Studies on Thermal and Mechanical Properties of Glass Fiber-Reinforced Unsaturated Polyester/Benzoxazine Composites

M. B. Kulkarni[1], **Hussein Ali Abed**[2]

Department Polymer Engineering, Maharashtra Institute of Technology, Kothrud, Pune, 411038, India.

Abstract: ***Unsaturated polyester/benzoxazine copolymer was employed to prepare polyester/benzoxazine/glass fiber composite laminates and their mechanical, morphological, and thermal properties were investigated. Compared with those of 100UPR/0PBZ/10GF composites, the tensile strength and flexural strength of 90UPR/10PBZ/10GF composites with 10 wt % polybenzoxazine content were increased by 10 % and 6 %, respectively. The enhancements in mechanical properties are mainly due to the strong interfacial adhesions between glass fiber and UPR/PBZ matrices, which were confirm by the SEM images of fracture surfaces of the composites. Curing behavior of glass fiber filed composite was investigated by differential scanning calorimetry analysis. All UPR/PBZ/GF composite laminates are thermally stable up to 270 ^{0}C in air. Furthermore, TGA thermograms revealed that the degradation temperatures of UPR/PBZ/GF composite increased with compare UPR/GF composite. UPR/PBZ/GF composite laminates will have potential applications in the areas where require of excellent mechanical properties and high temperature resistance.***

Keywords: Thermal, mechanical properties, lass fiber, reinforced unsaturated polyester, Benzoxazine composites

1. Introduction

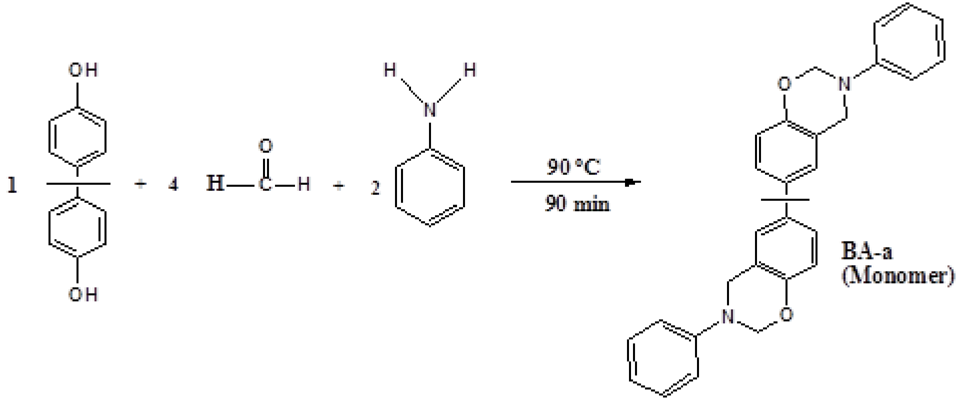
Glass fiber (GF)/polymer composite are well known for their low weight to high strength ration, excellent stiffness and low density. These polymers composite have been considered as next-generation high-performance materials for marine, aerospace and ground facility applications and the most promising materials in numerous fields such as automotive industries, wind mill industries. The performance of the GF/polymer composites may vary a lot depending on the types of GFs, matrices, and fiber-matrix interface [1, 2]. Now it was realized that the key difficulty in the use of GF/polymer composite laminates was weak interfacial interactions between GFs and polymer matrices which results in inefficient load transfer and phase separation. Thus, molecular level design of the GF/polymer composite interface is essential for the fabrication of high-performance composite materials. Recently, the benzoxazine-based phenolic resins have attracted significant attention. Compared with the conventional phenolic resins, benzoxazine-based phenolic resin possesses outstanding advantages: low water uptake capacity, nearly zero shrinkage, high char yield, high glass transition temperature, excellent flame retardant properties, very long shelf life, no requirement of curing agents, no release of by-products and thus crack-free structures, high molecular design flexibility, highly compatible to blend with other number of resin [3-7]. However, its processability needs to be further improved. Unsaturated polyester (UPR) resins are well-known for their outstanding properties such as mechanical properties, good chemical resistances and excellent processability. UPR resins-based composites have been extensively used in various fields such as marine industries, coatings, adhesives, automobile and electrical insulating materials. However their disadvantages are the poor thermal and thermal-oxidative stabilities, higher water uptake capacity, lower dimensional stability. In this study, to expand various advantages and applications of benzoxazine and UPR materials, especially in the fields required high mechanical and thermal properties, we are expecting to improve the processability of benzoxazine and the interface of final GF-filled benzoxazine composite through copolymerizing benzoxazine with UPR with the help of the low viscosity, excellent wetting properties, and bond forming of UPR. The differential scanning calorimetric analysis was used to investigate the curing of UPR/GF and UPR/PBZ/GF composite system. Furthermore, the mechanical, morphological, and thermal properties of UPR/GF and UPR/PBZ/GF composites were investigated. The results showed that UPR/PBZ/GF composites exhibited much better mechanical and interfacial properties than UPR/GF composites and all UPR/PBZ/GF composites could stand high temperatures up to 270 ^{0}C.

