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Environmental effects on bamboo-glass/polypropylene hybrid composites

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The effects of environmental aging and accelerated aging on tensile and flexural behavior of bamboo fiber reinforced polypropylene composite (BFRP) and bamboo-glass fiber reinforced polypropylene hybrid composite (BGRP), all with a 30% (by mass) fiber content, were studied by exposing the samples in water at 25°C for up to 1600 h and at 75°C for up to 600 h. Reduction in tensile strength for BFRP and BGRP was 12.2% and 7.5%, respectively, after aging at 25°C for about 1200 h. Tensile and flexural strength of BFRP and BGRP were reduced by 32%, 11.7%, and 27%, 7.5% respectively, after aging at 75°C for 600 h. While the strengths of the bamboo fiber reinforced composites reduce with sorption time and temperature, the environmental degradation process can be delayed by adding a small amount of glass fiber. Moisture sorption and strength reduction are further suppressed by using maleic anhydride polypropylene (MAPP) as a coupling agent in both types of composite system. *© 2003 Kluwer Academic Publishers*

1. Introduction

Natural fibers such as jute, coir, sisal, and bamboo etc. and their products have been widely used in engineering materials in various industries such as textile, paper, chemical, and construction. Over the past decade natural fiber reinforced composites are employed as substitutes for synthetic fiber reinforced composites used in the building/construction industry because the reinforcement is low cost and from renewable resources. Durability of a material becomes a critical issue when it is intended for prolonged period of usage. Polymer composites are sensitive to environmental conditions in that their physical and mechanical properties are influenced by hygrothermo-mechanical loads. Moisture diffuses into all organic matrices during aging under humid environment, and the mechanical properties of fiber reinforced polymer composite are degraded as a result of attacking by absorbed moisture to the fiber, the fiber/matrix interface/interphase region, and the matrix itself. The degree of deterioration and reversibility of properties of the composite materials are largely dependent on the extent of moisture sorption [1, 2]. Natural fibers readily absorb moisture because they contain abundant polar hydroxide groups, which results in a high moisture sorption level of natural fiber reinforced polymer matrix composites (NFRC), and is a major obstacle for preventing extensive applications of these materials. Another limiting factor for natural fibers to be used as reinforcement to the polymer matrix is that they are thermally unstable at elevated temperatures. Generally, the properties of most natural fibers are thermally weakened at about 160°C.

Effects of temperature and moisture on the thermal and mechanical properties of some natural fiber reinforced polymer composites have been reported in a few studies [3–9]. It has been shown that the extent of water sorption of NFRC depends on the relative humidity of the environment, fiber volume fraction, type of polymer used, sorption time, as well as temperature. Mechanical properties (tensile, flexure, impact) of these composites drastically decrease with soaking time and temperature. The saturated moisture content and level of deterioration is greater under aging at elevated temperature [3]. Pretreatment of natural fiber using chemical methods (for instance, use of coupling agent such as silane compound) enhances the adhesion at the fiber-matrix interface and reduces moisture sorption of these fibers. As a consequence, retention in mechanical properties of NFRC under environmental aging is improved. In addition, the amount of moisture sorption can be reduced significantly by replacing of natural fiber with a small amount of synthetic fiber such as glass or carbon [10–18]. However, the effect of long term hygrothermal loading on the mechanical properties of bamboo fiber reinforced polymer matrix composites and their hybrid composites have not been studied in detail.

In this work, the effect of environmental aging on retention of tensile and flexural properties of bamboo fiber reinforced polypropylene composites (BFRP) and bamboo-glass fiber reinforced polypropylene hybrid composites (BGRP) were studied. The effects of

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coupling agent (MAPP) on the mechanical properties of both types of composites were also examined, and qualitative correlation to between results from aging and accelerated aging is discussed.

2. Material and method

2.1. Sample fabrication

Polypropylene with a density of 0.908 g cm^{-3} and melt flow index of 9 and maleic anhydride polypropylene (MAPP) with a density of 0.902 g cm^{-3} (melting temperature at 140°C by DSC measurement) were obtained for this study. Bamboo fiber extracted from locally grown bamboo, and E-glass fiber with the density of 2.25 g cm^{-3} were used to fabricate short fiber reinforced composite samples. The physical and mechanical behavior of PP, bamboo fiber and glass fiber is described in Table I.

Bamboo fibers of different lengths were obtained using a laboratory scale extraction technique. Cylindrical bamboo culms deprived of nodes were cut into smaller pieces of 1–1.5 m in length and soaked in water for 24 h. After soaking the culms were manually sliced into 1-cm wide strips with a knife. Thin bamboo rods approximately 1 mm in diameter were obtained by passing the wider strips through an extruder. Small chips of bamboo 1 mm × 10 mm in dimension were then obtained from cutting the longer rods. Short bamboo fibers were obtained by grinding bamboo chips with a high-speed blender for approximately half an hour. Ground bamboo fibers with four different size ranges: (1) 0.25 mm, (2) 0.5 mm, (3) 1–6 mm, and (4) 6–12 mm were obtained using sieves with different aperture sizes. The extracted fibers were dried in an oven at 105°C for 72 h in order to remove moisture. Glass fibers 6 mm in length was obtained by cutting from continuous fiber roving using an electronic fiber-cutting machine. These short glass fibers were also dried in an oven at 105°C for 24 h to remove surface moisture.

Bamboo fiber length (6–12 mm) is used to prepare bamboo fiber-polypropylene composites (BFRP) without coupling agent to study the effect of bamboo fiber loading to the composite. For the environmental tests, bamboo fiber length (1–6 mm) and glass fiber length (6 mm) is used to prepare six different types of samples with total fiber content 30% by mass with and without coupling agent. Coupling agent MAPP (10% by mass) is used for making the sample with PP/MAPP matrix. The sample code and their contents are listed in Table I. BFRP and BGRP samples were prepared by first melt mixing the constituents using a torque rheometer (Hakkae rheocord 90) at 190°C and a rotor speed of 40 rpm for 8–10 minutes. After mixing, the mixture of bamboo fiber, glass fiber, and PP (with or without MAPP) was transferred to and homogeneously distributed in a stainless steel mold and then pressed at 190°C and 3.2 MPa for 30 minutes. The resulting material was a randomly oriented short fiber composite or hybrid composite plate of dimension 20 cm × 20 cm × 0.3 cm.

TABLE I Sample code for various types of BFRP and BGRP. Length of glass fiber is 3 mm, length of bamboo fiber is 1–6 mm

Sample code	Glass fiber content (wt%)	Bamboo fiber content (wt%)	Matrix type
BFRP (B)	0	30	PP
BGRP (H1)	10	20	PP
BGRP (H2)	20	10	PP
BFRP (BM)	0	30	PP/MAPP
BGRP (HM1)	10	20	PP/MAPP
BGRP (HM2)	20	10	PP/MAPP

TABLE II Physical and mechanical properties of neat PP, Bamboo fiber (BF), glass fiber (GF), and wood fiber

	Density g cm^{-3}	Tensile strength (Mpa)	Modulus of elasticity (Gpa)	Average diameter (μm)
PP	0.98	18	2.2	–
Bamboo fiber	1.4	450–800	18.5–30	60–100
Wood fiber	0.6	400	13.5	14
Glass fiber	2.25	1470–1460	72.5	12

2.2. Tensile testing

Dog-bone shaped samples of BFRP and BGRP with dimensions 60 mm × 12 mm × 3 mm were produced from the composite plates and then tested according to ASTM standard D639. Samples were tested to failure under tension at a cross-head speed of 1.5 mm $\cdot$ s^{-1} using an Instron® tensile tester. An extensometer was attached to the gauge section of the sample for strain measurement. Five samples were tested for each type of sample. Tensile strength, failure strain, and tensile modulus were recorded. Experimental tensile test results of BFRP and BGRP is compared to the theoretical data according to modified Bowyer and Bader model.

2.3. Flexural testing

Four-point bend tests were performed on BFRP and BGRP samples of dimensions 60 mm × 12 mm × 3 mm according to ASTM D790M. A cross-head speed of 1 mm min^{-1} was used. An extensometer placed under the tensile side of the sample at the mid-span was used to measure the mid-span deflection of the composite beam. Flexural strength and strain to failure were determined. Four samples were tested for each type of sample.

2.4. Environmental aging and accelerated aging

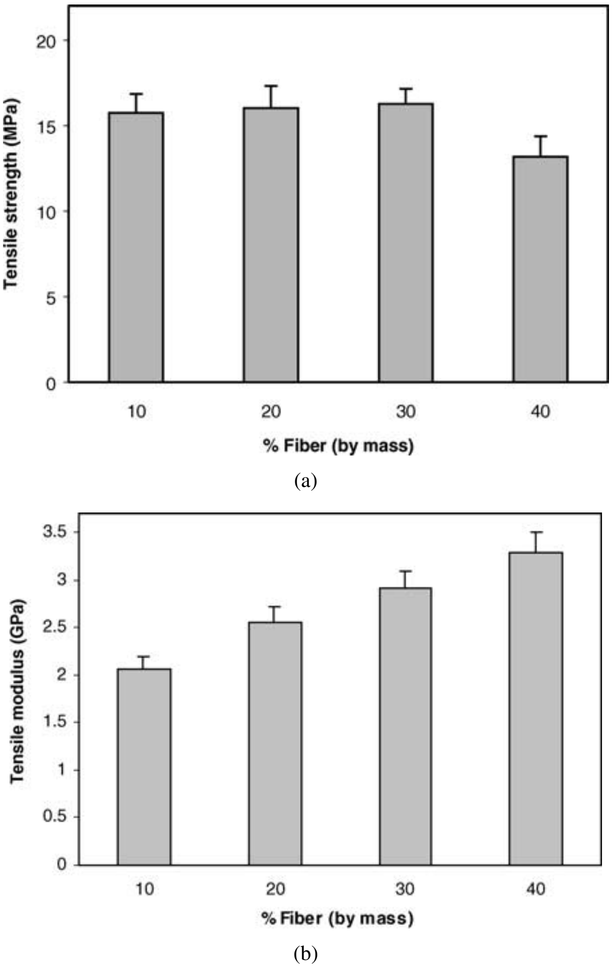
Dog-bone shaped BFRP and BGRP samples were fully immersed in water at 25°C for up to 1600 h. Mass change of the samples was recorded using an electronic balance at regular time intervals. Tensile tests were performed after 520 h and 1200 h to determine residual strength and modulus after aging. Tensile and flexure strength of BFRP and BGRP samples were also measured after immersing in water at 75°C in an environmental chamber for 600 h. Fracture surfaces of failed samples after tensile and flexural test (before and after aging) were examined using scanning electron microscope (SEM) to interpret the effect of absorbed moisture on the fibers, the matrix, and the fiber/matrix interface/interphase region.

