

Mechanical and Thermal Properties of Hemp Fiber-Unsaturated Polyester Composites Toughened by Butyl Methacrylate

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Hemp fiber-reinforced unsaturated polyester (UPE) composites were prepared by hand lay-up compression molding. The UPE resins were modified with butyl methacrylate (BMA) to improve the flexibility and toughness of the hemp-UPE composites. The results indicate that the toughness of the composites significantly increased as BMA usage increased. Compared to the unmodified UPE composites, the composites obtained from BMA-modified UPE resins had 27.4, 63.0, and 36.6% greater elongation at break, flexural strain, and impact strength, respectively. The optimum BMA usage to achieve an adequate balance of stiffness and toughness is 20 to 30%. Dynamic mechanical analysis (DMA) indicated that incorporation of BMA significantly decreased the storage modulus and glass transition temperature of the composites and increased its damping parameter due to the introduction of flexible segments into the UPE resins. Thermogravimetric analysis showed that the thermal stability of the composites decreased slightly following the incorporation of BMA. Scanning electron microscopy images of the impact-fractured surfaces of the composites revealed that BMA incorporation improved interfacial adhesion between hemp fibers and UPE matrices and that the main mechanism for the increase in the toughness of the composites was the added ductility of the matrices.

Keywords: Hemp fibers; Unsaturated polyester; Composites; Toughness; Butyl methacrylate; Mechanical properties; Thermal properties

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INTRODUCTION

Unsaturated polyester (UPE) resins are one of the most widely used types of thermosetting polymer matrices because of their low cost, ease of processing, high strength, excellent chemical corrosion resistance, good thermal and electrical properties, and curing capability at room temperature. The UPE resins have been extensively used in fiber-reinforced composites for applications in the aerospace, automotive, marine structure, infrastructure, military facilities, and sporting goods industries (Sharmila *et al.* 2007). However, applications of UPE resins are limited by the brittle nature of the resin due to its high degree of crosslinking and the significant shrinkage that take place during the curing process, and its poor resistance to crack propagation (Acha *et al.* 2003).

Natural fibers offer low pollutant emissions, non-toxicity, enhanced energy recovery, and good biodegradability (Wambua *et al.* 2003). Ever-increasing environmental concerns and shortages of petroleum resources have led to a demand for

natural fibers from bamboo (Tran *et al.* 2013), hemp (Dhakal *et al.* 2007), flax (Bozaci *et al.* 2013), kenaf (Hussein *et al.* 2013), sisal (Prasad and Rao 2011), and jute (Dhakal *et al.* 2014) to replace conventional glass- and petroleum-based fibers as reinforcements in UPE-based composites.

Compared with neat UPE resins, the natural fiber-reinforced UPE composites showed superior fracture toughness due to the flexibility of the natural fibers. The UPE composites prepared with bamboo fibers at 50% fiber volume fraction (vol.%) had 340% greater fracture toughness than the neat UPE resins (Wong *et al.* 2010). Hughes *et al.* (2002) investigated the fracture toughness of UPE composites reinforced with jute and hemp fibers (20 vol.%), finding that the fracture toughness and critical strain energy release rate in the jute-UPE composite were improved by 313 and 870%, respectively, and by 466 and 1740%, respectively, in the hemp-UPE composite. A similar study showed that the introduction of hemp fibers into UPE resins significantly increased the load bearing capability and impact energy absorption of the resulting hemp-UPE composites (Dhakal *et al.* 2007). Although the use of natural fibers to reinforce UPE resins can reduce the volume shrinkage of the resins to some extent, problems such as internal voids and cracks in resins, interfacial cracks between fibers and matrices, and others due to polymerization shrinkage cannot be completely avoided. As a result, the flexibility and toughness of natural fiber-UPE composites still need to be further improved to broaden their high value-added applications. Generally, the fracture properties of UPE resins (most notably, the impact strength and resistance to crack propagation) can be enhanced by using rubber particles, tougher thermoplastics, solid particles, or through interpenetrating polymer network (IPN) formation (Li *et al.* 2000; Singh *et al.* 2002; Bakar and Djaider 2007; Duan *et al.* 2009; Ahmadi *et al.* 2012). These methods also improved the toughness of natural fiber-UPE composites. The addition of a small amount of liquid natural rubber to kenaf-UPE composites noticeably increased the fracture toughness and impact strength of the composites (Ahmad *et al.* 2010). Haq *et al.* (2008) examined bio-based resins in which a partially-unsaturated polyester and a bio-based modifier (epoxidized methyl soyate) were used as the matrices to increase the toughness of the resulting nanoclay-hemp-reinforced hybrid bio-based composites. These composites have good stiffness and hygro-thermal properties. Acha *et al.* (2003) investigated the effects of UPE modification with polymethylmethacrylate (PMMA) on the mechanical properties of the UPE resins and wood flour-UPE composites. The addition of PMMA significantly increased the flexural strain at break, impact energy, and toughness of the UPE resins but did not otherwise change the mechanical behavior of the composites.