2. Experimental Materials

The starting chemicals used were, bisphenol-A, paraformaldehyde and aniline (99 % Merck, India.), chloroform (99.7%, Qualigens Fine Chemicals, India), bezoxyl peroxide (BPO) (99 % Sigma Aldrich, India), orthophthalate unsaturated polyester resin (bis(1-(4-methoxy-4-oxobut-2-enoyloxy)propan-2-yl) isophthalate) diluted with styrene (UPR) (M_w = 1800 approx) (Polylite PD-5522, Reichhold, India). E-glass chopped stand Mat (EMC) supplied by Asia Composite Materials (Thailand) Co., Ltd, Rayong, Thailand. All chemicals were used as received.

Synthesis of benzoxazine monomer (BA-a)

Benzoxazine (bis (3-phenyl-3, 4-dihydro-2H-1, 3-benzoxazinyl) isopropane) (BZ-a) was synthesized using a solventless method by reacting bisphenol-A, aniline and paraformaldehyde [8]. In a typical synthesis, 6.21 gm of bisphenol-A, 3.26 ml aniline, 7.47 gm of paraformaldehyde were mixed in a round bottom flask and slowly heated at 90 ^{0}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 ^{0}C to remove traces of chloroform. The synthesis route and structure of BZ-a are shown in Scheme 1.



Scheme 1. Synthesis route and structure of benzoxazine (BZ-a)

Preparation of UPR/PBZ/GF and UPR/GF composite

Composites of benzoxazine (BZ-a), isopthalic unsaturated polyester resin (UPR) and glass fiber (GF) mat with several compositions were prepared by mixing benzoxazine monomer and isopthalic unsaturated polyester resin at 80 ^{0}C for 30 min until to get clear solution under stirring at 200 RPM then cool down the mixture to room temperature, then added the BPO into mixture and then immediately brush-coated on pre-calculated glass fiber mat with the viscous solution obtained above and dried at room temperature for 24 h. The ratio was designed to get a composite of 10% to 40% GF by weight. Composite filled stainless steel mold was kept into the hot air circulating over at 100 ^{0}C for 2 h, 140 ^{0}C for 1 h, 160 ^{0}C for 1 h, 180 ^{0}C for 1 h and 210 ^{0}C for 2 h respectively. All samples for UPR/PBZ/GF were prepared by the same way for comparison. In case of UPR/GF composite the added the BPZ into the pre-calculate UPR resin and mixed properly and then immediately brush-coated on glass fiber mat and then same curing profile followed as per above Figure 1 shows the representative specimen of both the composite. Various compositions of UPR/PBZ/GF and UPR/GF composites are listed in Table 1.