3. Results and discussion

3.1. Tensile tests

Effect of fiber loading on the randomly oriented bamboo fiber composites (without MAPP) is shown in Fig. 1. It is observed that the tensile modulus of the BFRP composites increases linearly with an increase in fiber content. Incorporation of 40% (by mass) fiber improved the modulus of neat PP by 50%. A 60% increase in tensile modulus is seen at 40% (by mass) bamboo fiber content compared to the case of 10% (by mass) bamboo fiber content in BFRP.

However, a notable reduction in the tensile strength of neat PP from 28.9 to 15.8 MPa was observed by addition of 10% fiber (by mass). This may be because of the fiber was behaving as flaws at low fiber loading [19]. The mean tensile strength is in marginal with further increase in fiber content up to 30% (by mass) and it is dropped by 16% at 40% (by mass) fiber content compared to the case of 10% (by mass) fiber content. The decrease in tensile strength at high fiber loading could be a reflection of poor fiber adhesion between fiber and matrix, which promoted micro crack formation at the interface as well as non-uniform stress transfer due to the fiber agglomeration in the matrix. Generally, fibers start reinforcing the matrix when the fibers are sufficient to restrain the matrix leading to uniform stress distribution. The tensile strength of the unfilled polymer initially drops up to a critical fiber volume fraction and above which the fiber reinforces the matrix. The minimum amount of fibers needed to restrain the matrix is smaller if the matrix strength is higher [20]. Strength of a composite can achieve their optimum condition only when it has a critical fiber volume fraction and perfect interfacial strength. The critical volume of a composite depends on the nature of fiber and matrix, fiber aspect ratio, fiber/matrix interfacial adhesion, etc.



(a)

(b)

Figure 1 Effects of fiber loading on (a) tensile strength (b) tensile modulus of BFRP without MAPP. (Bamboo fiber length 6–12 mm).

Moreover, the extent of fiber orientation significantly affects the performance of any short-fiber-reinforced polymer composite. The efficiency of stress transfer is optimum if fibers are aligned parallel to the direction of the applied force. Poor fiber alignment at lower fiber loading could be a result of larger free space for fiber to move around. At high fiber loading, however, aggregation of the fibers due to restricted freedom to orient themselves results in degrading the strength of the composite [21].

Enhancement in mechanical properties of BGRP over BFRP is expected when weaker and less stiff bamboo fiber (strength ranged between 450–800 MPa and stiffness about 18.5–30 GPa is replaced by stronger and stiffer E-glass fiber (with strength and stiffness about 1470 MPa and 72 GPa, respectively. The results of tensile tests of BFRP and BGRP samples, with and without MAPP in the PP matrix, are shown in Figs 2 and 3. In this case, fiber content was kept at 30% (by mass).

Improved in tensile properties of BFRP after hybridization with stronger and stiffer glass fiber can be observed in their stress-strain behavior. The overall stress-strain behavior of BFRP and BGRP under tensile loading is non-linear, typical curves are shown in Fig. 2. Usually, a linear behavior is displayed up to 0.25% strain, and the curve begin to level out at about 0.8% strain. The strain at maximum tensile stress for all types of samples ranged from 1.59–1.67%.

In Fig. 3, it is observed that tensile strength and modulus of BGRP samples (H1 and H2) are gradually increased compared to that of BFRP (b). For instance, the average tensile strength and modulus of BGRP (H2) has increased by 15% and 18%, respectively, compared with BFRP (b).

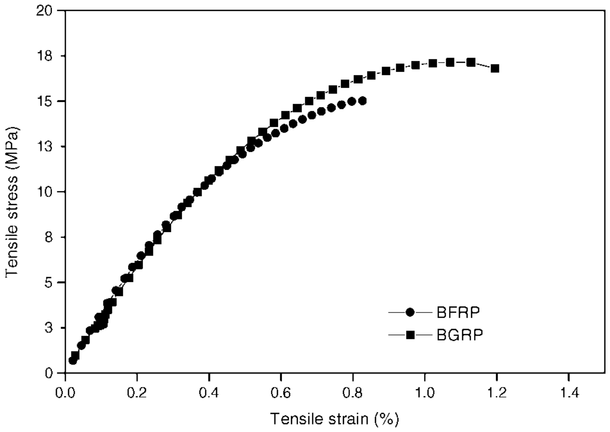


Figure 2 Typical tensile stress-strain curves of BFRP and BGRP.

All of the BFRP and BGRP samples failed under tension by a relatively planar crack through the matrix. The exhibited nonlinear stress-strain curves together

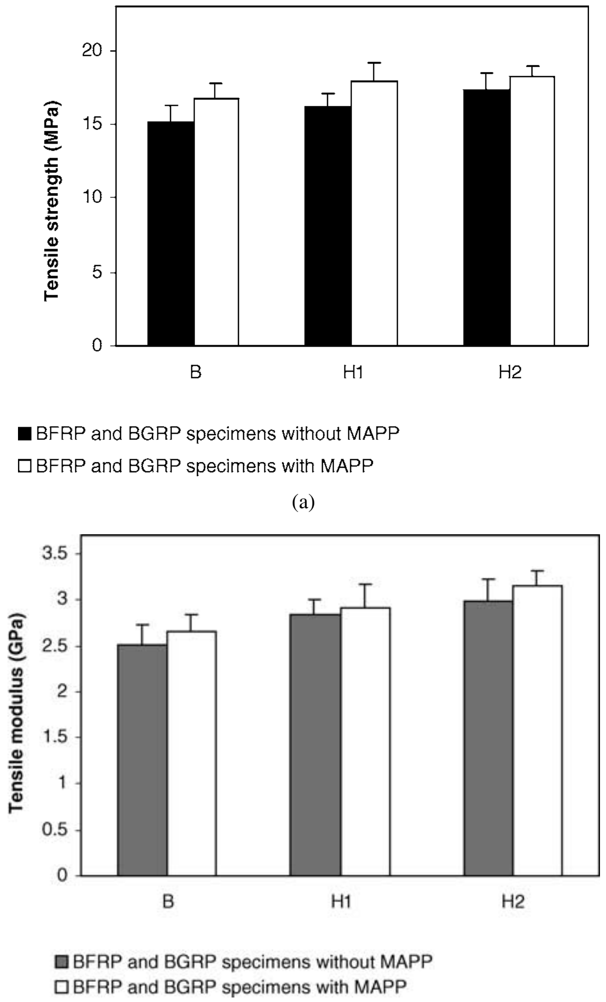


Figure 3 (a) Tensile strength (b) tensile modulus of BFRP and BGRP (with or without MAPP) before aging. (Fiber content- 30 mass%, bamboo fiber length- 1–6 mm, glass fiber length- 6 mm).

with extensive fiber pullouts seen for both glass and bamboo fiber suggest their reinforcing effect. However, large gaps between the fibers and the PP matrix indicate poor adhesion at the interface (Fig. 4).

With inclusion of a compatibilizer (MAPP), a further increase in tensile strength of about 5–11% was observed for all samples compared to their counter parts without MAPP as described in Fig. 3a. This is because enhanced adhesion between the reinforcing fibers and the PP matrix results in a more efficient transfer of stress along the fiber/matrix interface. However, the difference in tensile modulus of BFRP and BGRP (both with MAPP) are more or less the same compared to those without MAPP under statistical scrutiny ($P > 0.05$).

Bamboo and glass fibers do not generally adhere well to the PP matrix, a consequence of the chemical nature of these materials: the fibers are hydrophilic while PP is hydrophobic. MAPP can act as a compatibilizer in BFRP as maleic anhydride ($((CH_3CO)_2O)$) can be bonded strongly to the OH group on the bamboo fiber surface and the SiO group of the glass fiber, resulting in an improved interfacial adhesion between the matrix and both types of fibers.

Morphological evidence of improved adhesion between bamboo fiber and the MAPP-PP matrix is found, typical examples are shown in Fig. 5, taken from the tensile fracture surface of a sample. The bamboo fiber is well bonded to the PP-MAPP matrix (Fig. 5a), in contrast to detached fibers from the matrix (Fig. 4b). In this case fiber pullout is less extensive and improved interface is seen with the PP-MAPP matrix, shown in Fig. 5b, compared to those without MAPP.

It is noted that tensile strength of all BFRP and BGRP samples (with or without MAPP) could not reach to that of unfilled PP, however, obviously improved in tensile modulus is observed in all type of samples.

