

Thermosetting Blends of Acid Modified Polybenzoxazine and Unsaturated Polyester: Study on Intermolecular Specific Interactions and Their Thermal, Mechanical Properties

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Abstract: Acid modified polybenzoxazine (PBA-aa) /unsaturated polyester (UPR) blends were prepared by an in situ curing of acid benzoxazine monomer (BA-aa) in the presence of UPR. It was expected that after curing, the PBA-aa/UPR blends would be miscible since the phenolic hydroxyls and acid carbonyl group in the PBA-aa molecular backbone have the potential to form intermolecular hydrogen-bonding interactions with the carbonyls of UPR and thus would fulfil the miscibility of the blends and finally lead to enhance the thermal and mechanical properties. Fourier-transform infrared spectroscopy (FT-IR) conformed that there were intermolecular hydrogen-bonding interactions between PBA-aa and UPR after curing. Thermal properties of the blends have been investigated by using DSC and TGA. Thermal stability of the blends increased with increasing amount of polybenzoxazine in the composition. Fracture morphology study has been done by SEM. The best miscibility effect was achieved for 10 wt% loading level polybenzoxazine in the blend, while at this level of blend mechanical properties were found to be higher. The increase in mechanical properties of the blend indicated improved interfacial interaction between the two discrete phases (polybenzoxazine and unsaturated polyester) induced by the functional groups. The composition having 10 wt% polybenzoxazine and 90 wt% unsaturated polyester resin possesses highest mechanical properties with comparatively higher thermal stability.

Keywords: Polybenzoxazine, unsaturated polyester resin, blend, hydrogen bonding

1. Introduction

Polybenzoxazine is a novel class of thermosetting polymeric material which has various outstanding properties such as slow water uptake, high thermal stability, no requirement of catalyst for curing, dimensional stability, no by product after curing, no toxic gases release during curing, molecular design flexibility, near zero shrinkage after processing, etc [1]-[4]. Nevertheless, polybenzoxazine is a phenolic resin, i.e. it has some unique limitation of phenolic resin that is their brittleness and difficulty in processing at high temperature and pressure, however, polybenzoxazine possess an important property that is their ability to be blend with various other resins such as epoxy, polyurethane, etc therefore, this leads to their easy processability and improved mechanical and thermal properties in addition to some unique properties and application [5]-[7]. Therefore, in recent year's polybenzoxazine blends have attracted considerable

attention by researcher, engineers and polymer industries because of their unique physical, mechanical and thermal properties as well as easy processability with wide range of applications as compared to neat polybenzoxazine. In particular, the polybenzoxazine blend finds some applications in many areas, such as prepreg components, in manufacturing composites, casting of electrical components, for lamination and impregnation process, etc [8]-[10]. Consequently, the blending of benzoxazine with other resins was reported by many researchers. For example, the addition of epoxy to the polybenzoxazine network greatly increases the crosslink density of the thermosetting matrix and strongly influences on its mechanical properties. Though, The poly(benzoxazine-urethane) alloys were synthesized from urethane prepolymer and mono-functional or bi-functional benzoxazine resins. It was reported that during polymerization, there could be intermolecular reaction between hydroxyl groups (-OH) of benzoxazine monomer and isocyanate groups (-NCO) of urethane prepolymer. That means even small amount of benzoxazine added in the polyurethane could increase the thermal stability of the polyurethane [11]. Huang and Yang et al., [10] prepared the blends between bisphenol-A/methylamine-based benzoxazine resin (BA-m) and poly(ϵ -caprolactone) (PCL) via solution blending method. The miscibility and thermal behaviors of the blends were studied. The enhancement of flexural properties of the polybenzoxazine/poly(ϵ -caprolactone) blends was reported. In this paper, we report the preparation of acid modified benzoxazine-unsaturated polyester blend with variation in their ratios. The variation of properties of this acid modified benzoxazine-unsaturated polyester blend with changing compositions was investigated.