Table 1. Composition of composite

Sample code	UPR (wt%)	BA-a (wt%)	GF (wt%)	BPZ (wt%)
100UPR/0PBZ/00GF	100	0	0	2
100UPR/0PBZ/10GF	100	0	10	2
100UPR/0PBZ/20GF	100	0	20	2
100UPR/0PBZ/30GF	100	0	30	2
100UPR/0PBZ/40GF	100	0	40	2
90UPR/10PBZ/00GF	90	10	0	2
90UPR/10PBZ/10GF	90	10	10	2
90UPR/10PBZ/20GF	90	10	20	2
90UPR/10PBZ/30GF	90	10	30	2
90UPR/10PBZ/40GF	90	10	40	2

Figure 1: (a) UPR/GF composite and (b) UPR/PBZ/GF composite

Sample characterization

Thermogravimetric analysis (TGA) and Differential scanning calorimetric (DSC) analysis were carried out for the neat polymers and composites by using DTG-60 and DSC-60 (Shimadzu, Japan), respectively. Thermal analysis was performed from 30 to 650 ^{0}C at a constant heating rate 5 ^{0}C/min in air atmosphere. Tensile measurements were performed according to ASTM D 638 standard using a universal testing machine (INSTRON 3366, USA). Room temperature measurements were carried out at a constant crosshead speed of 5 mm/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 mm/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 Discussions

DSC Analysis

DSC heating curves for benzoxazine monomer, uncured polyester with benzoyl peroxide (initiator), cured UPR/GF and UPR/PBZ/GF composite are shown in Figure 2 (A). For benzoxazine monomer the exothermic peak at 204 ^{0}C attributed for the ring opening polymerization of benzoxazine to polybenzoxazine [9] (Figure 2 (A) (a)). In case of uncured polyester with benzoyl peroxide, the exothermic peak appeared at 95 ^{0}C is a broad exothermic peak. The broadness of this peak is mainly due to the presence of higher heat of reaction (Figure 2 (A) (b)), which corresponds to the thermally activated free radical polymerization of polyester resin in presence of benzoxyl peroxide [10]. In case of cured UPR/GF and UPR/PBZ/GF composite (Figure 2 (A) (c) and (d)) the exothermic free radical polymerization peak of polyester resin and ring opening polymerization exothermic peak for benzoxazine was absent (Figure 2 (A) (c) and (d)). This indicates that, UPR/GF composite and UPR/PBZ/GF composite, polyester were fully polymerized by cross linked with styrene (co-monomer) and benzoxazine completely polymerize to polybenzoxazine during composite preparation as curing was performed at 210 ^{0}C. Moreover, the thermal stability of cured UPR/GF composite was also performed by DSC and compared with UPR/PBZ/GF composite (Figure 2 (B) (a) and (b)). In case of 100UPR/0PBZ/30GF composite (Figure 2 (B) (a)), an exothermic peak at 356 ^{0}C and 497 ^{0}C were observed, which was due to the thermal-oxidative decomposition of polyester resin [11]. However, in case of 90UPR/10PBZ/30GF composite, an exothermic peak observe at 372 ^{0}C and 519 ^{0}C. These results indicate that, the thermal stability of composites has higher than the 100UPR/0PBZ/30GF composite. This may be due the presence thermally stable polybenzoxazine and lead to delay the thermal degradation of polymeric matrix of 90UPR/10PBZ/30GF composite, as comparative to 100UPR/0PBZ/30GF composite. This result indicates that, prepared UPR/PBZ/GF composite material has the more thermal stability than UPR/GF composite.