A comparison of results from theoretical model and experiments on tensile strength and modulus of BFRP and BGRP (without MAPP) at 30% (by mass) in fiber content is shown in Fig. 6. In the modified Bowyer and Bader's model, the tensile strength, T_c, and modulus, M_c, of a short-fiber composite are

$$T_c = T_f K_1 K_2 V_f + T_m V_m \tag{1}$$

$$M_c = M_f K_1 K_2 V_f + M_m V_m \tag{2}$$

where K_1 and K_2 are the fiber orientation factor and the fiber length factor, respectively. For fiber length $l > l_c$, $K_2 = l - l_c/2l$ and for fiber length $l < l_c$, $K_2 = l/2l_c$. l_c is the critical length of the fiber.

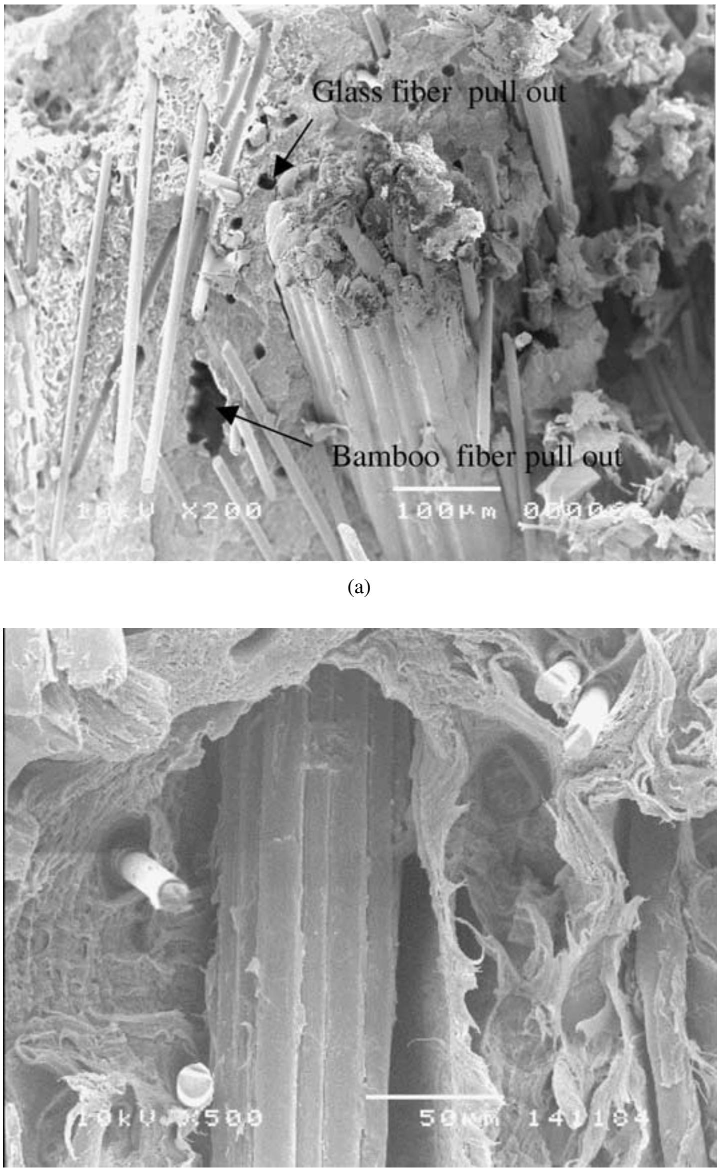
The fiber orientation factor, K_1, is 1.0 for perfectly aligned short fiber reinforced composites in the on-axis direction [22]. The same value of K_2 is obtained when fiber length, l, is equal to the critical fiber length, l_c, which is expressed in terms of fiber diameter, D, and interfacial shear stress, τ, and remote fiber stress, σ_f:

$$l_c = \frac{D\sigma_f}{2\tau} \tag{3}$$

Bamboo and glass fiber 3 mm in length is used as critical fiber length based on the previous results [20]. The fiber orientation factor K_1 for randomly oriented composites is 0.2 and K_2 is assumed to be 0.5 in our case [21].

It is observed that the experimental values of the Young's modulus of BFRP and BGRP are in agreement with the theoretical predictions. However, the gap between the experimental and theoretical results of the tensile strength is quite large. Low experimental tensile strength of the composites may be due to insufficient interfacial adhesion between the fiber and the matrix, as well as extent of fiber orientation. The highly hydrophobic nature of the bamboo fiber affects the mechanical strength of the composites because water on the fiber surface acts as a separating agent on the fiber/matrix interface. Moreover, pores appeared in the matrix due to moisture release from the fiber during processing might cab be viewed as internal damage. Both phenomena may lead to reduction in mechanical properties.

The interfacial adhesion strength between the fiber and the matrix plays a vital role on the mechanical properties of the composites. The adhesion between the bamboo fiber and PP resin is rather poor because of their different chemical nature. The poor wettability and adhesion characteristics of bamboo fiber towards polypropylene matrix are direct consequences of the hydrophilic nature of the bamboo fiber. Absorption of moisture by bamboo lowers its modulus and the presence of moisture at the bamboo-polymer interface



(a)

(b)

Figure 4 Fracture surface of a BGRP sample after tensile test (a) bamboo and glass fiber pulled out from the PP matrix, (b) weak interface between fiber and PP matrix.

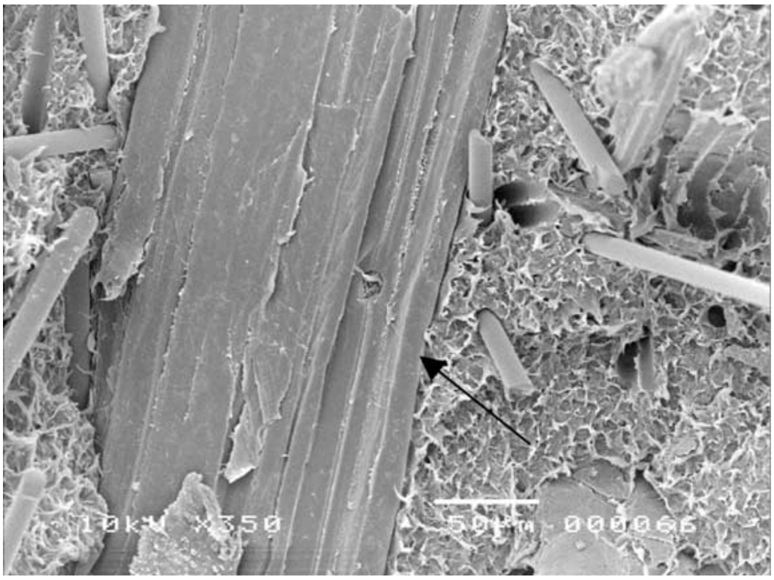
may contribute to initiate the debonding process between the fiber and the resin. The lack of interfacial interactions due to insufficient wetting on the fiber may induce the poor mechanical properties for the composites.

Previous results showed that using compatibilizer MAPP enhance the tensile properties of the composites. This may be affected by the improved adhesion at the interface, well dispersion of the fiber in the matrix, reducing the fiber attrition during processing and critical fiber length of the composite [23].

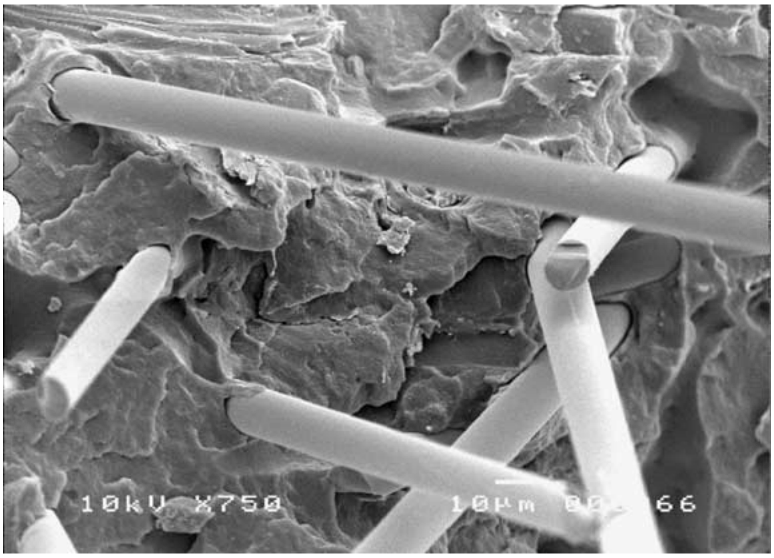
Moreover, in the case of short fiber composites the stress transfer depends on the fiber orientation, stress concentration at the fiber ends, and critical fiber length, etc. Poor fiber dispersion and fiber agglomeration in the composites without coupling agent may leading to non-uniform stress transfer between the fiber at the matrix at high volume fraction [24]. These aforementioned facts combine to produce a composite (BFRP) of less than desirable strength, toughness and also relatively poor environmental resistance.

3.2. Flexural tests

Both BFRP and BGRP samples displayed non-linear behavior under flexural loading, a typical load-displacement curve is shown in Fig. 7. The flexure strain of BGRP at failure ranged between 1.3–1.8% whereas 2–3% is found for BFRP. Damage in the form of matrix cracking initiated from the tensile side of the sample and propagated through the thickness of the sample, causing failure. The flexure strength and modulus of BFRP and BGRP with various glass-to-bamboo fiber ratio are shown in Fig. 8. BGRP (sample **H1**) is found to be considerably stronger and stiffer than BFRP (sample **B**). Replacing bamboo fiber by 10% (by mass) glass fiber in the PP matrix results in a 10 and 20% increase in flexural strength and modulus of the composite, respectively. The flexure strength and modulus have increased significantly in both all-bamboo-fiber and the hybrid composite, using MAPP-PP matrix. The flexural strength and modulus of sample **BM** is 25 and 35% higher than that of sample **B**, respectively; and they are 35 and 40% higher for sample **HM1** than sample **H1**,



(a)



(b)

Figure 5 (a) SEM image showing improved adhesion between the bamboo fiber and the PP-MAPP matrix. (b) SEM image showing glass fibers well bonded to the PP-MAPP matrix.

respectively, implying an improved fiber/matrix interfacial adhesion.

