

Bamboo Fiber Reinforced Thermosetting Resin Composites: Effect of Graft Copolymerization of Fiber with Methacrylamide

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ABSTRACT: Epoxy and polyester resins have been reinforced with methacrylamide (MAA) treated bamboo strip matting to develop bamboo fiber reinforced plastic composites. Bamboo mats were graft copolymerized with 1, 3, and 5% solution of MAA. The mechanical (tensile strength, elastic modulus, flexural strength, and flexural modulus), thermal, and water absorption properties of the composites were determined. One percent treatment of bamboo with MAA gave optimum results with epoxy resin. The mechanical properties were improved. TGA results reveal that the degradation temperature of the composite has improved after grafting. The weight loss of 1% MAA treated bamboo-epoxy composite reached a value of

95.132% at 795°C compared to 97.655% at 685°C of untreated bamboo-epoxy composite. Water absorption in the composites was studied by long term immersion and 2 h boiling in distilled water. The process of water absorption indicates Fickian mode of diffusion. MAA treatment results in reduced water uptake. There was improvement in the properties of pretreated bamboo-polyester matrix composite as well. Three percent treatment of bamboo with MAA gave optimum results with polyester resin. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1006–1013, 2010

Key words: bamboo; thermosetting resin; graft copolymerization; diffusion

INTRODUCTION

The use of biofibers, as opposed to synthetic fibers, has been well recognized due to the positive environmental benefits with respect to ultimate disposability and raw material used. In addition, it has properties like low cost, lightweight, high specific strength, and free from health hazard.

Graft polymerization is a well established technique used to modify properties of natural and synthetic fibers. Grafting on cellulose fiber may take place before or during compounding. In the former case, pretreatment of fibers by compatibilizing agents generally occurs in solution. The excess of (unreacted) compatibilizing agent is eliminated by washing.¹ Methacrylamide (MAA) has been widely applied as a grafting agent for natural and synthetic fibers. MAA is one of the most promising vinyl monomers because large polymer add-on can be easily obtained because of the hydrophilic nature of MAA.

It is highly water soluble, relatively less toxic, polar, and less expensive than other vinyl monomers.^{2–4}

The grafting of vinyl monomers onto cellulose and other cellulosic fibers has been extensively studied.^{1–5} Most of the studies have been done on silk fibers and cotton. The cross-sectional area of the tussah silk fibers was increased due to the MAA add-on. The rigidity of the fibers increased whereas breaking load was almost unchanged by the MAA treatment.² Celik³ carried out the graft polymerization of MAA onto acrylic fibers. Grafting of MAA increased the moisture content and water absorption of acrylic fibers due to polyMAA being hydrophilic in nature. Grafting also affects the fiber morphology. This is assumed to establish strong interactions between acrylic fiber and polymer by means of physical and/or chemical bonds. Tanobe et al.⁵ concluded that MAA results in a more severe treatment of the sponge-gourds fibers compared to alkali treatment. The MAA treatment results in very silky and nearly white colored fibers for all concentrations.

Bamboo is a natural material, and is an abundantly available natural resource in Asia and South America. It has been used traditionally as a structural material for fabrication of low cost houses. The ultra structure of bamboo fibers, proposed by Liese,⁶ is shown in Figure 1. The lamellation consists of alternating broad and narrow layers with different fibrillar orientation. In broader lamellae, fibrils are oriented at a smaller angle to the fiber axis whereas the narrow ones show mostly a transverse

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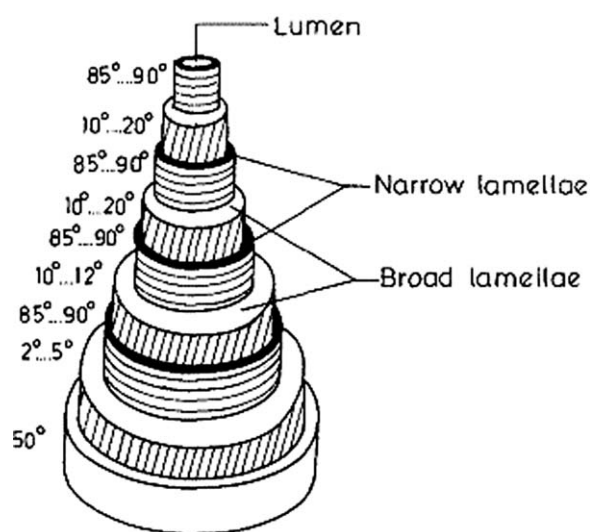