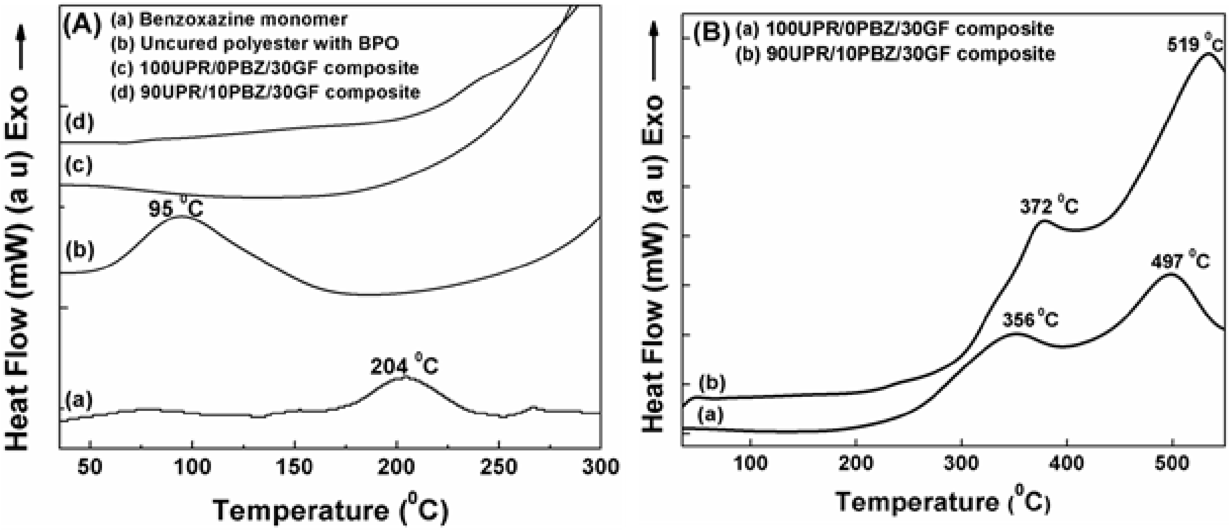


Figure 2: (A) DSC thermogram of (a) uncured polyester with BPO, (b) benzoxazine monomer, (c) cured UPR/GF composite and (d) cured UPR/PBZ/GF composite **(B)** DSC thermogram of (a) cured UPR/GF composite and (b) cured UPR/PBZ/GF composite

TGA analysis

TGA thermograms of cured UPR/GF composite and cured UPR/PBZ/GF composite are shown in Figure 3. These thermograms revealed that, the thermal stability of the cured UPR/PBZ/GF composite was found to be more than cured UPR/GF composite. The degradation of all the UPR/GF composite and UPR/PBZ/GF composites was found in the temperature range of 300-450 ^{0}C. The char yield at 650 ^{0}C for all the UPR/GF composite and UPR/PBZ/GF composites was found higher in cured polyester and polybenzoxazine. From TGA of UPR/GF composite and UPR/PBZ/GF composites, temperature at 5% weight loss ($T_{5\%}$), temperature at 10% weight loss ($T_{10\%}$) and char yield (%) at 650 ^{0}C in air were determined and listed in Table 2. It was observed that for all composition of UPR/PBZ/GF composite, the temperature at 5 and 10 % weight loss was found to be higher than the neat cure polyester resin and UPR/GF composite however less than neat polybenzoxazine. This may be due presence of inert and thermally stable glass fiber and higher thermally stable polybenzoxazine in composites enhances the overall thermal stability of the composites. Moreover, from the TGA thermogram of all UPR/GF composite and UPR/PBZ/GF composites, it was found that the amount of residual weight at 650 ^{0}C of the polyester/GF composites was close to the actual amount of added wt% GF in the composites. That may be due to the high thermal stability of glass fiber, thus glass fiber was not experienced any weight loss in the temperatures range of 30-650 ^{0}C. However, polyester resin and benzoxazine has been completely decomposed at same temperature. This indicates that, the amount of char in each composite composition corresponds to the amount of glass fiber present in the composites.

Table 2: Temperatures required for 5% and 10% weight loss of the composites due to thermal decomposition in air

Sample code	$T_{5\%}$ (0C)	$T_{10\%}$(0C)	Char yield (%) at 650 0C (approx.)
Neat UPR	197	259	1
100UPR/0PBZ/30GF composite	205	264	24
90UPR/10PBZ/30GF composite	217	283	27
Neat PBZ	300	390	2

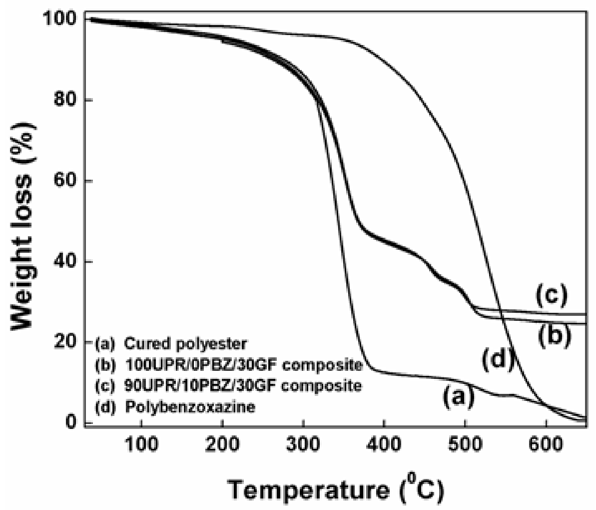


Figure 3. TGA thermograms of (a) cured unsaturated polyester, (b) 100UPR/0PBZ/30GF composite, (c) 90UPR/10PBZ/30GF composite, (d) polybenzoxazine.

