opening of BZ and the formation of polybenzoxazine–titanate composite at 180^0 C. Hence, this study overcomes the drawbacks associated with high temperature curing of polybenzoxazine.

3.2.2. DSC analysis for EBTA composites:

Fig-6a represents DSC thermo gram of TEA samples and precured sample of EBTA6. DSC curve of TEA does not show any curing reaction without initiator or catalyst and shows endothermic and exothermic thermal events at above 200^0C [46, 62] . DSC curve of EBTA6 shows the decrease in onset temperature to 115^0 C, peak exotherm to 213^0 C and heat flow area to 80.02 J/g respectively when compared to BZ sample. Shift of exothermic peak for EBTA6 towards low temperature and decrease in area of benzoxazine peak in the composite indicates acceleration of reaction due to acidic catalysis of titanium group [48,55-57,62,66,69] and insitu generated hydroxyl groups. This supports our hypothetical ring opening chemical reaction predicted by model compounds. Fig-6b represents the DSC scan of polybenzoxazine and EBTA composites after curing. EBTA0 has cured at curing temperature 200^{o}C [60,70] whereas, EBTA composites were cured at 180^{0} C which was represented in Fig-1a&1b. The disappearance of exothermic peaks in polybenzoxazine and EBTA composite samples indicates that all samples showed complete polymerization of BZ pre polymer in the mixture. Endothermic peaks at 242 and 281^{o}C for EBTA8 and EBTA10 indicates left over TEA in the mixture. All these results are in good agreement with our FTIR studies.

3.3. Network properties:

All composite samples were subjected to DMA studies to study the stiffness and cross link density from storage modulus; glass transition temperatures (Tg) and phase distribution from Tan δ.

3.3.1 Storage modulus: Stiffness and cross link density

Storage modulus scan for EBTA0 and ploybenzoxazine titanate composites were shown in Fig-7 and summarized in Table-2. Storage modulus of glassy plateau at 35^{0} C for the polybenzoxazine and EBTA composites EBTA4, EBTA6, EBTA8 and EBTA10 composites were found to be 1.3, 2.3, 2.6 4.7 and 5.8 GPa respectively. Polybenzoxazine composite showed relatively less stiffness when compared with other EBTA composites due to low link density caused by inter and intra molecular hydrogen bonding. In the case of EBTA composites, the increase of stiffness with incorporation of TEA in the benzoxazine matrix may be due to increase of reinforcement effect of uniformly distributed titanate and also due to formation of additional cross links.

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 [71-72].

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

Where, C is the cross link density, R is the gas constant, and T is the absolute temperature (i.e. at Tg + 30°C) and E'_R is the rubbery modulus at T. Table-2 shows that cross link densities calculated for polybenzoxazine and EBTA composites EBTA4, EBTA6, EBTA8 and EBTA10 were found to be 4.4, 7.55, 8.12, 12.6 and 19.3. E6 g mole^{-1} respectively. These results indicates that cross link density of polybenzoxazine increased gradually with the increase of amount of TEA in EBTA composites. Hence, the disadvantages of having low link density in polybenzoxazines can overcome with the addition of TEA.

3.3.2. Service temperature and phase distribution:

Tan δ scan carried out as a function of temperature on polybenzoxazine and other EBTA composites were given in Fig-8. Appearance of a single Tan δ peak for each composite show that the monomeric precursors had copolymerized without any detectable phase separation. This uniform dispersion of titanate complex with in polybenzoxazine titanate complex might be due to insitu generated reactive multiple aliphatic branches of TEA. The Tan δ peak maxima's considered as Tg for EBTA composites are summarized in Table-2. From the Fig-8 and Table-2, the Tg's of the EBTA0, EBTA4, EBTA6, EBTA8 and EBTA10 were found to be 175, 187, 190, 187 and 186^{o} C respectively. It was observed that Tg of all EBTA composites were higher when compared to polybenzoxazine composite due to lower segmental mobility with fewer relaxing species. This indicates high degree of cross linking density for EBTA composites. The increase of Tg of EBTA4 (16.5 wt% TEA) when compared to EBTA0 is may be due to increase in cross link density. The relative decrease of Tg for EBTA4 over EBTA6 (23 wt% TEA) is may be due to low cross link density with less stoichiometric quantity of TEA. The increase of Tg of EBTA6 when compared to polybenzoxazine and other EBTA composites is may be due to increase of cross link density with the stoichiometric quantity of TEA. The gradual decrease of Tg of EBTA8 (28.57 wt% TEA) and EBTA10 (33 wt% TEA) when compared to EBTA6 is due to non stoichiometric excess of TEA which may acts as a plasticizer . This is in good accordance with our assumptions made with DSC and FTIR studies.

In EBTA composites, addition of TEA enhances Tg, cross link density, brittleness of the material due to formation phenoxy titanate rigid structures. At the same time insitu generated hydroxyl flexible aliphatic groups improves cross link density and lowers the brittleness and Tg. Hence, selection of quantity of TEA in polybenzoxazine-titanate composites plays an important role in obtaining high service temperature.