The toughness of composites depends on the fiber properties, polymer matrices, and the nature of the interaction between the fibers and the polymer matrices. Although the toughness of pure UPE resins has been studied in depth, few similar studies on natural fiber-UPE composites have been conducted.

Butyl methacrylate (BMA) is synthesized from methacrylic acid and n-butyl alcohol. It is usually used to generate acrylate polymer and copolymer. Gagliardi (2013) investigated the effect of macromolecular composition and drug loading on thermal and mechanical properties of methyl methacrylate and BMA copolymer. Aji (2006) discussed the coverage of butyl acrylate, butyl methacrylate, styrene, acrylamide, acrylonitrile, and unsaturated polyester styrene resin onto wood samples and the effects on tensile and compression strength of the wood/polymer composites, respectively. In previous studies, however, BMA was not used in natural fibers reinforced UPE

composites. In this study, butyl methacrylate (BMA) was used as a modifier and crosslinking agent for UPE resins. The use of BMA could reduce the usage of styrene, which has been deemed a carcinogen, during the manufacture of UPE-based composites. Such a change would be good for the environment and for human wellbeing. Compared to styrene, there may be better compatibility between BMA and fiber, which could mean improved composite mechanical behavior. The addition of BMA is done to introduce flexible molecular chains into UPE resins and further improve the toughness of hemp-UPE composites. Butyl methacrylate is also expected to participate in the free-radical polymerization process, tightly crosslinking with the UPE-styrene system, decreasing the shrinkage of resins, and reducing interfacial cracks between fibers and polymer matrices. Dynamic mechanical properties and thermogravimetric analyses were used to study the viscoelastic behavior and thermal degradability of the composites, respectively. The fractured morphology of UPE matrices and the interfacial adhesion between hemp fibers and UPE resins was examined using scanning electron microscopy.

EXPERIMENTAL

Materials

Hemp fibers (average length, 3.86 cm; average fiber fineness, 7.69 dtex) were obtained from the Sanxing Hemp Industry (Anhui, China). The UPE resins (9231-1TP) were purchased from Shangwei Fine Chemical (Shanghai, China). Butyl methacrylate (BMA), styrene, cobalt naphthenate, and methyl ethyl ketone peroxide (MEKP) were purchased from Sinopharm Chemical Reagent (Shanghai, China).

Methods

Modification of UPE resins

The BMA was mixed with 9231-1TP resins at weight ratios of 90:10, 80:20, 30:70, and 60:40 (resin:BMA) in an Erlenmeyer flask. Then, 1 wt.% styrene (based on the weight of BMA-UPE mixture) was added to the mixture to increase its flowability. The resulting solution was mechanically stirred at room temperature (RT) for 30 min until BMA was uniformly in the UPE resins. The solutions were then used to fabricate composites.