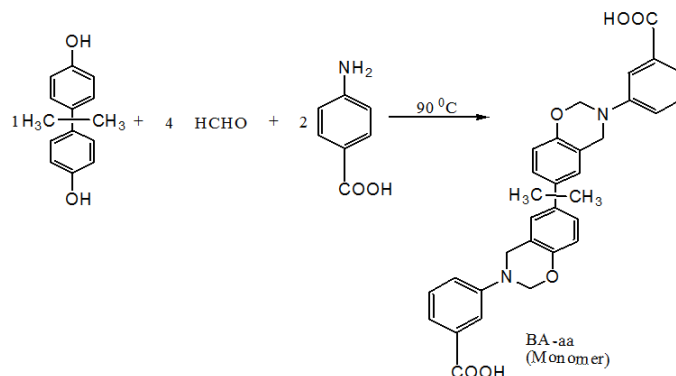
2. Experimental

2.1. Materials

The chemicals used were Starting chemicals used were, bisphenol-A, paraformaldehyde and para-amino benzoic acid (PABA) (99 % Merck, India.), chloroform (99.7%, Qualigens Fine Chemicals, India), benzoyl peroxide (BPO) (99 % Sigma Aldrich, India), isophthalate unsaturated polyester resin (bis(1-(4-methoxy-4-oxobut-2-enoyloxy)propan-2-yl) isophthalate) diluted with styrene (UPR) ($M_w = 1700$ approx) (Rafnol, India). All chemicals were used as received.

2.2 Synthesis of Acid Modified Benzoxazine Monomer (BA-aa)

Acid modified benzoxazine (bis (3-phenyl-3, 4-dihydro-2H-1, 3-benzoxazinyl) isopropane) (BA-aa) was synthesized using a solventless method by reacting bisphenol-A, para-amino benzoic acid (PABA) and paraformaldehyde. In a typical synthesis, 6.21 gm of bisphenol-A, 3.26 ml para-amino benzoic acid, 7.47 gm of paraformaldehyde were mixed in a round bottom flask and slowly heated at 90 °C in an oil bath for 90 min. After cooling the resulting material was dissolve in CHCl_3 and filtered. CHCl_3 was then evaporated to obtain benzoxazine monomer. Synthesized benzoxazine monomer was dried in a vacuum oven for 48 hr at 65 °C to remove traces of chloroform. The synthesis route and structure of BA-aa are shown in Scheme 1.



Scheme 1: Synthesis route of acid modified benzoxazine monomer (BA-aa)

2.3 Preparation of Acid Modified Benzoxazine-unsaturated Polyester Blend

Blends of benzoxazine (BA-aa) and isophthalic polyester resin (UPR) with several compositions were prepared by mixing benzoxazine monomer and isophthalic polyester resin (mass ratio: 10/90) at 70 °C for 30 min, subsequently cool down the blend mixture to room temperature and added the calculated amount of benzoyl peroxide (BPO) pest and mix thoroughly for next 10 min at room temperature. The sample was degassed under vacuum for another few minutes to remove the air bubbles. The semi viscous reaction mass was immediately poured in to metal mould and kept at room temperature for 1 hr to complete the free radical polymerization of unsaturated polyester and thus obtained the semi-viscous mass then the resulting semi-viscous mas was further cured by using a curing profile as shown in Table 2 to ensure the complete curing of benzoxazine monomer. All the samples for property measurements were prepared by casting their blends into a metal mould and curing with a profile as shown in Table 2. Samples for PBA-aa-IP were prepared by the same way for comparison. Various compositions of blends are listed in Table 1.