3.4 Thermal degradation and thermal stability properties.

Fig-9 represents thermal degradation of polybenzoxazine and EBTA composites. Thermal degradation temperature (T_d) at 5% wt loss, char yield at 600^0 C and maximum thermal stability temperature for all composites are summarized in Table-3. Initial thermal degradation of EBTA0 composite below 300^0 C is due to pyrolytic evolution of aniline derivative of mannich bridge, intermediate degradation between 300^oC and 400^0C and the final degradation above 400^0 C are due to evolution of substituted phenolic derivative and the evolution of phenol respectively [24]. All EBTA composites samples showed low T_d when compared with polybenzoxazine composite which indicates the fast release of low temperature resistant aliphatic flexible and amine groups over a small temperature range. The reduction of T_d values for EBTA composites is may be due to incorporation of flexible aliphatic and amine groups in the network structure [24, 71, 73]. Further, the char yield of EBTA composites increases when compare to polybenzoxazine composite up to 23 wt % of TEA addition. EBTA4 and EBTA6 composites with fiber volume content 59 and 60% and void content 1.0 & 1.1 % respectively shows char yield 79.35 and 82.34 % respectively when compared to polybenzoxazine composite which is having fiber volume content 58 % , void content 1.2% and char yield 78.61%. This increase of char yield for EBTA4 and EBTA6 when compared to polybenzoxazine composite is due to steady increase in cross link density with TEA [54, 66]. Other EBTA composites EBTA8 & EBTA10 with fiber volume content 59% and 58% and void content 0.8 and 0.9 % respectively shows char yield 76.88 and 73.08 % respectively when compare to polybenzoxazine composite is may be due to additional flexible cross links caused by excess of TEA. This is in good accordance with our assumptions made with FTIR, DSC and DMA studies.

Thermal stabilities for EBTA composites determined from differential thermo gravimetric analysis were shown in Table-3. All EBTA composites showed improved thermal stability when compared to EBTA0 composite. EBTA composites EBTA4, EBTA-6, EBTA8 and EBTA10 showed increase in thermal stability from 517^0C/mg of polybenzoxazine composite to 531, 550, 523 and 520 ^{0}C/mg respectively. It was observed that steady increase in thermal stability for EBTA4 and EBTA6 is may be due to increase in cross link density up to 23 wt. % TEA. The other EBTA composites EBTA8 and EBTA10 showed steady decrease in thermal stability when compared EBTA4 and EBTA6 is may be due to combine effect of increase in cross link density and plasticization effect of non stoichiometric excess of TEA. Hence, EBTA composites up to 23 wt % of TEA shows high char yield and thermal stability in comparison with polybenzoxazine composite.

3.5. Water absorption studies:

Water absorption studies carried out for EBTA0 and EBTA composites are shown in Table-3. EBTA composites shows steady decrease in water absorption till 23 wt% of TEA and than increases with increase of TEA content when compared to EBTA0 composite. The decrease in water absorption of EBTA4 and EBTA6 from 4.56 % of polybenzoxazine composite to 4.3 and 3.6 % is due to increase of cross link density that prevents water absorption [74]. Slight increase in water absorption of EBTA8 and EBTA10 from 4.56% of EB composite to 4.73 and 5.43 % is may be due to increase of non aromatic, aliphatic, hydroxyl and amine groups caused by the non stoichiometric excess of TEA [75]. Water absorption studies shows that EBTA composite EBTA6 having 23 wt % of TEA shows highest water absorption resistance among all the composites.

3.6 Flame retardant property:

Flame retardant tests carried out for EBTA0 and EBTA composites are given in Table-4. It was observed that all EBTA composite samples showed flame extinguishing time less than 6 seconds on each flame of first ignition and less than 23 seconds on second ignition flame. All EBTA composite samples does not show flammability up to the holding clamp and also any dripping of the particle for flaming cotton present below the testing samples is to be seen. This indicates that flame retardency of all EBTA composites are non combustible and comes under V1 category and retained the flame retardency of polybenzoxazine composite. The reason that EBTA composites were not achieved more flame retardency than EBTA0 is may be due to the combine effect caused by increased cross link density with rigid, thermal stable phenoxy titanate structures and flexible, aliphatic, hydroxyl and amine groups of TEA.

3.7. Micro structure study:

SEM pictures obtained from the fracture surfaces of polybenzoxazine and other EBTA composites were shown in Fig-10. Fig-10a representing the fracture surface of polybenzoxazine composite shows poor adhesion between fibres and polymer with the smooth surfaces of the fibres that are pulled out from the matrix and cavities within the composite [41]. The fracture surfaces of all EBTA composites shown in Fig-10b-10e are rough when compared with polybenzoxazine composite which indicates good interfacial adhesion between BZ-TEA copolymer and E Glass reinforcement. This good interfacial adhesion in the EBTA composites is may be due to the formation of stable phenoxy titanate and aliphatic structures with hydroxyl groups of E glass fabric [76]. The schematic representation of possible chemical bonds between E glass fabric with benzoxazine and BZ-TEA copolymer is given in Fig-11. The increase of interfacial adhesion of BZ-TEA copolymer with E glass fabric causes effective increase in thermo mechanical properties. This is in good accordance with DMA and TGA studies.