Figure 1 Model of the polylamellate wall structure of a bamboo fiber.

orientation. The narrow lamellae exhibit higher lignin content than the broader ones. The polylamellate wall structures of the fibers lead to an extremely high tensile strength. The polylamellate structures do not exist in the cell wall of the fibers of the normal wood. Based on its anatomical properties, ultra structure and plant fracture mechanism bamboo establishes itself as a superior natural fiber among other known natural fibers (like jute, coir, sisal, straw, banana, etc.) Physical properties of a few natural fibers are given in Table I. Amongst these various lingo-cellulosic fibers, bamboo has 60% cellulose with a considerably higher percentage of lignin (~ 32%), its microfibrillar angle being relatively small (2°–10°). These facts about bamboo, support its high tensile strength.^{7–9} As a cheap and fast-grown resource with superior physical and mechanical properties compared to most wood species, bamboo offers great potential as an alternative to wood. Although there are many works^{1–5,10–15} and views on the effects of chemical treatment of various bamboo fibers, there is hardly any information about MAA treated bamboo fiber reinforced polymer (thermosetting/thermoplastic) composite. In this article we have studied the effect of MAA treatment of bamboo fiber on the mechanical, thermal, and water absorption behavior of bamboo–epoxy and bamboo–polyester composites.

Kinetics of water absorption

The poor resistance of the fibers to water absorption can have undesirable effects on the mechanical properties and the dimensional stability of the composites.^{16–18} Therefore, it is important to study in detail the water absorption behavior to estimate not only

the consequences that the water absorbed may have, but also how this water uptake can be minimized in some way. Moisture absorption into the composite materials is considered by three major mechanisms and they include. (i) diffusion of water molecules inside the microgaps between polymer chains; (ii) capillary transport of water molecules into the gaps and flaws at the interface between fibers and the polymer due to the incomplete wettability and impregnation; and (iii) transport of water molecules by microcracks in the matrix, formed during the compounding process.^{19–21} Although all three mechanisms are active, the overall effect can be modeled conveniently considering the diffusion mechanism.

In general, diffusion behavior in glassy polymers can be classified according to the relative mobility of the penetrant and of the polymer segments. With this, there are three different categories of diffusion behaviour.²¹ Case I, or Fickian diffusion, in which the rate of diffusion is much less than that of the polymer segment mobility. The equilibrium inside the polymer is rapidly reached and it is maintained with independence of time. Case II (and Super Case II), in which penetrant mobility is much greater than other relaxation processes. This diffusion is characterized by the development of a boundary between the swollen outer part and the inner glassy core of the polymer. The boundary advances at a constant velocity and the core diminishes in size until an equilibrium penetrant concentration is reached in the whole polymer. Non-Fickian or anomalous diffusion occurs when the penetrant mobility and the polymer segment relaxation are comparable. It is then, an intermediate behaviour between Case I and Case II diffusion. These three cases of diffusion can be distinguished theoretically by the shape of the sorption curve represented by

$$M_t/M_s = kt^n, \quad (1)$$

where, M_t is the moisture content at time t ; M_s is the moisture content at the equilibrium; and k and n are constants. k is a constant characteristic of the sample, which indicates the interaction between the sample and water and n indicates the mechanism of sorption. The values of n and k were determined by linear

TABLE I
Composition of a Few Natural Fibers

Natural fiber	Density (Kg/m ³)	Microfibril angle	Cellulose (%)	Lignin (%)
Coir	1.15	30–49	43	45
Banana	1.35	11	65	5
Sisal	1.45	20–25	70	12
Jute	1.45	8.1	63	11.7
Bamboo	0.6–0.8	2–10	60.8	32.2

regression analysis. The value of coefficient n shows different behaviour between cases; for Fickian diffusion $n = 0.5$; whereas for Case II $n = 1$ (and for Super Case II $n > 1$). For anomalous diffusion, n shows an intermediate value ($0.5 < n < 1$). Moisture absorption in natural fiber reinforced plastics usually follows Case I Fickian behaviour, so, further attention will be focused on its study. As mentioned earlier, apart from diffusion, two other minor mechanisms are active in moisture exposure of composite materials. The capillary mechanism involves the flow of water molecules into the interface between fibers and matrix. It is particularly important when the interfacial adhesion is weak and when debonding of the fibers and the matrix have started. On the other hand, transport by microcracks includes the flow and storage of water in the cracks, pores, or small channels in the composite structure. These imperfections can be originated during the processing of the material or due to environmental and service effects.