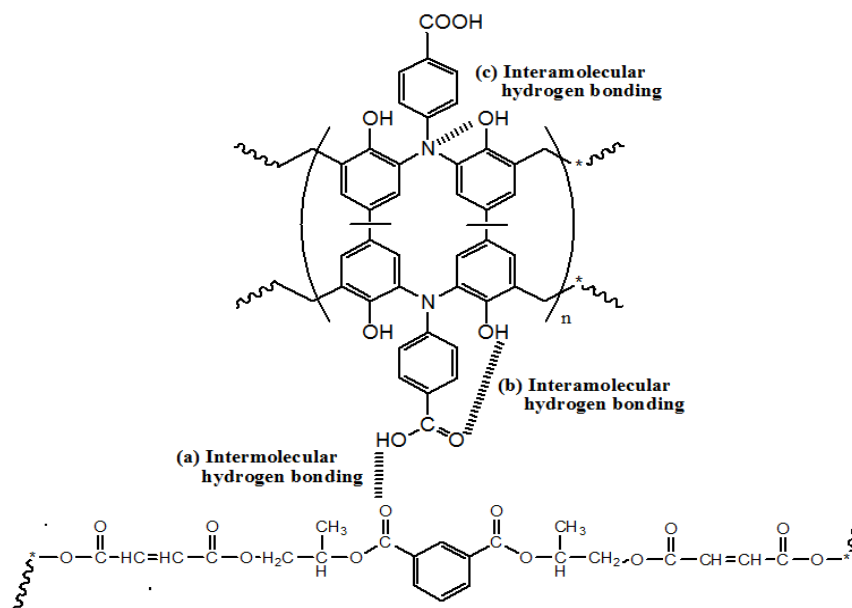
Table 1. Compositions of the blend

Sample code	BA-aa (wt%)	UPR (wt%)
10PBA-aa/90UPR	10	90
20PBA-aa /80UPR	20	80
30PBA-aa /70UPR	30	70
40PBA-aa /60UPR	40	60
50PBA-aa /50UPR	50	50

Table 2. Curing schedule for PBA-aa/UPR blend

Temperature (°C)	Time (hr)
100	2
120	1/2
140	1/2
160	1
180	1
200	2

Scheme 2: Three types of hydrogen bonding that could possibly occur in polybenzoxazine-unsaturated polyester blend. (a) intermolecular hydrogen bonding between two hydroxyl groups of polybenzoxazine with carbonyl group of polyester, (b) interamolecular hydrogen bonding between acid carbonyl groups of polybenzoxazine and hydroxyl groups of polybenzoxazine, and (c) intramolecular hydrogen bonding between hydroxyl groups and nitrogen atom on the Mannich bridge.



2.4 Sample Characterization

Fourier transform infrared (FT-IR) spectra of the samples were acquired using a Shimadzu IR Spectrophotometer (Model 840, Japan), equipped with a potassium bromide (KBr) beam-splitter. All spectra were recorded with 50 scans at a resolution of 4 cm^{-1} and spectral range between $4000\text{--}400\text{ cm}^{-1}$. Thermogravimetric analysis (TGA) and Differential scanning calorimetric (DSC) analysis were carried out for the neat polymers and blends by using DTG-60 and DSC-60 (Shimadzu, Japan), respectively. DSC analysis was performed from $30\text{ to }300\text{ }^{\circ}\text{C}$ at a constant heating rate $5\text{ }^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere while the TGA analysis was performed from $30\text{ to }700\text{ }^{\circ}\text{C}$ at a constant heating rate $5\text{ }^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. Tensile measurements were performed according to ASTM D 638 standard using a universal testing machine (INSTRON 3366, USA). Type I specimens with the overall dimensions of $165 \times 19 \times 3.2\text{ mm}$ were prepared for tensile testing. Room temperature measurements were carried out at a constant crosshead speed of $5\text{ mm}/\text{min}$. The flexural properties of the neat polymers and blend were determined in accordance with ASTM D 790 using a universal testing machine (INSTRON 3366, USA) with 10 kN load cell. Specimens were tested in a three point loading with 50 mm support span at crosshead speed of $5\text{ mm}/\text{min}$ at room temperature. The surface morphology of the composites was studied using a scanning electron microscope (SEM) (EVO 18, ZEISS, Germany).

3. Results and Discussion

3.1 FT-IR Analysis

FT-IR spectra of pure benzoxazine monomer, uncured UPR and cured blend (PBA-aa-10/UPR-90) as shown in Fig. 1 (A). It has been observed that, the peaks at 945 cm^{-1} and 1497 cm^{-1} of pure benzoxazine monomer (Fig. 1 (A) (a)), attribute to the tri-substituted benzene ring in benzoxazine monomer [12]. In case of uncured UPR, the peaks at 1652 cm^{-1} and 1732 cm^{-1} attributed for the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ respectively (Fig. 1 (A) (b)). However, in case of cured blend, peak at 1732 cm^{-1} along with a very small shoulder peak at 1717 cm^{-1} was observed (Fig. 1 (A) (c)). This is might due to the formation of hydrogen bonding between pendent $-\text{COOH}$ group and free $-\text{OH}$ group of polybenzoxazine with $\text{C}=\text{O}$ group of polyester. The peak at 1717 cm^{-1} assigned for hydrogen bonded carbonyl groups and 1732 cm^{-1} peak attribute for non-hydrogen bonded carbonyl groups (Fig. 1 (B)) [13]. There are three types of hydrogen bonding could possibly occur in PBA-aa/UPR blend are shown in Scheme 2. Intermolecular hydrogen bonding, between two hydroxyl groups of