Composites preparation

Hemp fibers were formed into a long mat with dimensions of about 100 cm width and 0.5 cm thickness. The mat was cut into pieces of fiber-mats (22 cm × 22 cm) and oven-dried at 103 °C for over 24 h. The pure UPE or BMA modified-UPE resins (90 g), cobalt naphthenate (0.5 g), and MEKP (3 g) were blended with a spatula for 1 min to generate a UPE mixture. The UPE mixture was immediately, evenly poured onto the surfaces of a hemp-fiber preform (90 g), which was unidirectionally formed from a stack of 12 to 15 fiber mats. Then, the resin-coated fiber preform was moved into the chamber of a stainless steel mold (22 cm × 22 cm × 0.3 cm). The mold was pressed at 6 MPa for 5 min at RT, allowing the UPE mixture to flow and wet the preform. Maintaining the same pressure, the mold was then pressed at 110 °C for 5 min and hot-pressed at 140 °C for 30 min. The mold was removed from the press and cooled to RT (6 MPa, 60 min) in another press. Finally, the hemp-UPE composite panel obtained was removed from the mold for mechanical property testing. The composites prepared with BMA-modified UPE resins

containing 0, 10, 20, 30, or 40 wt.% BMA were labeled control, BMA-10, BMA-20, BMA-30, or BMA-40, respectively.

Mechanical properties tests

Dumbbell-shaped specimens with a gage length of 50 mm and a narrow section width of 10 mm were prepared from the rectangular samples (150 mm × 20 mm) for tensile strength testing according to ISO standards 527-2 (2012). Rectangular specimens (80 mm × 10 mm) were used in the flexural properties and non-notch impact strength tests in according to ISO standards 178 (2010) and 179-1 (2010), respectively. The tensile strength and flexural property tests were carried out using a CMT6104 universal testing machine (MTS Systems, Shenzhen, Guangdong, China) at a crosshead moving speed of 10 mm/min. The impact tests were conducted on a ZBC-25B Charpy Impact Tester (MTS Systems, Shenzhen, Guangdong, China). Five replicate measurements of the tensile, flexural, and impact property tests were taken.

Dynamic mechanical analysis (DMA)

Samples with dimensions of 55 mm × 10 mm × 3 mm were used for DMA measurements on a DMA Q800 V20.22 Build 41 (TA Instruments, New Castle, DE, USA) instrument in a single cantilever bending mode at a frequency of 1 Hz. The measurements were performed throughout a temperature range of 25 to 160 °C at a heating rate of 5 °C/min.

Thermogravimetric analysis (TGA)

The thermal stability of hemp-UPE composites was investigated using a STA 449 F3 Thermogravimetric Analyzer (NETZSCH, Selb, Germany). The scans were performed at a heating rate of 10 °C/min from room temperature to 600 °C with a nitrogen flow of 30 mL/min to maintain an inert environment.

Scanning electron microscope analysis

The fractured surfaces of the pure UPE composites and the BMA-modified UPE composites specimens from the impact tests were characterized with a JOEL JSM-7500F SEM (JOEL, Tokyo, Japan) at an accelerating voltage of 5.0 kV. Specimens were coated with elemental gold film (8 to 10 nm) before testing.

Statistical analysis

The mechanical property data obtained was analyzed with one-way ANOVA (analysis of variance) in combination with GraphPad Prism 3.0 software (GraphPad Software, La Jolla, CA, USA). The comparisons were made based on a 95% confidence interval.

RESULTS AND DISCUSSION

Mechanical Properties

Figure 1a indicates that the tensile strength of composite BMA-10 was comparable to that of the composite with pure UPE resin (the control). Further increasing the BMA usage to 20 or 30 wt.% did not significantly change the tensile strength of the

composites, whereas composite BMA-20 had a 12.0% increase of tensile strength compared to the control.

However, the addition of 40 wt.% BMA dramatically decreased the tensile strength of the composites by 20.6% compared to that of the control. The incorporation of BMA significantly increased the elongation at break of the composites (Fig. 1a) by 11.0, 17.9, 24.5, and 27.4% in composites BMA-10, BMA-20, BMA-30, and BMA-40, respectively.

The flexural strength of the composites did not change significantly after 10 wt.% BMA incorporation but increased by 12.2% in composite BMA-20 (Fig. 1b). When the BMA usage was greater than 20 wt.%, the flexural strength of the composites decreased and reached the lowest level in composite BMA-40.