In most cases, moisture absorption processes often follow the prediction of Fick's law, where the mass of water absorbed increases linearly with square root of time, and then gradually slows until equilibrium plateau. The diffusion coefficient, D can be determined from:

$$M_t/M_s = (4/h)(D/\pi)^{1/2}t^{1/2}, \quad (2)$$

where h is the sample thickness.

EXPERIMENTAL

Materials and methods

Orthogonal bamboo strip mats were acquired from the local market. The cross section of the strip used in the mats is $4.25 \times 0.5 \text{ mm}^2$. Commercial grade cycloaliphatic epoxy resin (CY-230, Ciba Geigy product, epoxy equivalent 4.1–4.5 eq/kg), a pale yellow viscous liquid, and Aradur HY-951 hardener was used. The hardener was an aliphatic polyamine (triethylenetetramine). General purpose polyester resin, cobalt naphthenate, and methyl-ethyl ketone peroxide (MEKP) was obtained from the market

MAA 98% was obtained from Alfa Aesar. The bamboo mats were immersed in 1, 3, and 5% of MAA aqueous solution for 1 h, washed thoroughly with distilled water and then oven dried at 110°C for 24 h. Matrix was spread over the bamboo mats, placed one over another up to seven layers. This was placed in between two flat sheets, $300 \times 200 \text{ mm}^2$, and pressed in the hydraulic press under a pressure of 170 KN for 24 h for epoxy based composites and 6 h for polyester based composites. The Epoxy and polyester composites were cured at 80°C for 4 and 1.5 h, respectively in an oven. The volume

TABLE II
Materials Analyzed

Sample	Specification
BE	Bamboo–epoxy composite
BMAE1	Bamboo–epoxy composite with 1% MAA treated bamboo
BMAE3	Bamboo–epoxy composite with 3% MAA treated bamboo
BMAE5	Bamboo–epoxy composite with 5% MAA treated bamboo
BP	Bamboo–polyester composite
BMAP1	Bamboo–polyester composite with 1% MAA treated bamboo
BMAP3	Bamboo–polyester composite with 3% MAA treated bamboo
BMAP5	Bamboo–polyester composite with 5% MAA treated bamboo

percent of bamboo mats was $64 \pm 1\%$ in the composites. This was maintained all throughout. The composite prepared are described in Table II.

The percent graft yield ($G\%$) was calculated from the increase in weight of the fibers by using the following equation³:

$$G\% = (W_2 - W_1)/W_1 \times 100,$$

where W_1 and W_2 are the weights of the original and grafted fibers, respectively.

Thermogravimetric analysis

The thermogravimetric analysis was run under nitrogen atmosphere with a flow rate of 200 mL/min using Perkin Elmer thermal analyzer. The heating rate was $20^\circ\text{C}/\text{min}$ and the temperature range studied was from the room temperature to 800°C .

Scanning electron microscopy

The surface morphology of ungrafted and grafted bamboo fibers were examined by means of a CARL ZEISS EVO 50 scanning electron microscope, after silver coating.

Mechanical test

The tensile test was performed according to the ASTM D638. Samples were tested to failure under tension at a cross head speed of 2 mm/min on INSTRON 3369. Three-point bending test was performed according to ASTM D790. Support separation was 70 mm and test speed was 10 mm/min.