Mechanical properties

Overall, the trend of mechanical properties for UPR/GF and UPR/PBZ/GF composite is that the tensile and flexural properties were increased with the increase of glass fiber content that is due to the reinforcement effect of glass fiber (Figure 4). However it is very important to note that, the UPR/PBZ/GF composite did exhibit much better mechanical properties in comparison with those of only UPR/GF composite. The tensile and flexural strength of 100UPR/0PBZ/10GF composites was 48 MPa and 78 MPa, respectively while 90UPR/10PBZ/10GF composites with 10 wt% benzoxazine content exhibited high tensile strength of 53 MPa and high flexural strength of 82 MPa, increased by 10 % and 6 % in comparison with 100UPR/0PBZ/10GF composites, respectively (Table 3). Generally, mechanical properties of polymer/GF composites depends on some primary components such as the nature of glass fiber, loading level of glass fiber, and importantly the interaction between the matrix and reinforcement material. Since the glass fiber is well known for its better stiffness and high strength with both in tension and compression at the same time the matrix also play very important role for the enhancement of mechanical properties of polymer/GF composite. Here, in this case enhancements of mechanical properties can be due to improvement of interfacial adhesions by the copolymerizing of UPR/PBZ metrics. In addition, due to contribution of the excellent wetting properties of polyester and polar groups such as phenolic hydroxyl groups generated by the ring-opening of PBZ and UPR may further promote interfacial adhesions [12], which were confirmed by the SEM images of fracture surfaces of the 100UPR/0PBZ/30GF and 90UPR/10PBZ/30GF composites, as shown in Figure 5 (a) and (b) respectively. It can be seen from Figure 5 (a), the fracture surfaces of 100UPR/0PBZ/30GF composites had less covering of UPR showing with bare GFs. In addition, the UPR on the glass fiber surfaces tends to less adhesion to form uneven contact with bare glass fiber bars, and the fracture occurred between the polymeric matrix and glass fiber because of the poor interfacial adhesion strength. On the other hand, the fracture surface of 90UPR/10PBZ/30GF composites, it can be seen that the glass fibers were homogenously covered by the benzoxazine and UPR metrics. This may be because that the better binding properties of benzoxazine in presence of UPR and can offer conveniences to make GF be well wetted during the brush-coating process. Moreover, polar groups (free -OH groups after polymerization) of polybenzoxazine may give better polar interaction with glass fiber in presence of UPR and lead to promote interfacial adhesions the surface of glass fiber with metrics, this indicating strong interfacial adhesion between glass fiber and metrics. These structures could lead to effective stress transfer and prevent crack initiation and propagation. All these results confirmed the enhancement of mechanical performances.

Table 3: Tensile and flexural properties of the composites having various loading level of glass fiber

Sample code	Tensile strength (MPa)	Flexural strength (MPa)
100UPR/0PBZ/00GF	29	42
100UPR/0PBZ/10GF	48	78
100UPR/0PBZ/20GF	62	89
100UPR/0PBZ/30GF	73	98
100UPR/0PBZ/40GF	85	105
90UPR/10PBZ/00GF	32	49
90UPR/10PBZ/10GF	53	82
90UPR/10PBZ/20GF	67	93
90UPR/10PBZ/30GF	79	103
90UPR/10PBZ/40GF	91	109