The flexural strain of the composites increased significantly after the incorporation of BMA (Fig. 1b). Although the flexural strains of composites BMA-10 and BMA-20 were comparable and slightly higher than that of the control, there were 37.1 and 63.0% increases in the flexural strains of composites BMA-30 and BMA-40, respectively, compared to that of the control.

The change in the impact strength of the composites exhibited a similar trend as the elongation at break and flexural strain (Fig. 1). The impact strength of the composites increased steadily with the increase of BMA content (Fig. 1c). The impact strength increased by 6.2, 12.8, 24.8, and 36.6% in composites BMA-10, BMA-20, BMA-30, and BMA-40, respectively, compared to that of the control.

The tensile strength and flexural strength of the hemp-UPE composites increased significantly as the BMA usage increased to 20 wt.% and decreased dramatically when the BMA usage exceeded this threshold. However, the elongation at break, flexural strain, and impact strength of the composites increased with increasing BMA usage. The carbon-carbon double bond of BMA was expected to form covalent linkages with the UPE resins during the free radical polymerization of the UPE-styrene system. The BMA increased the crosslinking density of the UPE resins when the BMA usage was lower than 20 wt.%.

Compared to styrene, BMA molecules seemed to be more compatible with hemp fibers because the carboxylic ester group of BMA may easily interact with the hydroxyl groups of hemp fibers through H-bonding or other polar-polar interactions (Yampolskii and Bondarenko 1998). This might improve interfacial adhesion between the fibers and matrices after BMA is introduced, improving the tensile strength and flexural strength of composites BMA-10 and BMA-20. The long molecular chains of BMA in the composites helped disperse instantaneous loading and effectively prevented stress concentration when the composites were loaded (Bibo *et al.* 1996). This is responsible for the increase in the elongation at break, flexural strain, and impact strength of the composites with 10 or 20 wt.% BMA.

There was a significant decrease in the stiffness of the composites when the BMA usage exceeded an optimum value (20 wt.%). Homopolymerization of BMA, forming polybutyl methacrylate (PBMA), could occur because of excessive BMA addition. The PBMA molecular chains efficiently dispersed stress, improved the toughness, and decreased the stiffness of the mixed BMA-UPE resins during curing. The incorporation of 30 or 40 wt.% BMA significantly improved the elongation at break, flexural strain, and impact strength of the resulting composites by sacrificing their tensile and flexural strengths.