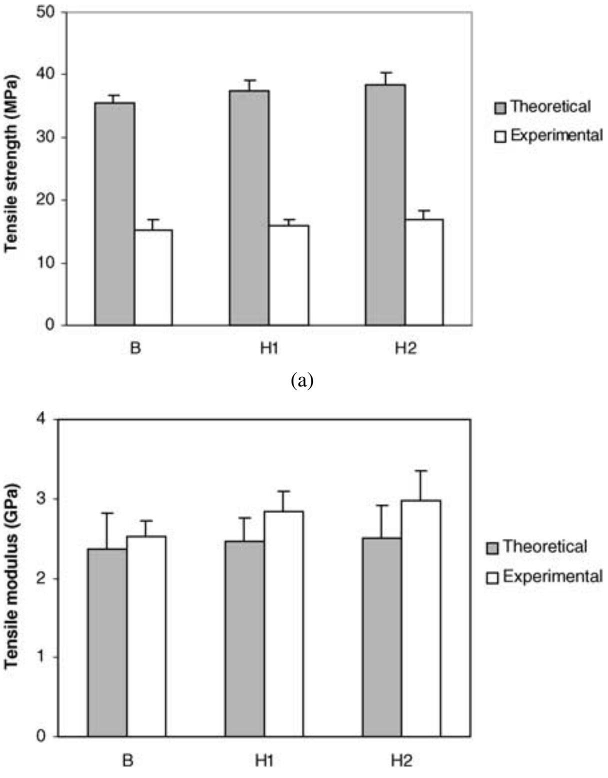
3.3. Sorption behavior

Water diffuses through the composite sample mainly by two possible mechanisms: water molecules diffuse directly into the matrix and reach the fibers, or they enter the composite by capillary action along the fiber-matrix interface, followed by diffusion from the interface into the bulk resin. The rate of water diffusion depends on external environments such as temperature and applied stress, as well as internal material states such as debonding at the fiber-matrix interface, matrix cracking, and the inherent sorption property of the constituent materials.

Percent mass gain during aging, $\Delta M(t)$, is calculated according to

$$\Delta M(t) = \frac{M_t - M_o}{M_o} \times 100 \tag{4}$$

where M_o and M_t are the mass of the sample measured before and during aging, respectively. The sorption curves at 25°C, shown in Fig. 9, where mass change is plotted against the square root of soaking time, all display Fickian-like behavior with a saturation level attained after about 1600 h. The saturated moisture level for BFRP (about 13%) is substantially higher than that of most glass fiber reinforced polymeric composites, attributed primarily to high moisture uptake of the bamboo fiber. Replacing bamboo with glass fiber results in reduced moisture sorption of the composite since moisture uptake is negligible for the latter. The saturated moisture level for samples **B**, **H1**, and **H2** after 1600 h are 13, 11.5, and 9.5%, respectively. Use of PP-MAPP matrix further reduces water uptake by about 1.5–2% for both BFRP and BGRP samples. This reduction in moisture level is attributed to an improved fiber/matrix interfacial bonding that reduces water accumulation in the interfacial voids and prevents water from entering the bamboo fiber.



(a)

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Figure 6 A comparison of the experimental and theoretical value of (a) tensile strength (b) tensile modulus of BFRP and BGRP (without MAPP).

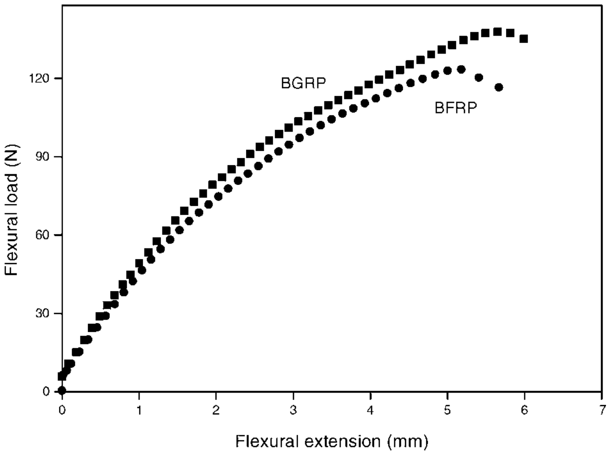
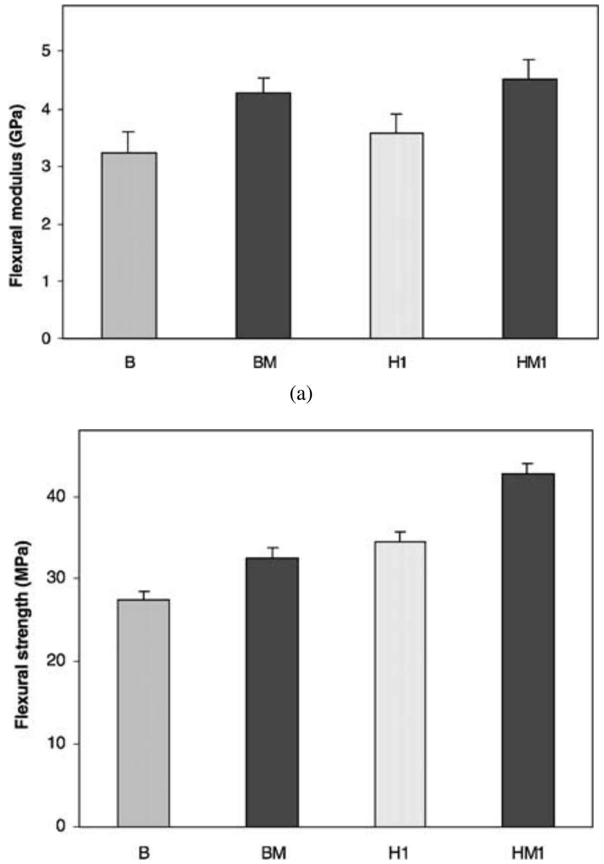


Figure 7 Typical load-displacement curve under flexural load of BFRP and BGRP.



(a)

(b)

Figure 8 (a) Flexural strength and (b) Flexural modulus of BFRP and BGRP before aging.

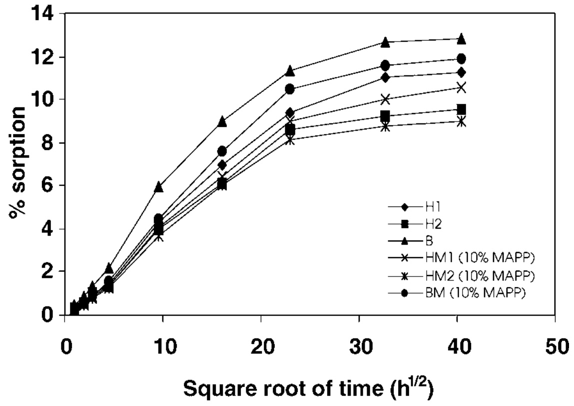


Figure 9 Sorption behavior of BFRP and BGRP at 25°C.

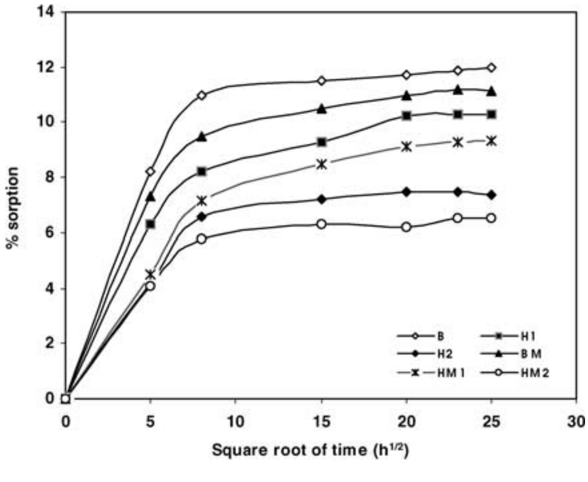
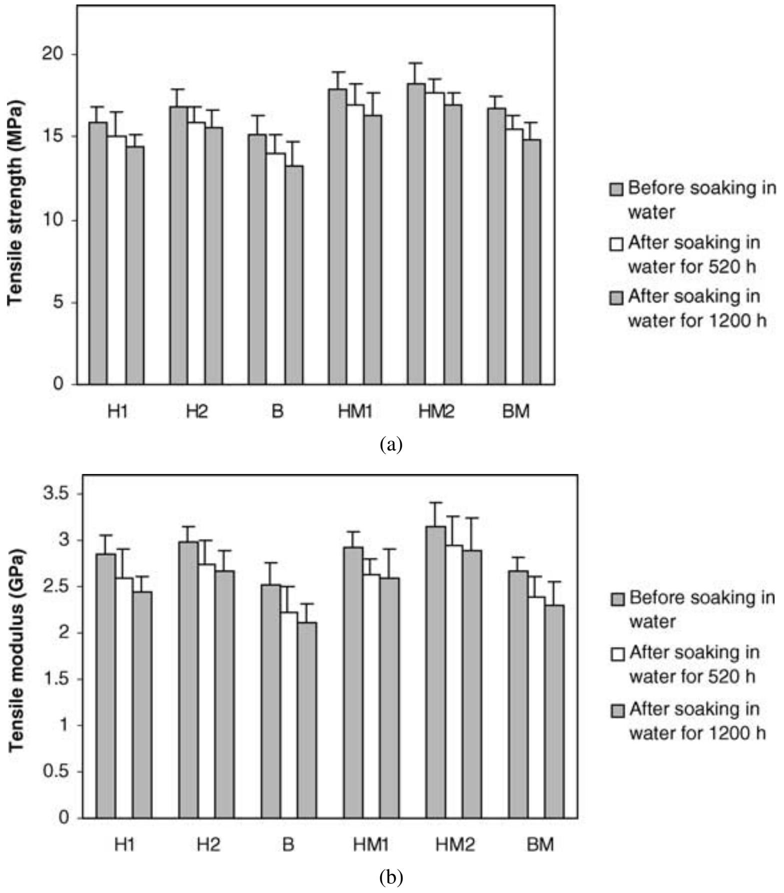


Figure 10 Sorption behavior of BFRP and BGRP at 75°C.