4. Conclusion:

In this study, for the first time insitu generating reactive multiple branched aliphatic titanate i.e., triethanol amine titanate (TEA) chelate complex in various ratios were utilized along with E glass fabric reinforced bisphenol F benzoxazine resin. The hypothetic chemical reaction between BZ & TEA was understood by studying the reactivity between model compounds such as phenol, tera isobutoxy titanate and triethanol amine. Curing conditions were optimized and final cure temperature was established for EBTA composites using FTIR and DSC studies. FTIR and DSC showed that EBTA composites with TEA up to 23 wt. % were completely cured. DMA studies were carried out to study the stiffness, cross link density, phase distribution and service temperature for all the EBTA composites and found to be improved when compared to the homo polymerized polybenzoxazine composite EBTA0. TGA showed higher char yield and thermal stability for EBTA6 composite with 23% TEA when compare to EBTA0 composite. Similarly, water absorption resistance of EBTA6 shows more than EBTA0 composite. Flame retardency of all EBTA composites comes under V1 class and retained the flame retardency of EBTA0 composite. SEM carried out for all EBTA fractured composite samples showed improved interfacial adhesion between E glass fabric and BZ-TEA copolymer. Hence, the newly developed polybenzoxazine titanate composites showed low cure temperature, with improved service temperature, cross link density, stiffness, water absorption resistance, thermal stability and char yield when compared to E glass fabric polybenzoxazine composites. These new material looks promising to overcome many of the traditional shortcomings associated with polybenzoxazine and conventional resin composites.

Acknowledgements

The authors wish to thank Director, ASL and Director, DRDL for supporting this study.

Notes and references

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Tables:

Table-1: Sample codes and formulation details of EBTA composites

Sample codes	E Glass fabric, meters	Benzoxazine resin (BZ), wt, g	n-butoxy triethenol amine titanate (TEA), wt, g	Benzoxazine wt %	Triethanol amine titanate, wt%
EBTA0	1.25	200	0	100	0
EBTA4	1.25	200	40	83.33	16.66
EBTA6	1.25	200	60	76.93	23.07
EBTA8	1.25	200	80	71.43	28.57
EBTA10	1.25	200	100	67	33

Table-2 : Thermo-mechanical properties of EBTA composites

Sample codes	E’			Tanδ
	RT, GPa	Tg+30^0 C, MPa	Cross link density, g mole^{-1}	Tg , °C
EBTA0	1.3	5410	4.49787E6	175
EBTA4	2.3	9090	7.55743E6	187
EBTA6	2.6	9773	8.12527E6	190
EBTA8	4.7	15203	1.26398E7	187
EBTA10	5.8	23332	1.93982E7	186

Table-3: Physical properties, TGA and water absorption properties of EBTA composites

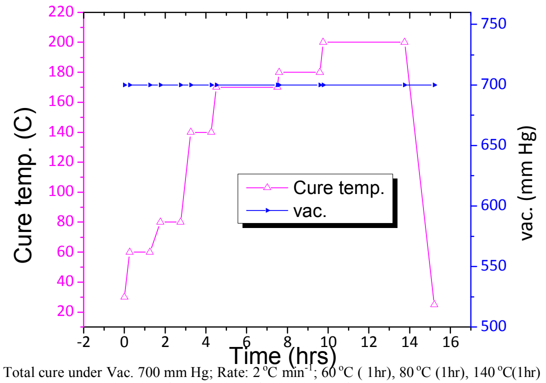
Sample codes	Density, g/cc	Fiber Volume content %	Void content	TGA			Water absorption , %
				T_d, ^{0} C (5% wt loss)	Char Yield, 600^0 C in air, %	Thermal stability, ^{0}C/mg	
EBTA0	1.83	58±1.7	1.2±0.9	455.2	78.61	517	4.56
EBTA4	1.89	59±0.9	1.0±0.7	412	79.35	531	4.3
EBTA6	1.92	60±0.8	1.1±0.5	391	82.34	550	3.67
EBTA8	1.88	59±1.2	0.8±0.5	346	76.88	523	4.735
EBTA10	1.87	58±0.6	0.9±0.4	331	73.08	520	5.435

Table-4 Flame retardency values for EBTA composites

Sample codes	No. of Samples : 4		sum of 1st ignition, Sec.	sum of 2nd ignition, Sec.	Sum of 1st+ 2nd ignition, Sec.	UL94 V Class
	1st ignition, Sec.	2nd ignition, Sec.				
EBTA0	3.41, 1.59, 2.17, 2.81	18.32, 13.74, 8.04, 12.13	9.98	52.23	62.21	v1
EBTA4	0.5, 0.3, 2.9, 4.0	14.30, 14.36, 17.92, 15.42	7.7	62	69.7	v1
EBTA6	3.6, 2.63, 2.5, 2.5	16.50,16.37, 16.5, 17.5	11.23	66.87	78.1	v1
EBTA8	3.5,2.5, 2.0, 2.5,	15.5,14.5, 20.0, 13.0	10.5	63	73.5	v1
EBTA10	5.5, 6.5, 3.4, 6.0	18.1, 18.5, 13.0, 23.1	21.4	72.7	94.1	v1