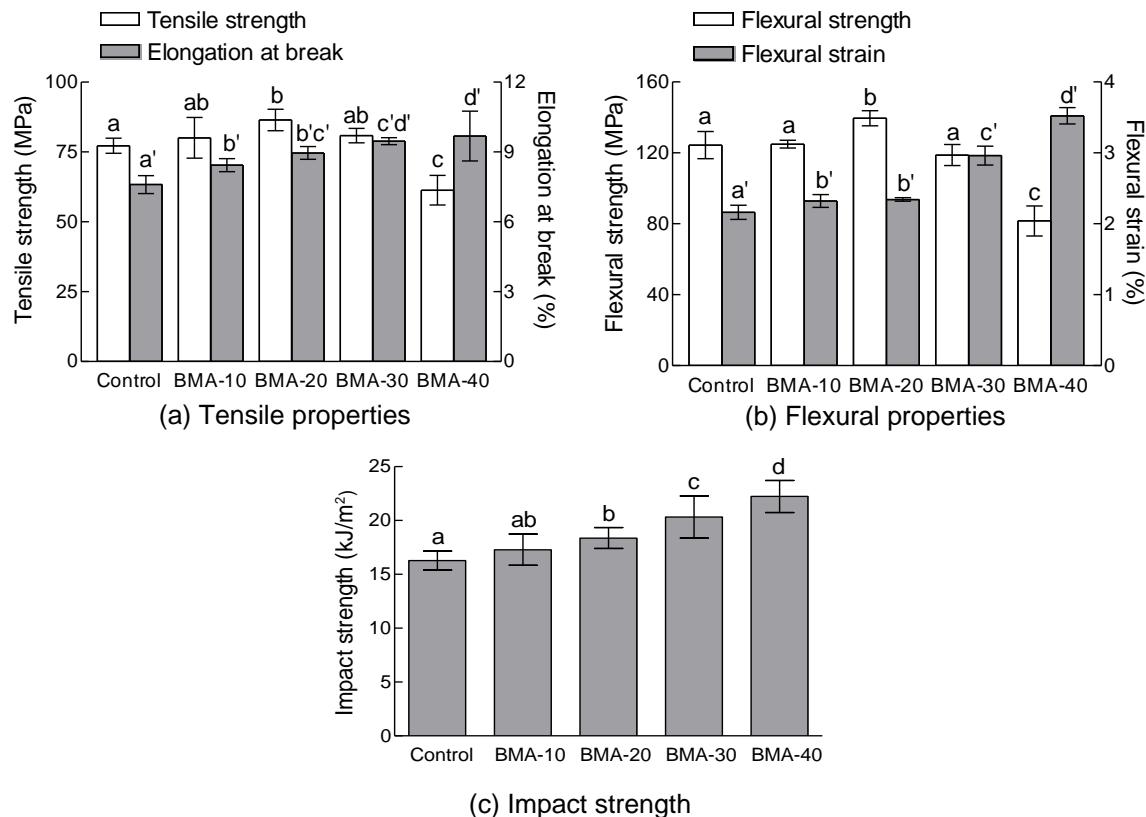


Fig. 1. Effects of BMA content on the mechanical properties of hemp fiber-UPE composites. The number following BMA represents the usage of BMA based on the weight of the UPE resin. It is the same in the following figures and table. The error bar at the top of each column represents two standard deviations above and below the mean. The groups do not significantly differ from one another when same letter is presented at the top of the columns.

Dynamic Mechanical Properties

The storage modulus (E') of the composites, which measured the stiffness and shape stability of the specimens, decreased sharply when the temperature increased from 50 to 120 °C and then flattened out at higher temperatures (Fig. 2a). This is likely due to the increased molecular mobility of the polymer chain in the vicinity of the glass transition temperature (T_g). The E' values of the composites BMA-10 and BMA-30 (9545 and 9617 MPa, respectively) at 50 °C were lower than that of the control (11929 MPa). Although the decline rate in E' with increasing temperature for composite BMA-30 was lower than that of composite BMA-10, the E' values at 50 and 130 °C of composite BMA-30 were comparable with those of composite BMA-10. The decrease of E' after the addition of BMA indicated the increased flexibility and decreased crosslinking density of the UPE molecular chains.

The $\tan \delta$ curves of all the composites only had one T_g , corresponding to the peak $\tan \delta$ (Fig. 2b) and indicating that the phase separation in the composites was not obvious. This is because the BMA molecules could participate in the polymerization of the UPE-styrene system. The BMA molecular chains could also be covalently bonded onto the UPE resin. However, when the BMA usage exceeded the optimum value, the homopolymerization of BMA monomers may occur. Compared with that of the control, the T_g of the BMA-modified UPE composites decreased from 113.7 to 102.7 and 94.5 °C

with the addition of 10 and 30% BMA into the UPE resins, respectively (Fig. 2b). Also, the relaxation peak height, associated with molecular mobility, increased with increasing BMA usage. These confirmed that the incorporation of BMA into UPE resin resulted in composites with improved molecular mobility and reduced thermal stability.