Water sorption behavior of BFRP and BGRP samples at 75°C displayed a pseudo-Fickian behavior up to 600 h where a saturated moisture level had not been seen, as shown in Fig. 10. A plausible cause is that internal damage (such as interfacial debonding that accumulates water) continues to develop with soaking time. Sorption rate is significantly higher compared to those aged at 25°C during the initial stage. Moisture content ranged from 6.2–12% for BFRP and BGRP samples, after 400 h. The mass gain during aging decreases with an increase of glass fiber content and with the use of MAPP-PP matrix, a trend that is seen previously for samples aged at 25°C. Compared to those aged at 25°C, mass gain is lower when aged at 75°C after about 600 h, caused by dissolution of components of the bamboo



(a)

(b)

Figure 11 (a) Tensile strength and (b) tensile modulus of BFRP and BGRP before and after aging in water at 25°C for 520 h and 1200 h.

fiber (e.g. lignin) and the PP matrix, which is visually evident under scanning electronic microscope (more will be said on this later). Thus the mass gain recorded at 75°C does not represent the true moisture level absorbed by the material, rather, it is a quantity resulting from both moisture ingress and mass loss from the material itself.

3.4. Tensile tests after aging at 25°C

Moderate drop in tensile strength and modulus for all of the samples were seen after aging in water at 25°C for up to 1200 h, results are summarized in Fig. 11. The results indicate that retention of mechanical properties of BGRP (with PP matrix) is better than BFRP (with PP matrix). For example, reduction in tensile strength of sample **B** (BFRP) is 7.3 and 12.2% after 520 h and 1200 h of aging, respectively, while for sample **H2** (BGRP) the reductions are 4.5% and 7.5%. The same data trend also applies to systems using the PP-MAPP matrix. Incorporation of MAPP in BFRP and BGRP enhance the retention in mechanical properties during aging. It is seen that retention of mechanical properties for samples with the PP-MAPP matrix is in general better than samples with the PP matrix. However, the difference is only moderate.

Degradation in bamboo fibers after aging is reflected by morphological changes of the fiber surface, shown in Figs 12 and 13. These SEM micrographs, taken from the tensile fracture surfaces of BGRP samples tested after aging, showed roughened bamboo fiber surface with cavities (Fig. 12) and splitting of bamboo fiber into thinner fibrils (Fig. 13). Although no significant change of surface morphology can be found on glass fibers, it has been confirmed by numerous studies that stress corrosion of glass fiber results in strength degradation [25]. Furthermore, obvious interfacial gaps between the fiber and the matrix are seen, presumably a result of dimensional instability as a consequence of moisture absorption. Some fine threads appeared on the fracture surface of the sample after aging, believed to be a result of swelling of the polymer matrix in moist environment (Figs 12 and 13).

Use of compatibilizer delays the degradation process during aging. Improved interfacial adhesion was found in samples with the MAPP-PP matrix. In such cases rough bamboo fiber surfaces similar to those shown in Fig. 12 were not seen after extensive examination under SEM. However, some threads are also found, believed to be from the PP-MAPP matrix.

3.5. Tensile and flexural tests after aging at 75°C

Results of tensile tests after aging in water at 75°C for 600 h are shown in Fig. 14. Similar to the previous case at 25°C, BFRP showed a greater reduction in tensile strength and modulus than those of BGRP, and retention in mechanical properties of the composites is enhanced by using the MAPP-PP matrix. For samples **B**, **H1**, and **H2**, reduction in tensile strength and modulus after aging for 600 h is quite substantial, ranged between 25–40% and 27–42%, respectively. It is worth mentioning that reduction in tensile strength of sample **B** is about

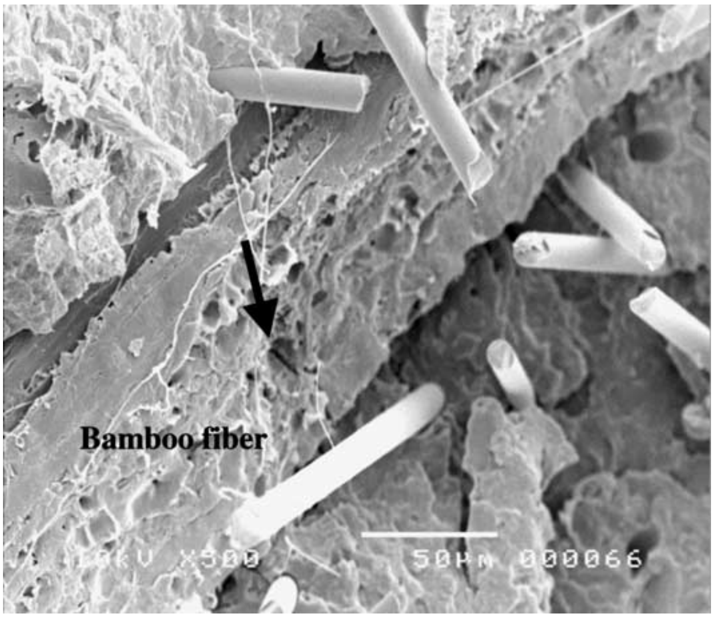


Figure 12 Effect of aging in water at 25°C for 520 h on BGRP (PP matrix) sample, showing roughened bamboo fiber surface.

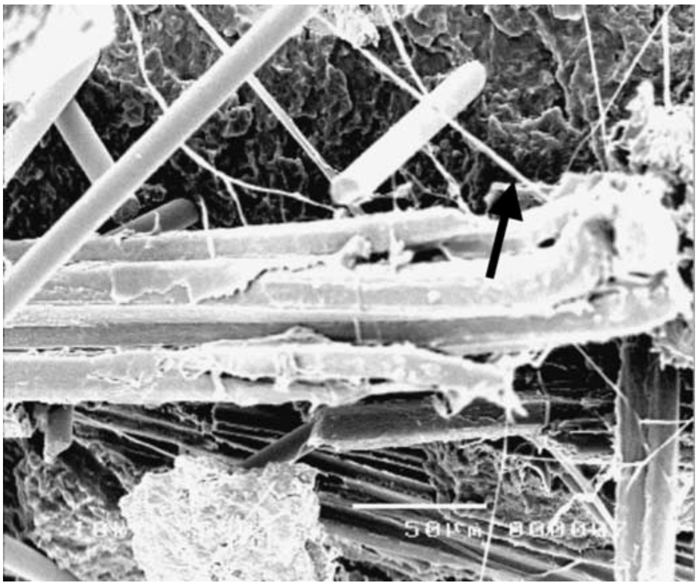
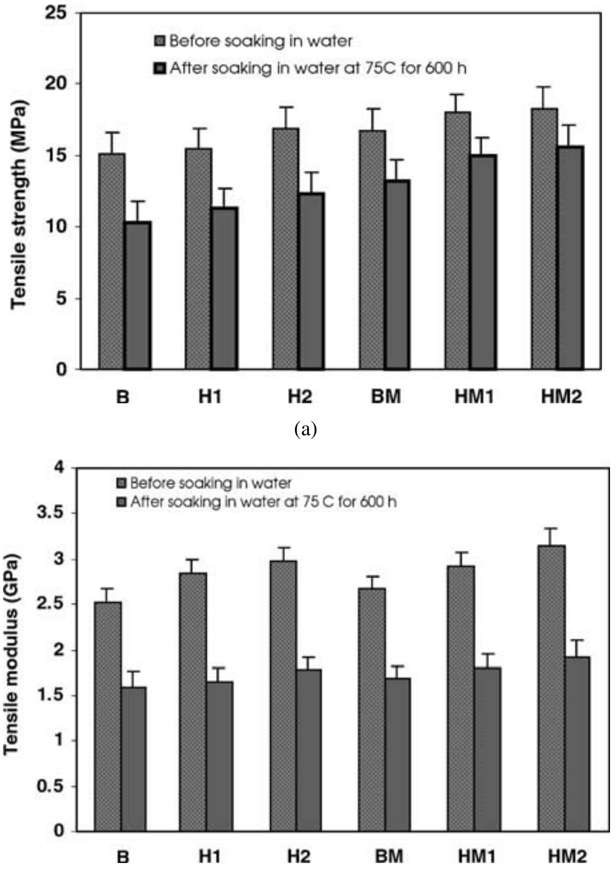


Figure 13 Effect of aging in water at 25°C for 1200 h on the BGRP showing roughened bamboo fiber surface and splitting of fibril. Thin strings of the polymer matrix are also seen on the fracture surface because of dissolution.

twice that of sample **HM2** under both aging conditions, suggesting the positive effect of hybridization and use of coupling agent in improving the durability. Also, from the sorption behavior, it is found that the moisture content of sample **HM2** is the lowest among all the systems, suggesting mechanical properties are strongly influenced by the amount of water absorbed.