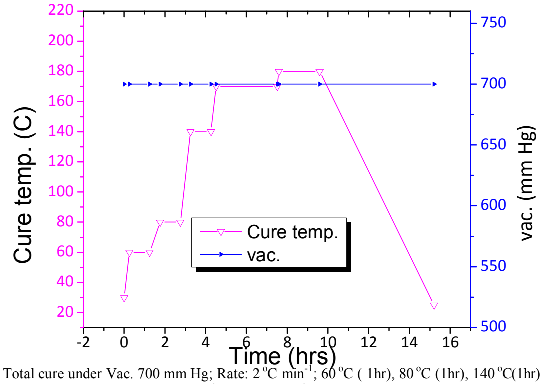
Figures:

Fig-1a : Cure cycle for model compounds and EBTA0 composite:



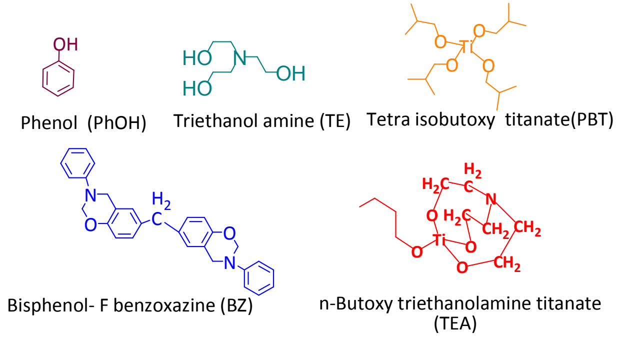
Total cure under Vac. 700 mm Hg; Rate: 2 °C min^{-1}; 60 °C (1hr), 80 °C (1hr), 140 °C(1hr) 170 °C (3 hrs), 180 °C (2hrs), 200 °C (4hrs)

Fig-1b : Cure cycle for EBTA composite:



Total cure under Vac. 700 mm Hg; Rate: 2 °C min^{-1}; 60 °C (1hr), 80 °C (1hr), 140 °C(1hr) 170 °C (3 hrs), 180 °C (2hrs)

Fig-2: Chemical structures of Bisphenol F benzoxazine resin , n-Butoxy triethenol amine titanate, Phenol, Tetra isobutoxy titanate and triethanol amine



Phenol (PhOH)

Triethanol amine (TE)

Tetra isobutoxy titanate(PBT)

Bisphenol- F benzoxazine (BZ)

n-Butoxy triethanolamine titanate (TEA)