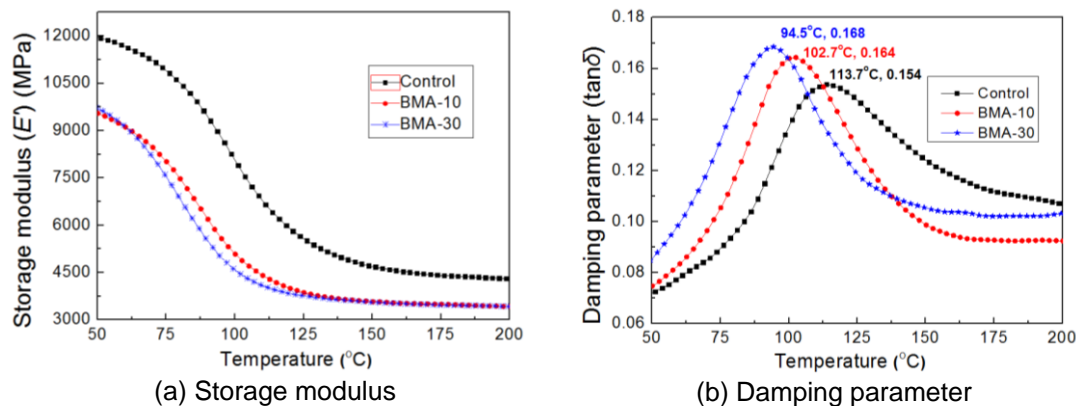


Fig. 2. DMA curves of untreated and BMA-treated UPE composites

Thermal Properties

The thermogravimetric (TG) and derivative of thermogravimetric (DTG) curves of BMA-10 and BMA-30 were similar to those of the control (Fig. 3), exhibiting a three-stage thermal degradation process. The first stage of degradation, occurring at about 150 to 320 °C, corresponds to the evaporation and decomposition of substances. The initial mass loss of the composites is below 330 °C, resulting from the loss of volatile material and moisture. The second stage, between 330 and 400 °C, is the fastest step of the degradation of the composites, due to the decomposition of matrices and fibers. The third stage of degradation is attributed to the transformation of fibers and matrices into ash, the conclusion of which was marked by constant mass. As summarized in Table 1, the thermal decomposition of the control began at 337.7 °C and was nearly complete at 389.8 °C. The onsets of thermal decomposition (T_{onset}) of the composites BMA-10 and BMA-30 were observed at 334.8 and 331.5 °C, respectively. These results represent declines of 2.9 and 6.2 °C compared to the control. Also, a reduction of 3.6 °C and 5.1 °C occurred in the final degradation temperature (T_{end}) of the composites BMA-10 and BMA-30, respectively, compared to the control. The degradation of the composites took place at lower temperatures in the presence of BMA, and both T_{onset} and T_{end} of composites decreased with the increasing BMA. This was also indicated by the fact that, although the maximum weight loss temperature (T_{max}) of the control and composite BMA-10 were comparable, composite BMA-30 had a significantly lower T_{max} than the control. The decrease in the thermal stability of the composites with the addition of BMA could be due to the presence of a thermoplastic molecular chain within UPE matrices, exhibiting easier internal molecular rotation. Further, the reduction in the thermal stability of the composites was more obvious at high BMA content due to decreased crosslinking density. Again, the amount of char residue formed in the composites at 600 °C decreased with the introduction of BMA into the UPE matrices.

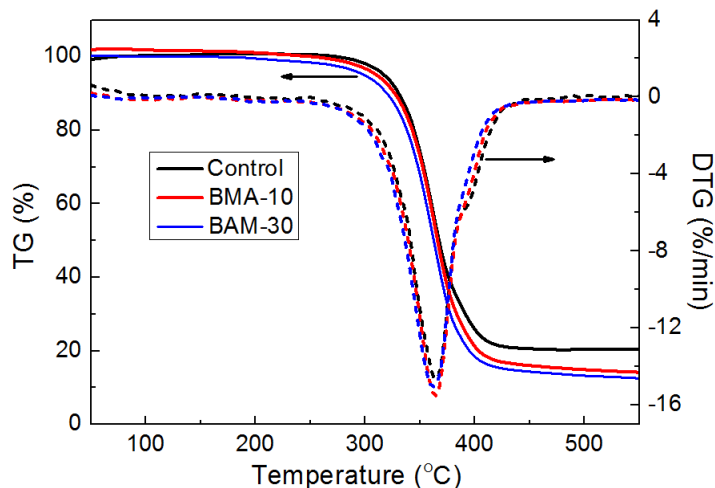


Fig. 3. TGA and DTG curves of untreated and BMA-treated UPE composites

Table 1. Thermal Properties of Untreated and BMA-treated UPE Composites

Samples	Degradation temperature (°C)			Char residue weight percentage at 600 °C (%)
	T_{onset}	T_{end}	T_{max}	
Control	337.7	389.8	364.5	20.7
BMA-10	334.8	386.2	364.1	13.7
BMA-30	331.5	384.7	361.9	11.8