Water absorption

Water absorption test was carried out according to ASTM D 570 –98. The samples with dimensions

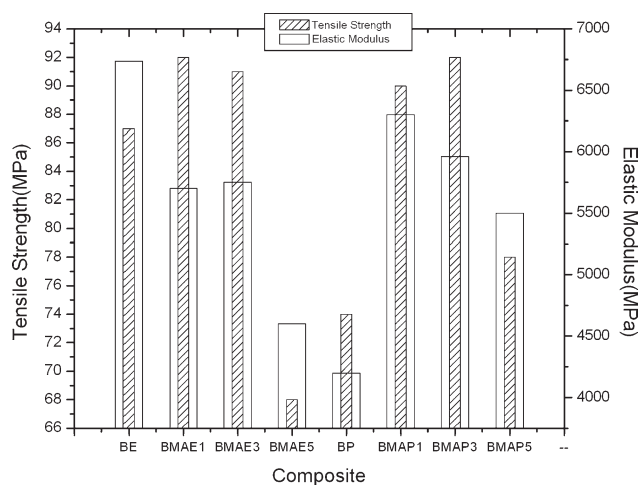
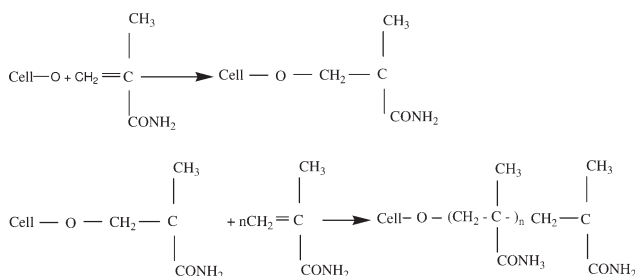


Figure 2 Tensile properties of composites.

76.2 mm long by 25.4 mm wide by the thickness of the laminates were used to examine water absorption behavior after drying at $50 \pm 3^\circ\text{C}$ for 24 h, cooled in desiccators, and immediately weighed. Two different procedures were adopted; long-term immersion and 2 h boiling. The wet weights were determined after sandwiching the samples between the filter paper. The water absorption of the samples was calculated from the weights of the wet and dry samples.

RESULTS AND DISCUSSION

In the presence of vinyl monomer the cellulose is added to the double bond of the vinyl monomer, resulting in a covalent bond between monomer and cellulose with creation of free radical on the monomer i.e., a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates the grafting reaction onto cellulose as follows¹:



Reaction with cellulose produces a brush like grafting on the fiber, which is favorable for the entanglement with the matrix chains. When a long-chain polymer is attached to a surface or interface, the mobility of the chains is restricted. Normally, the grafted chains would adopt a random-walk configuration to maximize their configurational entropy. However, under certain conditions, the

grafted chains may stretch away from the surface and form a brush like structure. Particularly important factors that affect the stretching tendency are graft density, the molecular weight of grafted chains, and the character of the surrounding medium.²²

Mechanical properties

The percent graft yield ($G\%$) at 1, 3, and 5% of MAA are 0.3, 1, and 1.6%, respectively. The tensile properties and flexural properties of the composites are shown in Figures 2 and 3, respectively. The tensile strengths of bamboo-epoxy composites were increased by 5.7 and 4.6% at 1 and 3% of MAA treated bamboo, respectively. The increase in tensile strength may be due to the enhanced strength of the bamboo. MAA treatment partially dissolves hemicellulose and lignin.⁵ This allows the cellulose fibrils to rearrange, decreasing the spiral angle and increasing the molecular orientation. This in turn would lead to a better load sharing and higher stress development in the fiber. Also, mechanical bonding between fiber and matrix is better as reaction with cellulose produces a brush like grafting on the fiber which is favorable for the entanglement with the matrix chains. At 5% MAA treatment the tensile strength show a 21% decrease compared to the untreated bamboo-epoxy composite. An increase in the amount of grafted MAA onto the bamboo results in a decrease in adhesion between the hydrophilic MAA and hydrophobic epoxy matrix. Scanning electron micrograph of fiber surface, Figure 4(c), of MAA treated fibers clearly indicates that 5% MAA treatment makes the fiber surface smooth, which lessens the mechanical bonding between fiber and matrix. Whereas, in Figure 4(a,b), pits are observed over the surface, which is the cause of mechanical interlocking between the fiber and matrix and hence the strength increases. The elastic modulus show a