Fig-3a: DSC of precured samples of BZ, TE and PBT

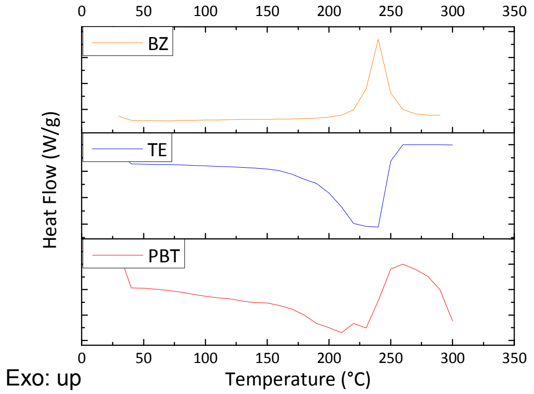


Fig-3b: DSC of precured samples of PhOH:PBT, BZ:PBT and BZ:TE mixtures

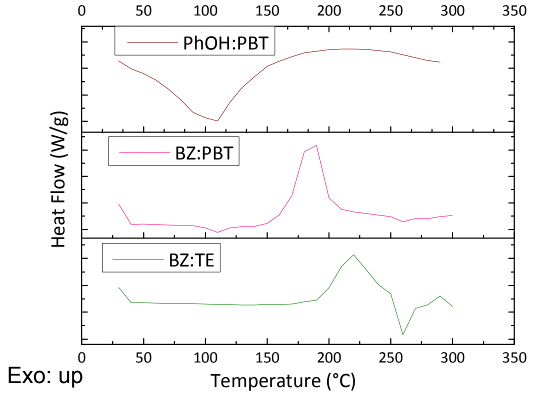


Fig-4a : FTIR of precured samples of BZ, PBT and TE

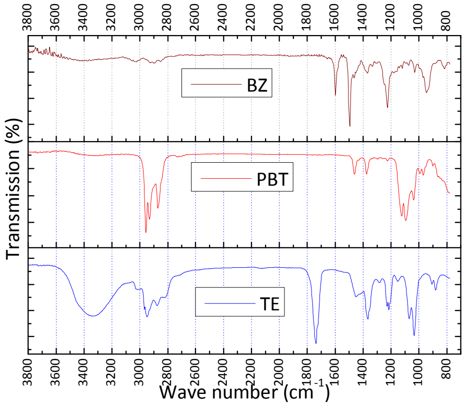


Fig-4b: FTIR of cured samples of PhOH:PBT and BZ:TE mixtures

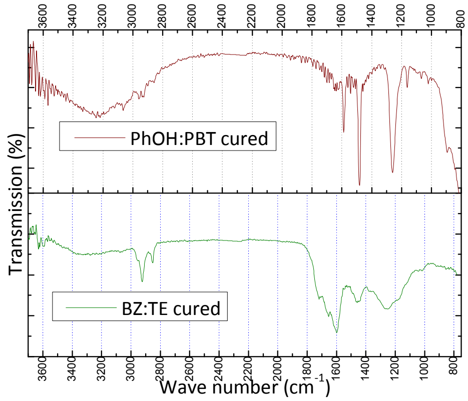


Fig-5a: FTIR of precured samples of TEA and EBTA6

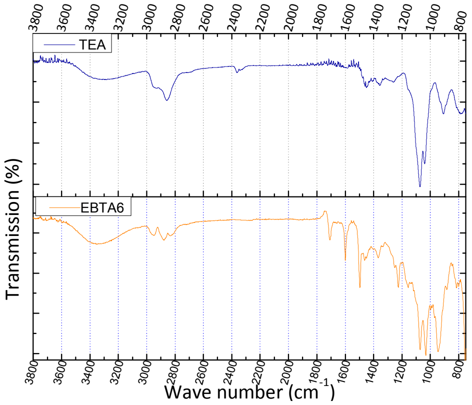


Fig-5b: FTIR of EBTA6 composite at various curing stages:

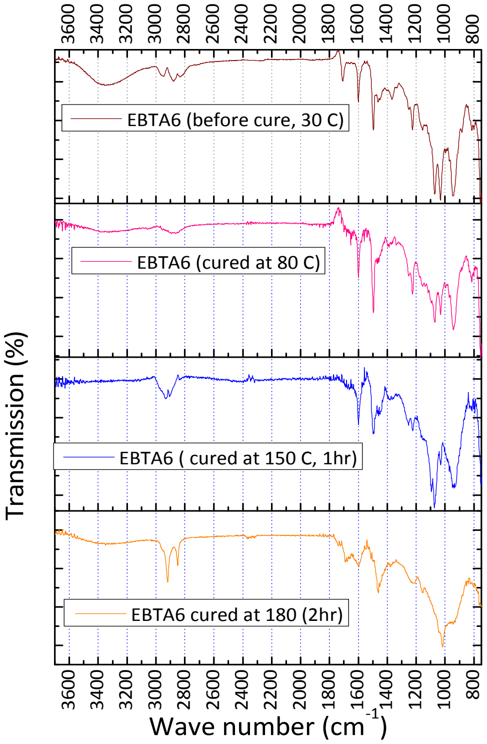


Fig-6a: DSC of precured samples of TEA and EBTA6 composite

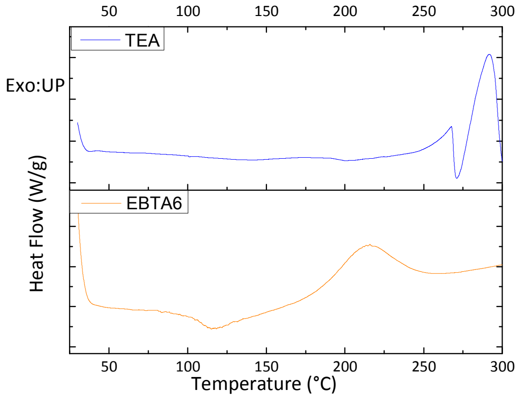


Fig-6b: DSC of cured samples of EBTA composites

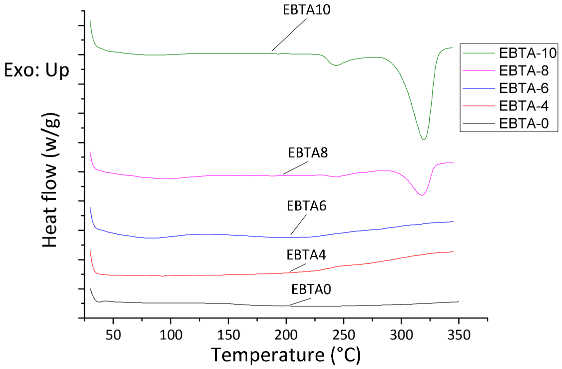


Fig-7: Storage modulus of EBTA0 and EBTA composites

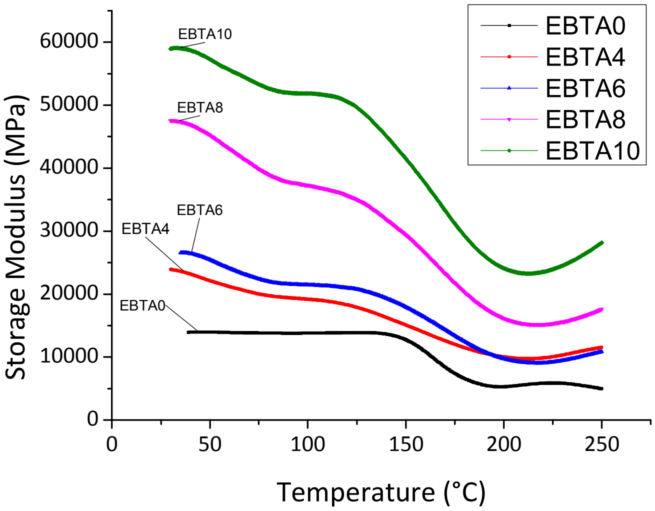


Fig-8: Tan δ of EBTA0 and EBTA composites

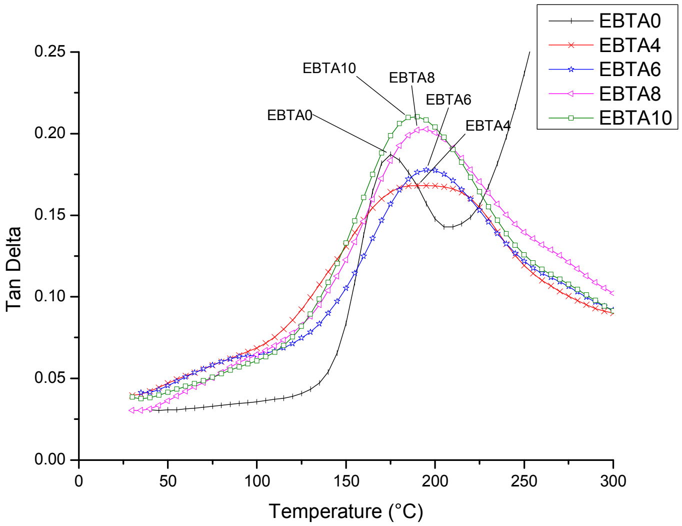


Fig-9: Thermal degradation curve of EBTA0 and EBTA composites

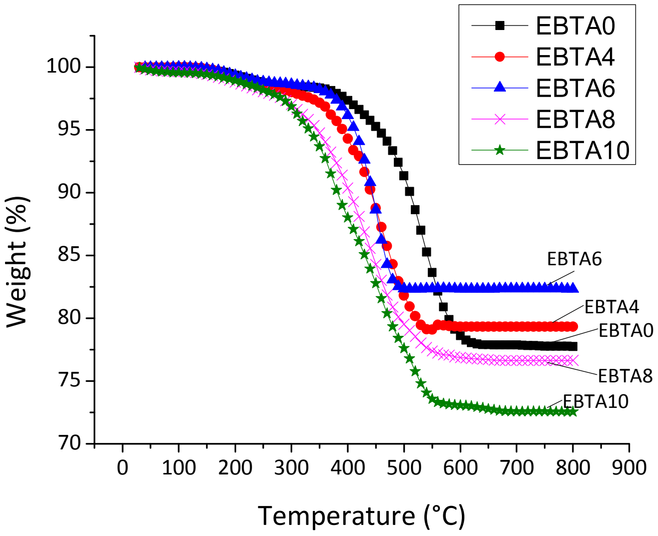


Fig-10a: SEM image of fractured sample of EBTA0

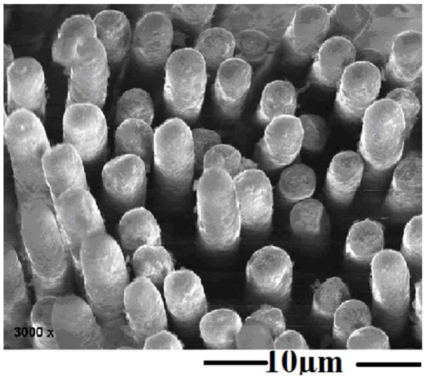


Fig-10 b to 10e: SEM images of fractured samples of EBTA composites, 10b: EBTA4, 10c: EBTA6, 10d:EBTA8, 10e:EBTA10