acid modified polybenzoxazine pendent acid group and carbonyl group of polyester, (Scheme 2 (a)) intermolecular hydrogen bonding between free hydroxyl group polybenzoxazine and carbonyl group of pendent acid group of polybenzoxazine, (Scheme 2 (b)) and intermolecular hydrogen bonding between free hydroxyl group of polybenzoxazine and of nitrogen of polybenzoxazine on the Mannich Bridge (Scheme 2 (c)). Absence of peak at 1652 cm^{-1} (for C=C group) indicated the crosslinking of double bonds occurred due to free radical polymerization reaction between unsaturated polyester and styrene and it was also observed that the peak at 949 cm^{-1} , corresponds to the tri-substituted benzene ring of benzoxazine, was disappeared in the blend samples. This indicates the complete formation of polybenzoxazine from benzoxazine occurred during blend preparation as shown in Fig. 1.

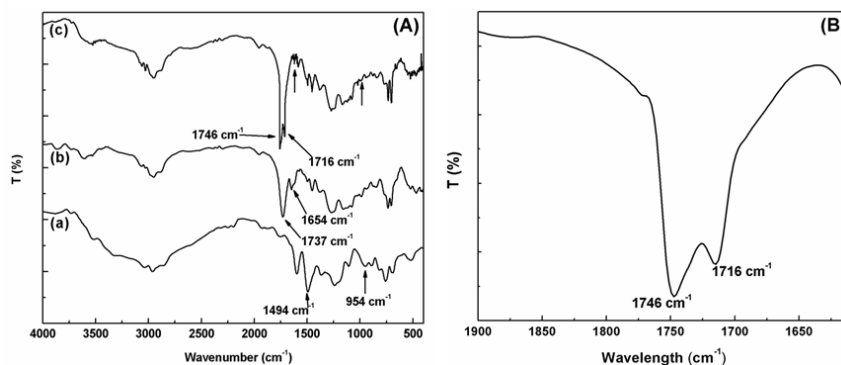


Fig. 1. (A) FT-IR spectra of (a) benzoxazine, (b) uncured UPR, (c) cured 10PBA-aa/90UPR blend, (B) cured 10PBA-aa/90UPR blend at carbonyl group region showing the presence of hydrogen bonding

3.2 Thermal Analysis

DSC analysis has been performed (Fig. 2) to investigate the polymerization of polyester resin, benzoxazine monomer and cured blend of PBA-aa/UPR. DSC thermogram for mixture of polyester resin with benzoyl peroxide, exothermic peak at $95\text{ }^{\circ}\text{C}$ was observed as shown in Fig. 2 (a), which can be attributed, to the free radical polymerization of unsaturated polyester [14]. In case of benzoxazine monomer the existence of an exothermic peak at $215\text{ }^{\circ}\text{C}$ indicated the ring opening polymerization benzoxazinemonomer (Fig. 2 (b)) [15]. However, in case of cured blends, it was observed that the exothermic peak at $215\text{ }^{\circ}\text{C}$ of ring opening polymerization of benzoxazine and peak at $95\text{ }^{\circ}\text{C}$ which is attributed for the polymerization of unsaturated polyester completely disappeared (Fig. 2 (c)). This indicates that the complete curing of blend has occurred during the processing of the blend with benzoyl peroxide for free radical polymerization of polyester and post thermal curing for the benzoxazine monomer.

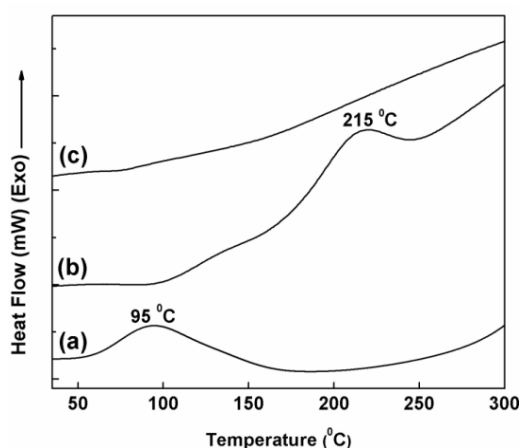


Fig. 2. (a) mixture of UPR and BPO, (b) benzoxazine monomer and (c) cured 10PBA-aa/90UPR blend