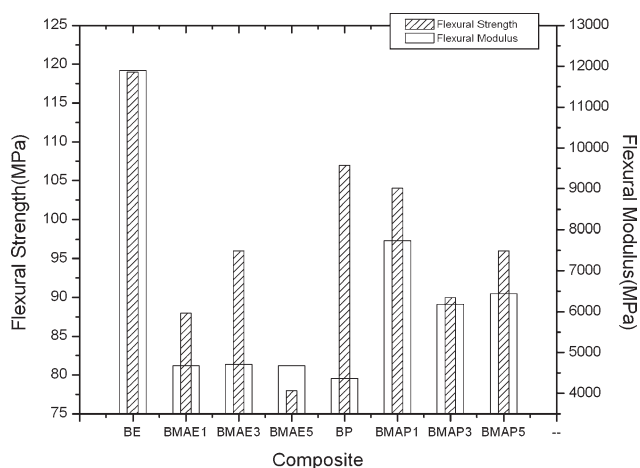


Figure 3 Flexural properties of composites.

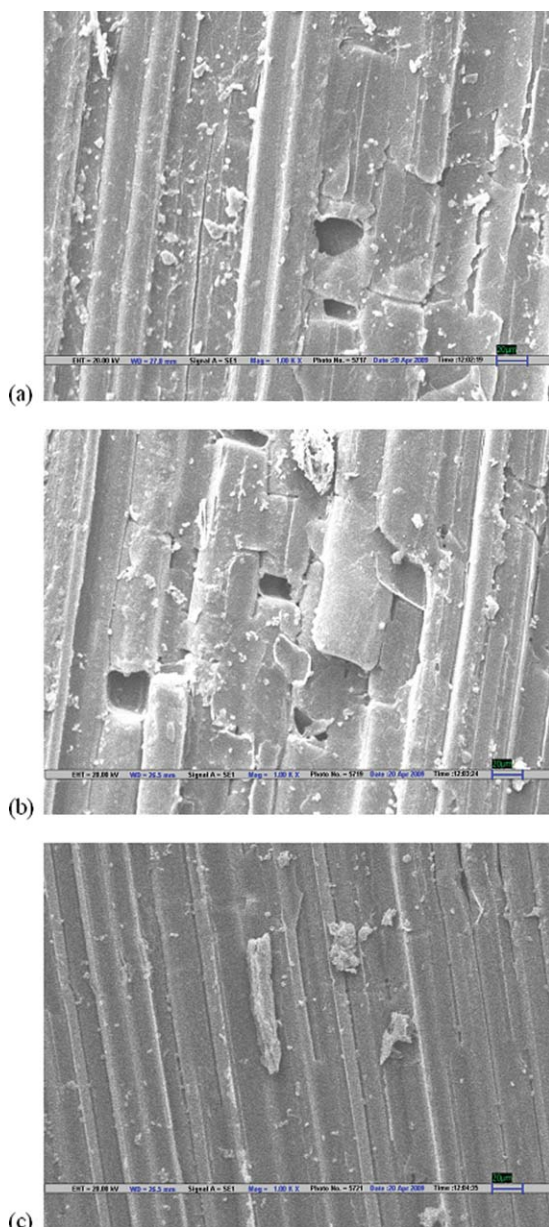


Figure 4 SEM micrographs of treated bamboo with (a) 1% MAA, (b) 3% MAA, and (c) 5% MAA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decrease in value at all percent of MAA treatment, least value is obtained at 5% MAA treatment. Flexural properties of bamboo–epoxy composites also decrease with increase in the percent of MAA.

The mechanical properties of bamboo–polyester composites show the same trend as bamboo–epoxy composites at different MAA treatments. However, bamboo–polyester composites have shown better improvement of mechanical properties. The percent increase in tensile strength of BMAP1, BMAP3, and BMAP5 are 21.6, 24.3, and 5.4, respectively. Higher tensile strength at 1% and 3% MAA treatments may be due to enhanced strength of bamboo and better

interfacial adhesion between the treated bamboo and polyester matrix. The flexural properties of these composites also show a decrease in values. However, decrease in flexural strength is less than that obtained for bamboo–epoxy composites. This may be due to better compatibility of polyester matrix with MAA.