A SEM micrograph of the tensile fracture surface of a BGRP sample after aging at 75°C is shown in Fig. 15. Small holes and cracks are clearly seen on the fiber surface and the bamboo fiber splits into thinner fibrils. After extensive examination, it is also found that the inner wall of the bamboo fiber become thinner compared with fiber before aging. The change in fiber morphology after accelerated aging can also be attributed to dissolution of chemical constituents of the bamboo fiber in hot water, resulting in weakened fiber. The evidence of the dissolution of the polymer matrix is also found in some part of the fracture surface of the sample (more will be said about this later). It is worth noticing that aging at elevated temperatures will also cause color change in samples. For the present case, the color of the sample became darker at higher temperature and longer aging times. The color of all of the samples changed from brown at 25°C to dark brown at 75°C. The change in color is usually associated with the dissolution of the coloring compound of the bamboo fiber and/or changing in refractive index of the matrix [2, 3].

Flexural strength and modulus of BFRP and BGRP samples were all dropped after accelerated aging, results are summarized in Fig. 16. Reductions in flexural strength and modulus for sample **B** (BFRP with PP matrix) are about 17 and 50%, respectively, for sample **H2** (BGRP with PP matrix), 7.3 and 33.3%; and for sample **HM2** (BGRP with MAPP-PP matrix), 3.4 and 20.3%. In general, retention in flexure properties is enhanced

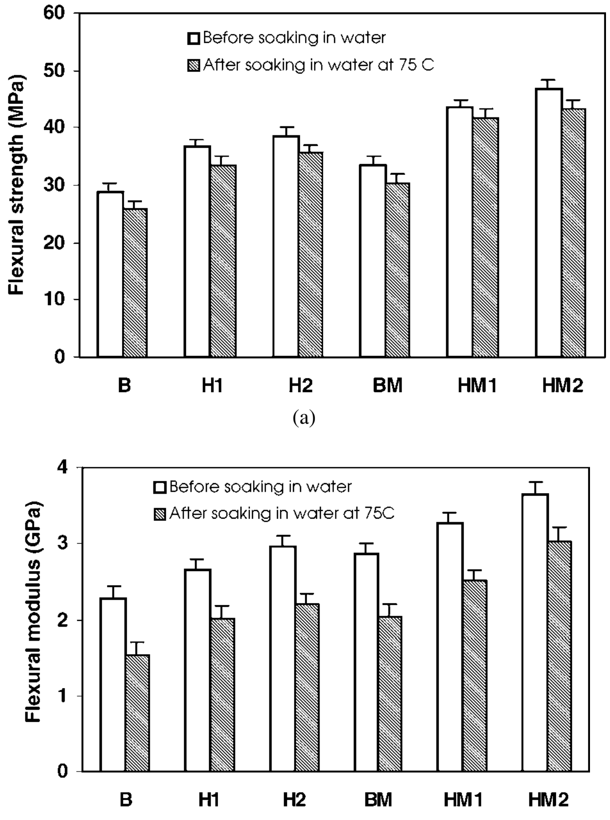


(a)

(b)

Figure 14 Effect of accelerated aging on (a) tensile strength and, (b) tensile modulus of BFRP and BGRP after aging in water at 75°C for 600 h.

by using MAPP in the PP matrix as well as with the addition of more durable glass fiber. Similar to tensile tests, SEM micrographs of BFRP and BGRP samples after flexure test also revealed change in bamboo fiber surface morphology, debonded fiber/matrix interface, and the degradation of the polymer matrix.



(a)

(b)

Figure 16 (a) Flexural strength and (b) Flexural modulus of BFRP and BGRP before and after aging in water at 75°C for 600 h.

3.6. Comparison of aging process at different temperatures

Accelerated aging is generally carried out in order to shed light on the long-term performance of material without actually carry out long-term test. Temperature is a key factor for accelerated aging in the processes of water diffusion and chemical degradation. Acceleration of test is justifiable if the accelerating parameter

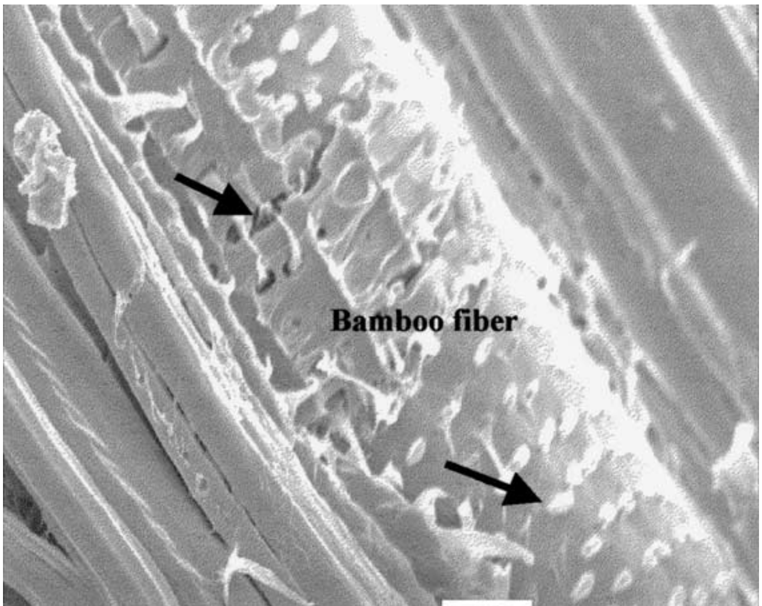


Figure 15 Tensile fracture surface of a BGRP sample after accelerated aging in water for 600 h, showing weakened bamboo fiber. Arrows indicate holes on the bamboo fiber surface and recrystallized polymer residues.

does not cause an change in the aging mechanism. The change in tensile and flexural properties of BFRP and BGRP during environmental aging is a consequence of the following degradation processes: (1) hygrothermal degradation of bamboo and glass fiber, (2) debonding at the fiber/matrix interface, and (3) dissolution and degradation of polymer matrix. Similarities and differences of these mechanisms will be compared at the two aging temperatures in terms of morphological evidence.

4. Fiber degradation

Degradation of the reinforcements plays an important role in strength reduction of fiber-reinforced composite as they are the major load-carrying constituents. It has been proposed that decrease in the tensile strength of glass fiber is caused by breaking of the Si—O—Si bond on the fiber surface by the attacking water molecules, and the process is accelerated at higher temperatures as can be best described by kinetic crack growth equation. Apparently, as suggested by most available data, temperature has no effect on the mechanism of crack growth [26, 27]. In our case, no morphological evidences indicate the different feature of glass fiber before and after aging.

Morphological features of bamboo fiber before and after aging in water at 75°C are shown in Figs 17 and 18. The ultra-structure of the bamboo fiber consists of alternating broad and narrow lamellae with different fibrillar orientation. Each layer is made up of lignin, pentosan, and cellulose compound and cellulose fibrils are embedded in the lignin-polyose matrix by hydrogen bonding [15]. The bonding between the layers of the bamboo fiber were loosen or broken during aging by the attacking water, leaving them detached from each other as the chemical constituents were being dissolved. Consequently, the diameter of the lumen (inner hole) of bamboo fiber became larger as the material in the inner layers was dissolved and transported out of the fiber. Increased diameter of the lumen of bamboo fiber is obviously in Fig. 18 compared to Fig. 17. Although similar morphological pattern is also seen from those aged at 25°C, exposure in elevated temperature has a much greater effect in terms of the extent of degraded morphology. Chain splitting of cellulose, as is obvious from the holes that are seen on the bamboo fiber surface (Fig. 18b), may be caused by the attack of water molecule during aging. Thus it can be concluded, based on morphological comparisons, that there is no fundamental difference in the degradation mechanism for the bamboo fiber at ambient and elevated temperatures.

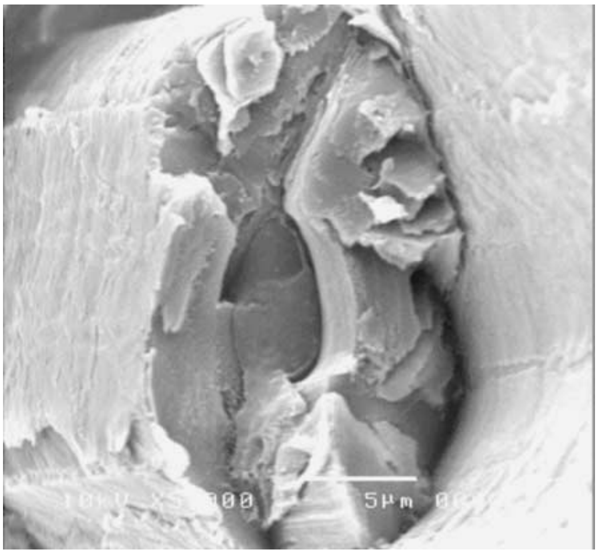


Figure 17 SEM micrographs of bamboo fiber (a) before aging, showing the lumen of bamboo fiber filled with polymer matrix.