To investigate the thermal stability of the cured blends with various composition Thermogravimetric analysis (TGA) was performed. From the TGA thermogram of cured polyester, polybenzoxazine and different composition of blends (Fig. 3) it was observed that the 4 % weight loss was occurred in the temperature range of 150-250 °C, might be due to loss of volatile content and major weight loss of ~ 52 % in temperature range 300-400 °C, this may be due to the decomposition of carbonyl groups and aromatic ring units from the main chain. In case of polybenzoxazine, decomposition started at 365 °C and 69 % weight loss occurred in the temperature range at 365-650 °C. However, thermal stability of cured blends was found to be increased with increasing polybenzoxazine quantity in the blend. In case of the entire blend composition, the major weight loss due to thermal decomposition occurred in the temperature range of 315-600 °C, however the char yield of the blends at 750 °C was found to be increasing with increasing polybenzoxazine amount in the blend. This indicates that presence of thermally stable polybenzoxazine enhances the thermal stability of the polyester and enhancement in char yield indicates that the prepared blend possesses the better flame retarding properties. Weight loss at 5%, weight loss at 10% and percentage of char yield of the cured blend was found to be increasing with increasing benzoxazine concentration in the blend and results are shown in Table 3.

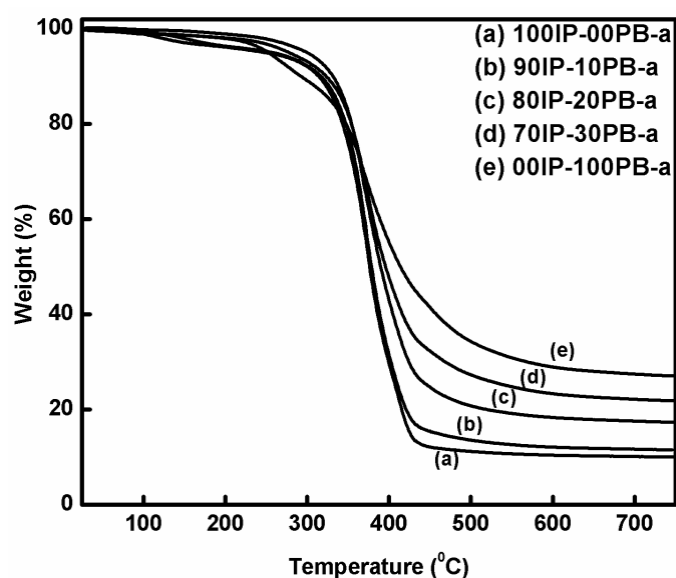


Fig. 3. TGA thermograms of (a) cured polyester, (b) 10PBA-aa/90UPR cured blend, (c) 30PBA-aa/70UPR cured blend, (d) 50PBA-aa/50UPR cured blend (e) polybenzoxazine

Table 3. Temperatures required for 5% and 10% weight loss of the blends due to thermal decomposition in an air atmosphere

Sample code	T _{5%} (°C)	T _{10%} (°C)	char yield (%) at 750 °C
100PBA-aa/00UPR	197	226	27
00PBA-aa/100UPR	245	308	10
10PBA-aa/90UPR	257	318	11
20PBA-aa/80UPR	298	330	17
30PBA-aa/70UPR	272	322	22
40PBA-aa/60UPR	250	293	24
50PBA-aa/50UPR	247	287	27

3.3 Mechanical Properties

The effect of composition of blends on mechanical properties was determined by flexural and tensile testing. Mechanical properties of polyester were found to be lower than the polybenzoxazine, may be due to the polybenzoxazine have three dimensional network structure which is more rigid than the ladder type crosslinking structure of polyester (Fig. 4) and results are tabulated in Table 4. However, in the case of cured blend the mechanical properties of the blends increased with increasing amount of benzoxazine content in the blend up to 10 wt% of benzoxazine content in the blend. This might be due to the increase of crosslinking density of blend with addition of 10wt% polybenzoxazine. However, beyond this composition the mechanical properties start decreasing (Fig. 4). This might be due to the influence of significant amount of PBA-aa in blend which enhances the crosslinking density of UPR beyond the certain level and lead to enhance inter molecular stress and finally resulted in to the brittleness of the overall blend system and subsequently lead to result in decreasing of mechanical properties. Table 4 summarizes the tensile and flexural properties of the blends having various amount of PBA-aa. SEM micrographs of the fractured surface of blend are also showed the enhancement of homogeneity of polyester and polybenzoxazine phases with increasing amount of polybenzoxazine up to 10 wt% (Fig. 5 (a)) beyond this level homogeneity found to be less with prominent phase separation (Fig. 5 (b) and (c)).