Morphology Analysis

Fibers with smooth surfaces and obvious gaps between fibers and resins were also observed, indicating a poor interface in the composites without BMA. This also suggests that the cracks in composites might propagate in a planar manner under impact loading (Liu *et al.* 2014). However, the failure surfaces of composite BMA-10 (Fig. 4b) were rougher and some filamentous materials appeared in the matrices, perhaps resulting from the broken and plastic-deformed fibers at the tip of the crack. The interfaces of the composites were more indistinct, indicating a typical ductile fracture. These images demonstrate that the incorporation of 10 wt.% BMA in UPE slightly improved the toughness of the matrices and the interfacial adhesion between the fibers and UPE resins. This characteristic was also observed in the SEM image of composite BMA-30 (Fig. 4c); the filaments shown in the SEM image were longer and more noticeable and the surface of the fracture was rougher. Although the fibers were pulled out of the matrix, some resin remained on the fiber surface. The rough and filamentous surfaces should result from the dissipation of impact energy due to shear deformation during the crack propagation (Liu *et al.* 2014). Furthermore, less distinct phase separation between the fibers and matrices was observed (Figs. 4b and 4c), compared to that of the control (Fig. 4a). This indicates that the incorporation of flexible molecular chains in UPE induced a yielding process within the matrix, thus increasing the energy required for the fracture of the composites (Mandhakini *et al.* 2012). A further explanation is that BMA is a monomer that more easily undergoes internal rotation, and when it was properly introduced into UPE, the crosslinking degree, deformability, and toughness of the resins increased to some extent after curing.

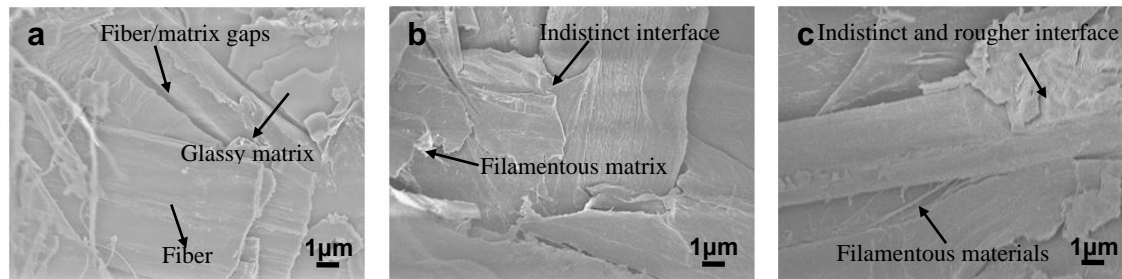


Fig. 4. SEM images of the impact-fractured surfaces of hemp-UPE composites: (a) Control specimen, (b) BMA-10 specimen, and (c) BMA-30 specimen

CONCLUSIONS

1. Hemp-UPE composites with properly-added BMA had significantly greater elongation at break, flexural strain, and impact strength properties without any decrease in their tensile or flexural strengths.
2. The toughness of the composites significantly increased as BMA usage increased. The composites with 20 to 30 wt.% added BMA exhibited a good stiffness-toughness balance.
3. The incorporation of BMA into UPE significantly decreased the storage modulus and glass transition temperature of the resulting composites and increased their damping parameters due to the introduction of flexible segments into the UPE resins.
4. The thermal stability of the composites decreased slightly after BMA was incorporated and the interfacial adhesion between hemp fibers and UPE matrices was improved.
5. The SEM graphs showed that fracture surface of the control exhibited brittle fracture in comparison of ductile fracture of the composites with the incorporation of BMA, which evidenced that the toughness of the composite was improved with proper usage of BMA.

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