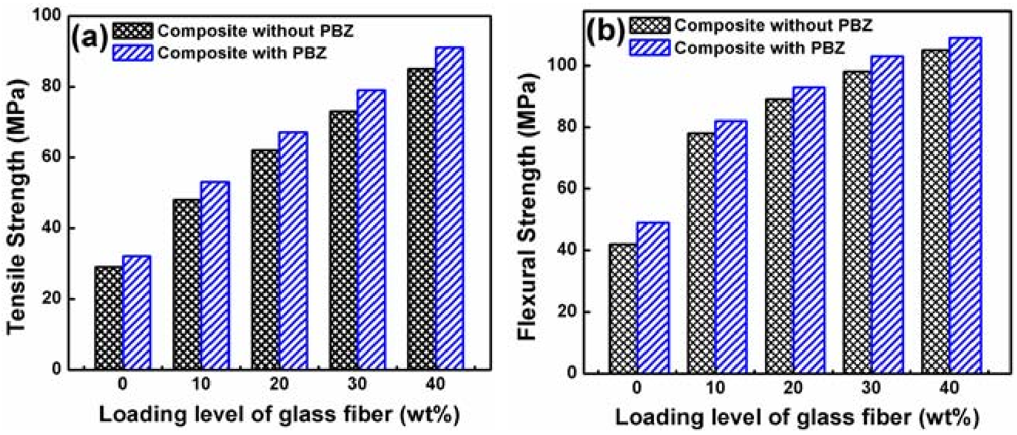


Figure 4. Change of (a) tensile and (b) flexural strength of the composites with the variation of loading level of glass fiber in the composition

Impact Energy was observe from the Table 5.5, that the 74.94 KJ/m2 (Impact Energy) is the value for UPR/PBZ/GF and 27.68 KJ/m2 (Impact energy) is the for UPR/GF composite respectively. From these results we can seen that the impact energy is higher for the composite contains the PBZ, moreover we can also examine from the Table 5.5 that impact energy is increasing with increasing the loading level of glass fiber in composite. This may be because of that the presence of glass fibers and higher strength PBZ result in absorbing the shock loads, thereby increasing the toughness of the composite. From the above results we can conclude that the because of presence of PBZ in the UPR/PBZ/GF composite the impact strength is higher than the UPR/GF composite. So theses type of composite can have the application where high impact energy requirement to subject.

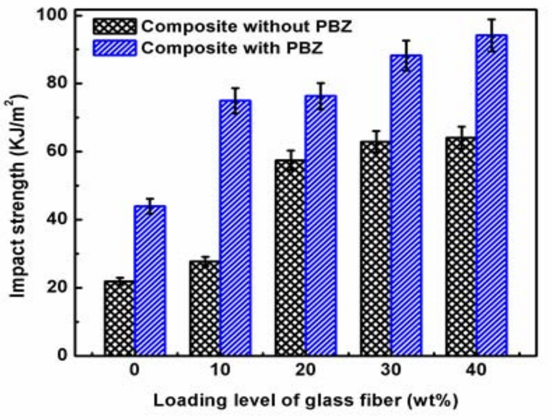


Figure 5: Change of Impact strength of the composites with the variation of loading level of glass fiber in the composition.