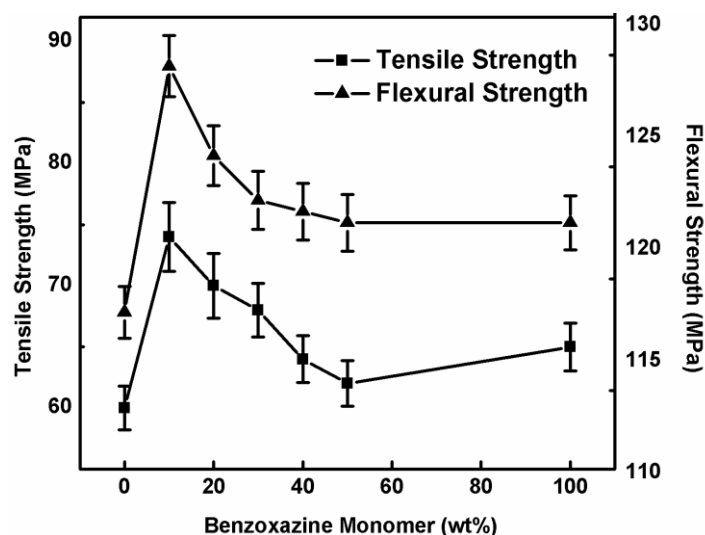


Fig. 4. Change of tensile and flexural strength of the blends with the composition of polybenzoxazine and polyester

Table 5. Change of mechanical properties of the blend with the variation of PBA-aa and polyester in the blend

Sample code	Tensile strength (MPa)	Flexural strength (MPa)
100PBA-aa/00UPR	65.69	120.06
00PBA-aa/100UPR	60.06	116.75
10PBA-aa/90UPR	74.07	127.07
20PBA-aa/80UPR	70.09	123.10
30PBA-aa/70UPR	67.75	121.79
40PBA-aa/60UPR	63.95	120.10
50PBA-aa/50UPR	61.87	120.33

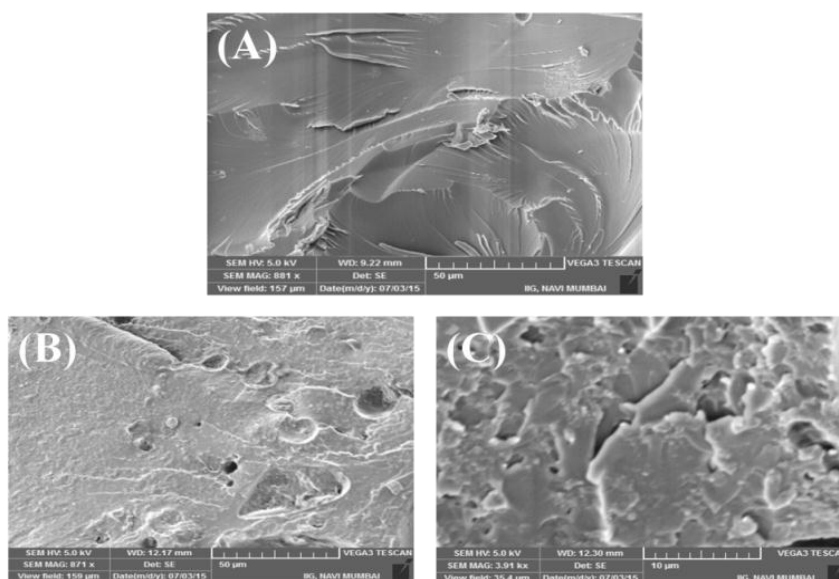


Fig. 5. SEM micrograph of fractured samples (a) cured 10PBA-aa/90UPR blend, (b) cured 30PBA-aa/70UPR blend, (c) cured 50PBA-aa/50UPR blend

4. Conclusions

Polybenzoxazine-unsaturated polyester based composites were prepared by blending polybenzoxazine with unsaturated polyester. Thermal stability of the blends was found to be increased with increasing polybenzoxazine content in the blend. Tensile and flexural testing of the blends revealed that 10 wt% is the optimum amount of polybenzoxazine that can be used in blend preparation. In summary, in this paper, blending method has been reported for preparation of polybenzoxazine-unsaturated polyester blend is very simple. Consequently, these blends can easily be prepared in large scale. As the prepared blends possess good better mechanical properties along with good thermal stability, these blends have the potential to be used in preparation of complex structures for FRP industries.

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