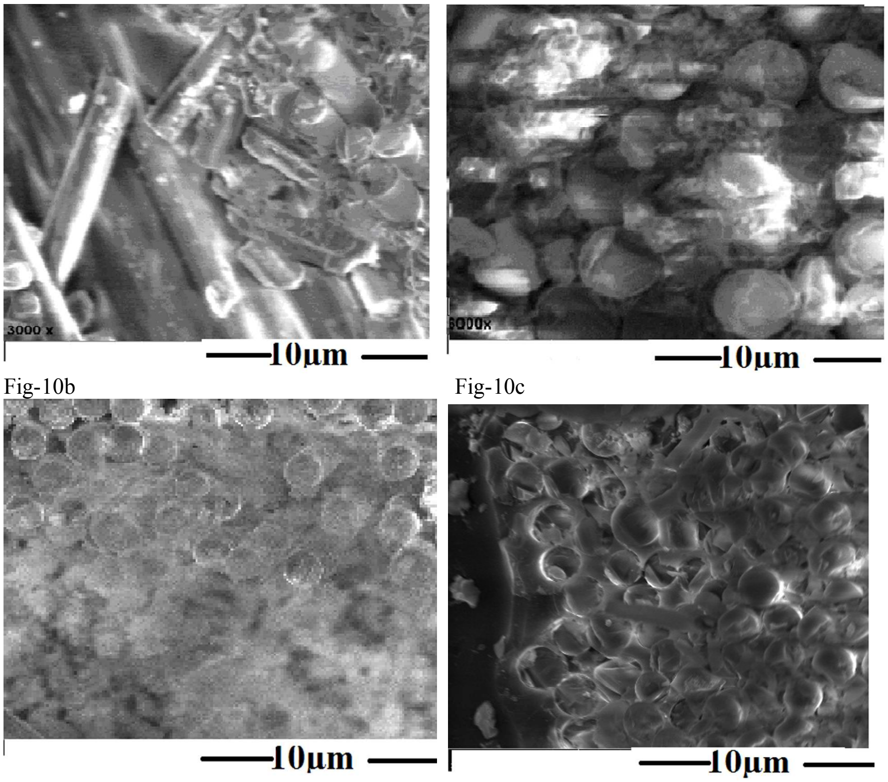


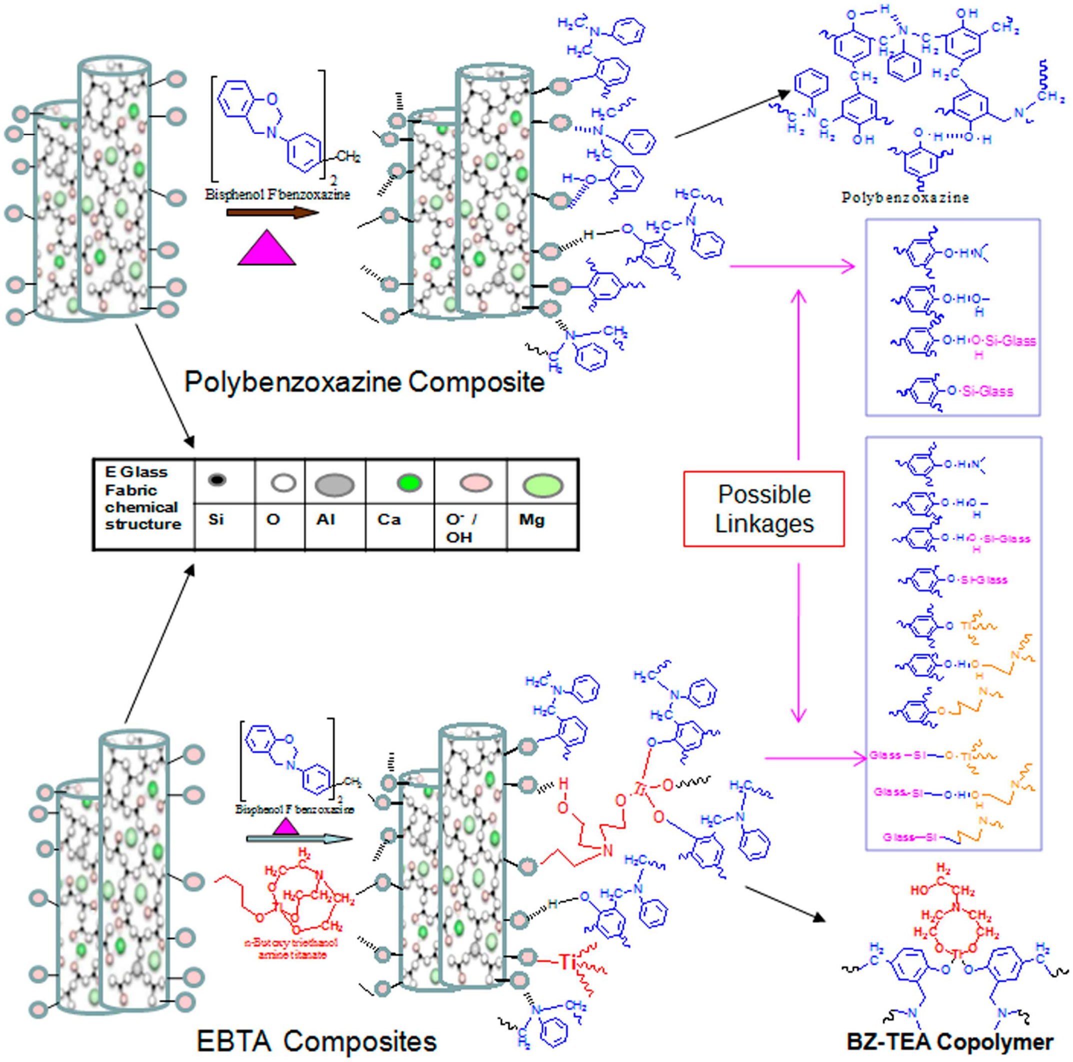
Fig-10b

Fig-10c

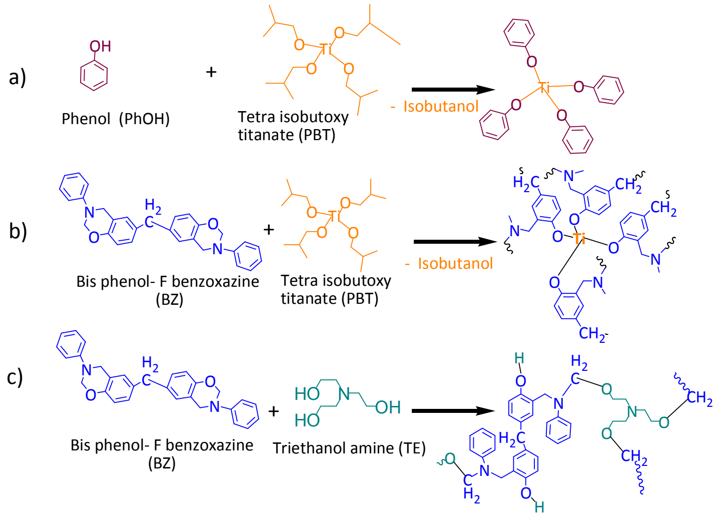
Fig-10d

Fig-10e

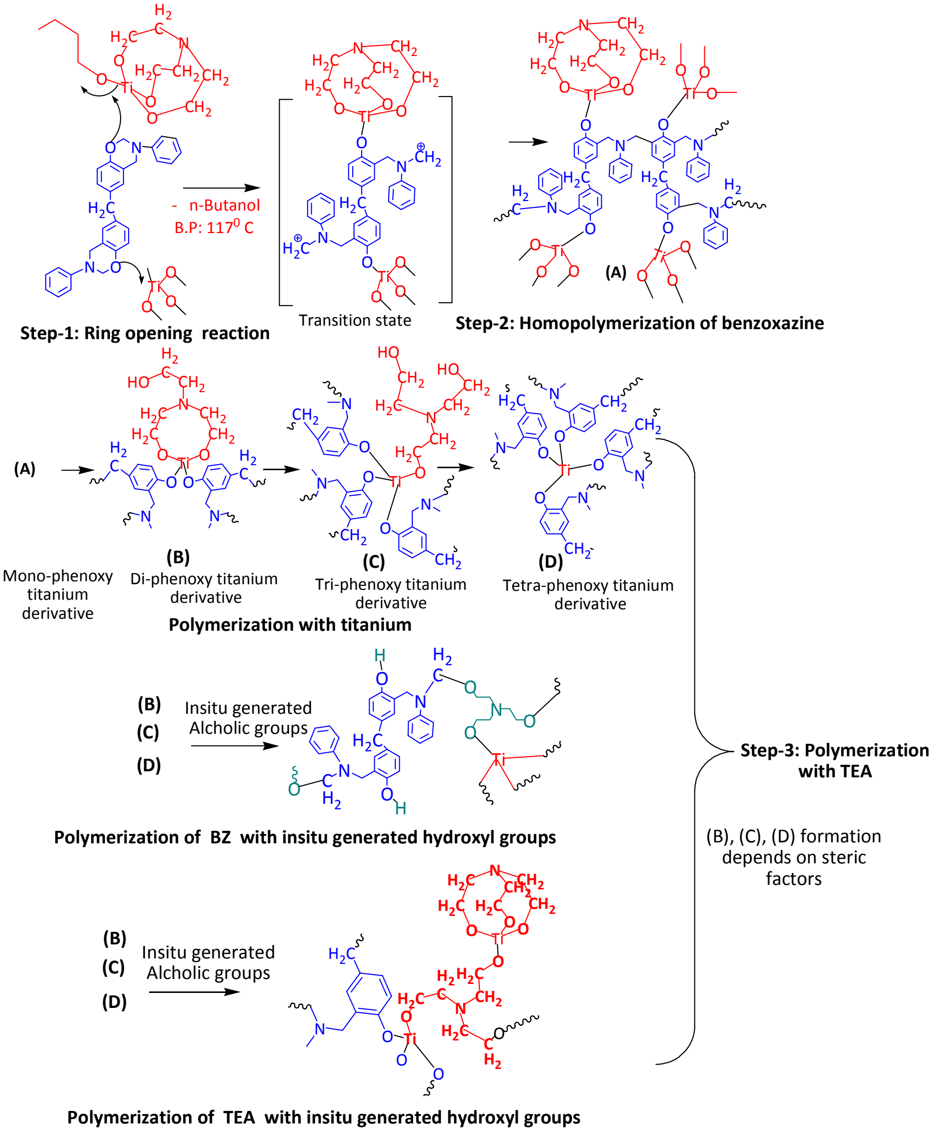
Fig-11: Schematic representation of chemical bonds between E glass fabric with benzoxazine and BZ-TEA copolymer



Scheme-1:


a)
Phenol (PhOH)
+
Tetra isobutoxy titanate (PBT)
- Isobutanol
b)
Bis phenol- F benzoxazine (BZ)
+
Tetra isobutoxy titanate (PBT)
- Isobutanol
c)
Bis phenol- F benzoxazine (BZ)
+
Triethanol amine (TE)

Scheme-2:


- n-Butanol
B.P: 117^0 C
Step-1: Ring opening reaction
Transition state
Step-2: Homopolymerization of benzoxazine
(A)
(A)
(B)
(C)
(D)
Mono-phenoxy titanium derivative
Di-phenoxy titanium derivative
Tri-phenoxy titanium derivative
Tetra-phenoxy titanium derivative
Polymerization with titanium
(B)
(C)
(D)
Insitu generated Alcholic groups
Polymerization of BZ with insitu generated hydroxyl groups
Step-3: Polymerization with TEA
(B), (C), (D) formation depends on steric factors
(B)
(C)
(D)
Insitu generated Alcholic groups
Polymerization of TEA with insitu generated hydroxyl groups