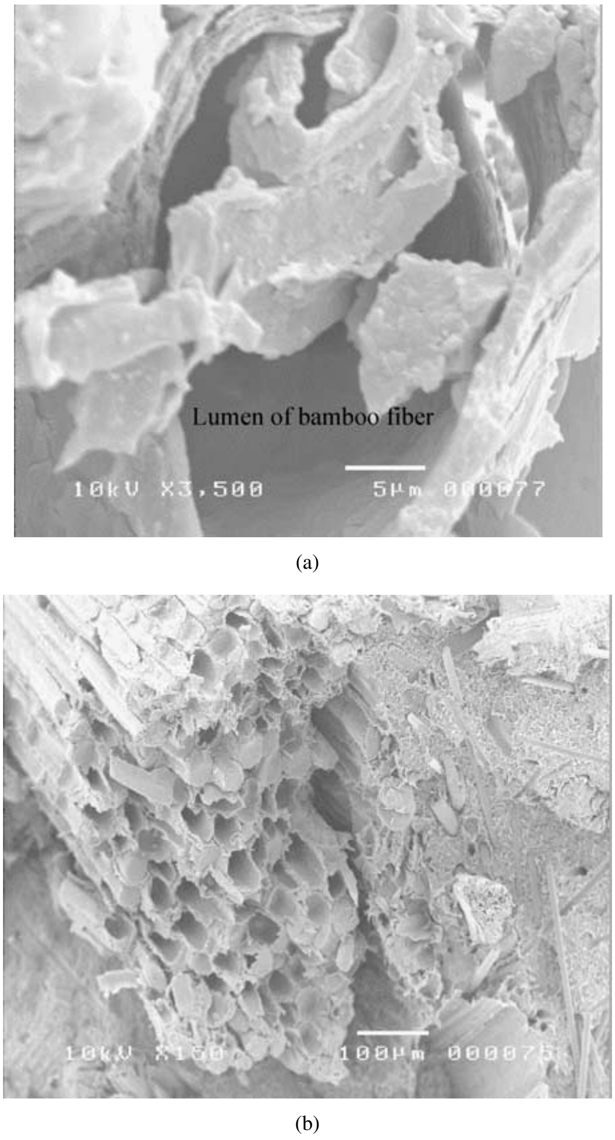


Figure 18 (a) SEM micrographs of bamboo fiber after aging at 75°C, showing the lumen with larger diameter because the detached inner layer was transported out of the fiber. (b) SEM micrographs of fracture surface of BGRP sample after accelerated aging in water for 600 h, showing weakened bamboo fiber bundle.

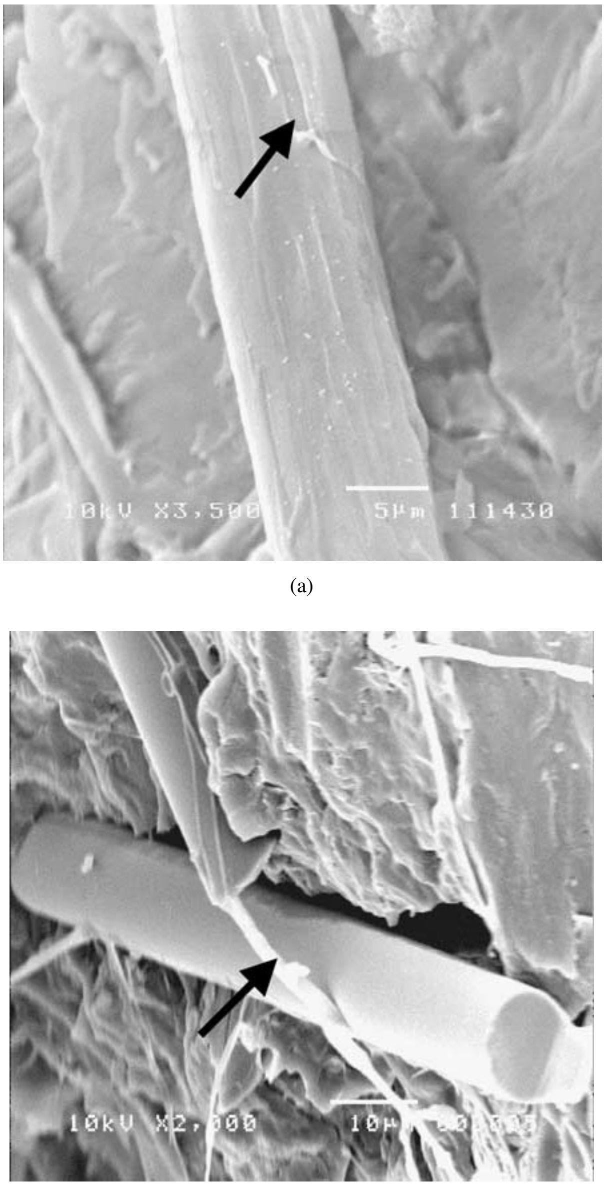
4.1. Matrix degradation

Physical and chemical changes may occur in the polymer matrix during hygrothermal aging. For instance, it is well established that plasticization of the matrix by water results in a lowering of its glass transition temperature (T_g), and generation of internal stress due to the accumulation of water molecules within the polymer network. T_g of a polymer is decreased by absorption of moisture because of the breaking of hydrogen bonds and making chain segment rotation possible. Softening of the materials results in a less efficient load transfer capability from the matrix to the fibers, and the fracture mode of the composites is changed from ductile to brittle [26–29]. As has been discussed earlier, water ingress is controlled by temperature and it follows that matrix plasticization is also controlled, at least in part, by temperature. However the interrelationship between water ingress, temperature, and matrix plasticization as well as the effect of the latter on the performance of the material cannot be elucidated without extensive experimentation.

Temperature also serves as a rate controlling parameter for other degradation mechanisms such as hydrolysis. Chemical changes occur due mainly to the hydrolysis of polymer bonds, dissolution, and leaching of the water-soluble species. Therefore, the extent of degradation of polymeric matrix at elevated temperature is expected to be greater than that at lower temperature [30]. In our case, depolymerization of semi-crystalline polypropylene matrix had occurred during aging. Well organized array of thin, short polymer rods are clearly seen on the bamboo surface, believed to be formed from deposition of depolymerized matrix (Fig. 15). In addition, compared to samples before aging where polymer coating can be seen on the glass fiber surface (Fig. 19a), a much smooth fiber surface with litter polymer coating is seen after aging at elevated temperature (Fig. 19b), suggesting that the polymer has been degraded. Some small strings are observed on the fracture surface of the specimens in aging at 25°C (Figs 12 and 13), also believe to be the consequence of polymer matrix swelling in moist environment. Thus degradation of the PP matrix is apparent in 25 and 75°C, however, morphology of the polymer residue deposited on the fiber surface after dissolution seems to indicate a different rate of depolymerization and deposition. What is not known in our case is whether internal damage is developed in the matrix at elevated temperature as a result of internal stress redistribution. Further studies are needed to clarify this point. Nevertheless, it has been shown that mechanical properties for many commonly used polymer systems for composites do degrade under environmental loads [31]. In addition to the aforementioned factors, dimensional instability of the matrix under the influence of moisture and temperature may result in debonding of the fiber/matrix interface, discussed as follows.

4.2. Degradation of the Interface/Interphase

The interfacial adhesion characteristics have a significant effect on the load carrying capacity of a fiber-reinforced composite. Under environmental aging, interfacial debonding occurs by penetration of water molecule, and water-filled voids or blisters may also develop at the interface. Differences in both the thermal and moisture expansion coefficients of fibers and matrix also contribute to progressive debonding and therefore weakening of the materials and it is more severe in accelerated aging because of the larger differences of temperature and moisture content [32]. Debonded fiber/matrix interface of the BFRP and BGRP (Fig. 20) is found in both PP or PP-MAPP matrix composite, compared to those before aging condition where the



(a)

(b)

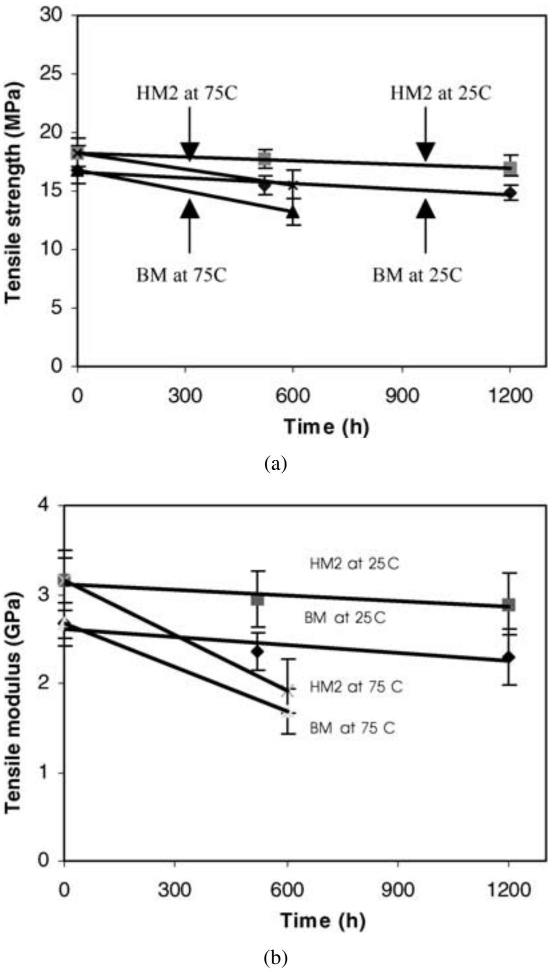
Figure 19 SEM micrographs of BGRP sample (a) before aging, showing glass fiber covered with a thin polymer layer, (b) after aging at 75°C. The thin thread pointed by the arrow is possibly recrystallized PP after dissolution.

Figure 20 Fracture surface of BGRP samples after aging at 75°C, showing gaps between bamboo fiber and the PP matrix.

fiber is still tightly surrounded by the matrix (Fig. 5a). Damage at the interface is more severe at high temperature as a result of dissolution of components of both fiber and matrix materials, and has caused a greater reduction in mechanical properties of the composite, compare to those aged at a lower temperature.

So far it has been shown that environmental aging do induce damage to bamboo fiber, PP and PP-MAPP matrix, and the fiber-matrix interface, and that aging at a higher temperature accelerates the process and intensifies the extent of those damages. Qualitative comparison on damage modes based on morphology reveals that the fundamental damage mechanisms appear to be the same. A comparison of tensile strength and tensile modulus of BFRP (sample **BM**) and BGRP (sample **HM2**) as a function of aging time at 25 and 75°C are presented in Fig. 21. While degradation in both tensile strength and modulus are gradual at 25°C, accelerated aging has a stronger effected on the stiffness of the composites as the dropping rate of tensile stiffness of both BFRP and BGRP is greater during aging at 75°C compared to that of tensile strength.