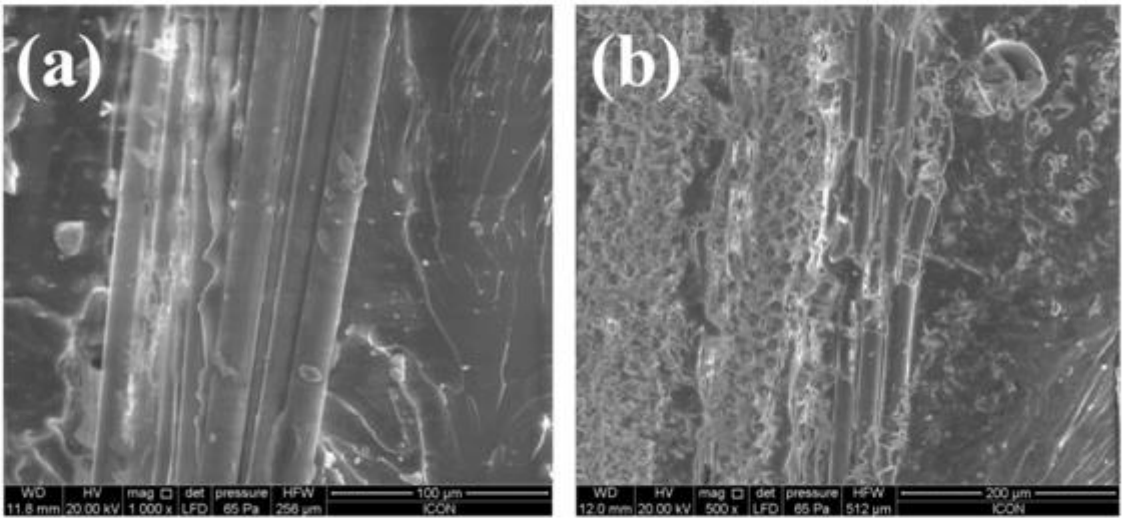


Figure 6: SEM micrographs of (a) 100UPR/0PBZ/30GF composite, (b) 90UPR/10PBZ/30GF composite

4. Conclusion

UPR/PBZ matrix were used to prepare UPR/PBZ/GF composite and their mechanical, thermal properties and morphological were investigated and compared with those of UPR/GF composite. The tensile strength and flexural strength of UPR/PBZ/GF and UPR/GF composites were increased with increasing the GF. However the mechanical properties of UPR/PBZ/GF composite were found higher than the UPR/GF composite, such mechanical enhancements can be due presence of benzoxazine on the interfacial interactions between matrix and reinforced glass fiber. Thermal properties revealed that all UPR/PBZ/GF composites could stand high temperature up to 270 ^{0}C in air. These characteristics could enable the UPR/PBZ/GF composites to find uses under some critical circumstances with requirements of excellent mechanical properties and high temperature resistance.

References

[1] Weisshaus, H., Kening, S., Kastner, E. and Siegmann, A. (1990). Morphology Development During Processing of Carbon-Carbon Composites, Carbon, 28: 125–135.

[2] F. Dillon, F.; Thomas, K.M.; Marsh, H. Carbon (1993) 31, 1337, DOI: 10.1016/0008-6223(93)90095-R.

[3] Takcichi T., Agag T. (2006). High performance polybenzoxazine as novel thermoset, High perform. 18, 777-797.

[4] Brunovska, Z.; Lyon, R.; Ishida, H. (2000). Thermal properties of phthalonitrile functional polybenzoxazines, Thermochim Acta, 357, 331-334.

[5] Ishida H., Allen D J., (1996). Physical and mechanical characterization of near zero shrinkage polybenzoxazines, J.Polym.Sci.BPolym.Phys. 34, 1019-1030.

[6] Ishida. H., Low H.Y. (1997). A study on the volumetric expansion of benzoxazinebased phenolic resin,Macromolecules, 30, 1099-1106.

[7] Jin, K. H.; Brunovska, Z.; Ishida, H. (1999). Molecular characterization of the polymerization of acetylene-functional benzoxazine resins, Polymer, 40, 1815.

[8] Brunovska Z., Liu J. P., Ishida H. (1999) 1,3,5-Triphenylhexahydro-1,3,5-triazine – active intermediate and precursor in the novel synthesis of benzoxazine monomers and oligomers, Macromolecular Chemistry and Physics, 200, 1745–1752.

[9] Sarangi P P, Naik,BVadera S R, Patra M K., Prakash, C., Ghosh N N. (2010). Preparation of Polybenzoxazine- Ni-Zn Ferrite magnetic

nanocomposite and its magnetic property, Materials Technology, 25 [5] 271- 275.

[10] Rajput A. B., Ghosh N. N. (2010). Preparation and Characterization of Novel Polybenzoxazine-Polyester resin Blends. International Journal of Polymeric Materials. 59, 1-13.

[11] Sugimura, Y., &Tsuge, S. (1979). Studies on Thermal Degradation of Aromatic Polyesters by Pyrolysis-Gas Chromatography. Journal of chromatography Science. 17, 269-272.

[12] Mingzhen Xu, Xulin Yang, Rui Zhao, Xiaobo Liu. (2013) Copolymerizing behavior and processability of benzoxazine/epoxy systems and their applications for glass fiber composite laminates, Journal of Applied Polymer Science, 128, 1176-1184.