Although no distinctive damage modes are identified from aging in ambient and elevated temperatures, different rates of degradation and interaction between damage modes at different temperatures render the entire aging process a coupled one, which may well result in an overall nonlinear behavior on property degradation over time. Therefore, assessing mechanical properties at longer terms under ambient temperature aging through linear extrapolation based on elevated temperature data may result in erroneous estimations. To date, there are very few examples concerning with the correlation of the data between the low temperature and high temperature aging effect on the service performance of the composite materials [28]. More extensive studies are needed to understand the relationships between different damage development in the thermo-mechano-chemical process of environmental aging. However, without a rigorous quantitative model, such complicated relationships could be hard to elucidate.



(a)

(b)

Figure 21 (a) Tensile strength as a function of aging time at 25 and 75°C, (b) Tensile modulus as a function of aging time at 25 and 75°C.

Since the strengths of fiber reinforced composites are themselves complicated issues, predicting property degradation during environmental aging pose additional challenges. Various degradation models for glass fibers, such as the power law model and the exponential model, under the influence of stress, time, temperature, and environment have been proposed based on subcritical crack growth concept. However, similar degradation model for natural fibers, to the author's knowledge, is still not available. Based on the morphology of the degraded bamboo fiber, such as those shown in Figs 12, 13, and 15, it seems that the strength degradation could be related to dissolution and mass transport. Description of the interfacial degradation is another major challenge. Nevertheless, interfacial damage is closely related to dimensional stability of the fiber and the matrix as well as its susceptibility to chemical attack. The former can be found based on data from simple experiments together with simple mechanics while the later usually can be described by chemical rate equations. Once degradation laws for the fiber(s), matrix, and the interface are found, incorporating into a micromechanics model seems to be a sensible way in tying them up for predicting long-term property degradation. We will report a modeling effort in a subsequent paper.

In summary, low price cellulose fiber such as bamboo has high stiffness, low density and recyclable. Incorporation of cellulose-base filler to thermoplastic reduces the cost per unit volume and improves stiffness. The effect of bamboo fibers on the tensile and bending strengths was poor when there was no coupling agent. Mechanical performance and environmental resistance of BFRP is enhanced by hybridization and adding coupling agent. Improved in performance of hybrid composites is due to the inclusion of relatively higher in strength and stiffness and moisture resistant glass fiber. Addition of MAPP as coupling agent in the composite enhances the composite performance by improving the interfacial strength between the fibers and PP. Improved environmental resistance of composites of BFRP and BGRP (with MAPP) is apparently due to the presence of a layer of hydrophobic resin moieties at the interface of the fiber and polymer matrix.

Neat polypropylene resins have been reinforced with bamboo fibers when sufficient stress transfers is achieved at the critical volume fraction with the critical fiber length in the composites. It has been reported that the optimum strengths of BFRP and BGRP were developed by improving the interfacial strength and varying the arrangements of fiber orientation [23].

Therefore, incorporation of bamboo fiber with high tensile strength and modulus to the polymer enhanced the mechanical properties of neat resin. The present results on the composites (BFRP and BGRP) reveal that bamboo fiber and their composites are tough engineering materials.

The thermoset and thermoplastic/bamboo-fiber composites with moderate strength to weight ratio and resistance to wear may be estimated for design purpose instead of commercially available glass fiber reinforced plastic composites in a number of applications. It can be used as structural materials such as wind mill funs, automobile carriage, low cost housing, instrument boxes, crash helmets etc. Some of them has already been produced using the thermoset/bamboo fiber composites and the results obtained so far have been potential [33].

Moreover, wood and wood fiber products such as fiberboard, fiber composites etc. have been widely used in interior decoration and in the furniture industry. It is urgently need to find out a material to be substitute in wood products due to the shortage of timber and serious global concern. Bamboo has been accepted as a tough structural material and already being used in its raw forms for the construction of building. In addition, bamboo is an abundant natural resource in Asia and it has a rapid growing rate and overall mechanical properties are comparable to those of wood [34]. Based on our present results bamboo-glass hybrid composites may be used instead of wood because it has low cost, light weighted, with improved durability, and possess adequate strength and stiffness for building and construction applications.

5. Conclusions

Based on our results, the following can be concluded:

- Although tensile strength of BFRP and BGRP (with or without MAPP) systems could not reach that of neat PP, tensile modulus is significantly improved by adding fibers to the polymer matrix.
- Tensile and flexural strength and stiffness of BFRP and BGRP both decreased after aging in water at 25 and 75°C for prolonged period. The extent of strength and stiffness loss depends on the aging time and temperature.
- BFRP samples showed a greater reduction in tensile and flexural strength and stiffness in a specific environment than BGRP.
- Tensile and flexural strength and stiffness are enhanced by inclusion of a compatibilizer, MAPP, in matrix material as a result of improved interfacial bonding.
- Bamboo fiber degrades by decomposition into thin fibrils and detached layers while the PP matrix degrades by dissolution.
- The hybrid approach of blending more durable glass fiber with bamboo fiber is an effective way to improve the durability of natural fiber composite under environmental aging.

References

1. N. P. CHEREMISINOFF (ed.), "Handbook of Engineering Polymeric Materials" (Marcel Dekker, New York, 1997).
2. S. K. DE and J. R. WHITE (eds.), "Short Fibre-Polymer Composites" (Woodhead, Cambridge, 1996).
3. R. D. ADAMS and M. M. SINGH, in "Durability of Polymer Based Composites Systems for Structural Applications," edited by H. Carbon and G. Verchery (Elsevier, Amsterdam, 1991).
4. A. C. KARMAKER and J. A. YOUNGQUIST, *J. Appl. Poly. Sci.* **62** (1996) 1147.
5. U. DEVI, S. S. BHAGAWAN and S. THOMAS, *ibid.* **63** (1997) 1739.
6. F. G. SHIN, X. J. ZHENG and M. W. YIPP, *J. Mater. Sci.* **24** (1983) 3483.
7. X. CHEN, Q. GUO and Y. MI, *J. Appl. Poly. Sci.* **69** (1998) 1891.
8. A. C. KARMAKER, *J. Mater. Sci. Lett.* **16** (1997) 462.
9. N. CHAND and S. A. R. HASHMI, *J. Mater. Sci.* **28** (1993) 6724.
10. A. VALADEZ-GONZALEZ, J. M. CERVANTES-UC, R. OLAYO and P. J. HERRERA-FRANCO, *Comp.* B: *Engin.* **30** (1999) 321.
11. I. YUAN, Y. ZHANG and X. ZHANG, *J. Appl. Poly. Sci.* **71** (1999) 333.
12. A. VALADEZ-GONZALEZ, J. M. CERVANTES-UC, R. OLAYO and P. J. HERRERA-FRANCO, *Comp.* B: *Engin.* **30** (1999) 309.
13. S. KUMAR, *Wood and Fiber Sci.* **26** (1994) 270.
14. S. SREENIVASAN, P. B. IYER and K. R. K. IYER, *J. Mater. Sci.* **31** (1996) 721.
15. A. K. BLEDZKI, S. REIHMANE and J. GASSAN, *J. Appl. Poly. Sci.* **59** (1996) 1329.
16. R. MOHAN and KISHORE, *J. of Reinf. Plast. Com.* **4** (1985) 187.
17. N. CHAND and P. K. ROHATGI, *Poly. Commun.* **28** (1987) 146.
18. C. PAVITHRAN, P. S. MUKHERJEE and M. BRAHMAKUMAR, *J. Reinf. Plast and Com.* **10** (1991) 91.
19. Y. LI, Y-W. MAI and L. YE, *Com. Sci. and Tech.* **60** (2000) 2037.
20. M. M. THWE and K. LIAO, *J. Mater. Sci. Lett.* **19** (2000) 1873.
21. G. KALARPRASAD, K. JOSEPH and S. THOMAS, *J. Mater. Sci.* **32** (1997) 4261.
22. X. CHEN, Q. GUO and Y. MI, *J. Appl. Pol. Sci.* **69** (1998) 1891.
23. M. M. THWE and K. LIAO, *Plast. Rub. Com.*, in press.
24. J. SEEMA and R. KUMAR, *Mater. and Manuf. Proc.* **9** (1994) 813.
25. K. LIAO, C. R. SCHULTHEISZ, D. L. HUNSTON and L. C. BRINSON, *J. Advan. Mater.* **30** (1998) 2.
26. S HALIM HAMID, B. A. MOHAMED and A. G. MAADHAH (eds.), "Hand Book of Polymer Degradation" (Marcel Dekker, New York, 1992).
27. J. COMYN (ed.), "Polymer Permeability" (Elsevier Applied Science, New York, 1995).
28. G. THOMAS and A. H. ZUREICK (eds.),"High Temperature and Environmental Effects on Polymeric Composites" (American Society for Testing and Materials, STP 1302, West Conshohocken, PA, 1997).
29. A. H. CARDON and G. VERCHERY (eds.),"Durability of Polymer Based Composite System for Structural Applications" (Elsevier Applied Science, New York, 1990).
30. J. I. KROSCHWITZ, in "Polymers," edited by H. S. Katz and J. V. Milewski (Van Nostrand Reinhold, New York, 1987).
31. J. R. MARTIN and R. J. GARDNER, *Poly. Eng. Sci.* **21** (1981) 557.
32. G. S. SPRINGER (ed.), "Environmental Effects on Composite Materials" (Technomic Publishing Company, Westport, CT, 1981).
33. J. LIU, G. B. TANG, G. J. QU, H. R. ZHOU and Q. GUO, *J. Appl. Poly. Sci.* **47** (1993) 2111.
34. K.-C. HO and M.-C. JENG, *Plast. Rub. Com. Proc. Appl.* **25** (1996) 469.

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