Thermogravimetric analysis

The thermal behavior of ungrafted bamboo–epoxy composite (BE) and 1% MAA-grafted bamboo–epoxy composite (BMAE1) was examined by TGA analysis under N_2 atmosphere at a heating rate of $20^\circ C/min$. The TGA curves for the thermal degradation of BE and BMAE1 are presented in Figure 5(a,b), respectively. The initial weight losses observed in the cases of BE and BMAE1 are due to the loss of moisture. The weight loss of BE started at $222.21^\circ C$ and reached a value of 97.655% at $685^\circ C$. The weight loss of BMAE1 started at $239.79^\circ C$ and reached a value of 95.132% at $795^\circ C$. MAA-grafted bamboo–epoxy composite exhibited rather higher weight retention value than the ungrafted sample.

The decomposition temperature and the weight retention value of BMAE1 were observed to increase. This clearly indicates that grafting increases the

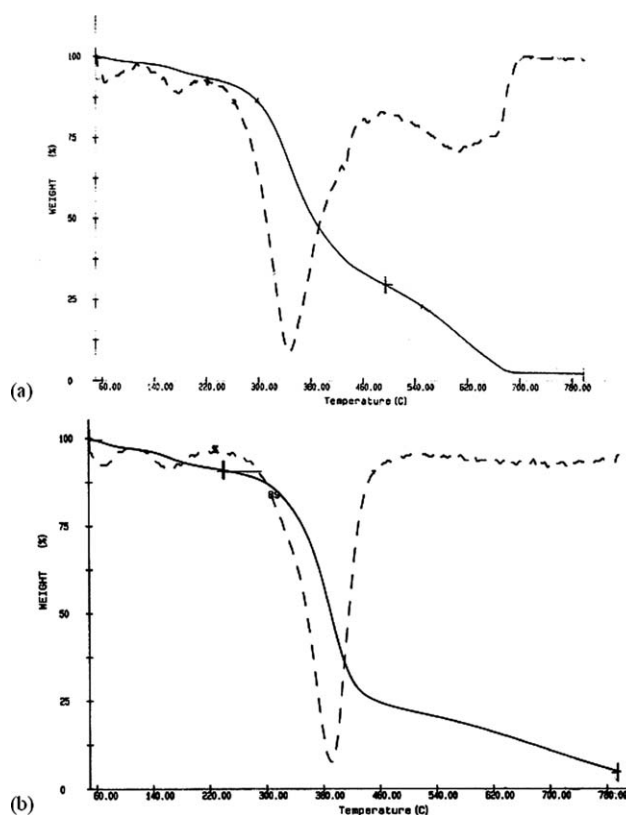


Figure 5 (a) TGA curves of untreated bamboo–epoxy composite and (b) TGA curves of 1% MAA grafted bamboo–epoxy composite.

thermal stability of bamboo composite, perhaps due to new crosslinkages formed after grafting.^{23,24}

Water absorption

It is clear in Figure 6 that the composites absorb water very rapidly at the initial stage, and later a saturation level was attained without any further increase in water absorption. In the case of untreated bamboo composites, higher water absorption, 41% may be due to poor wettability and adhesion between untreated bamboo and matrix, and defects such as voids. These lead to higher percentage of water absorption by the composites. Treatment of bamboo fibers with MAA results in slight decrease in water absorption, 36 and 39% by BMAE1 and BMAE3, respectively. Water absorption by BMAE5 is 63%. At 5% MAA treatment, interfacial bonding is less, due to hydrophilic nature of MAA and smoothing of fiber surface. The MAA attached with the bamboo fibers is not reacting with the epoxy resin, but attracting the moisture. Higher the percent deposition of MAA on the fiber, greater is the water absorption by the respective composites.

Figure 7 shows the water absorption curve of bamboo–polyester composites. MAA treatment results in lower initial rate of water absorption and less water absorption at saturation. Water absorption of BP, BMAP1, BMAP3, and BMAP5 are 51, 26, 24, and 37%, respectively. This is due to improved wettability and strong adhesion between MAA treated bamboo and polyester matrix.

Figure 8 shows the water absorption by the composites after 2 h of boiling in distilled water. Water absorption by untreated bamboo–epoxy composite is

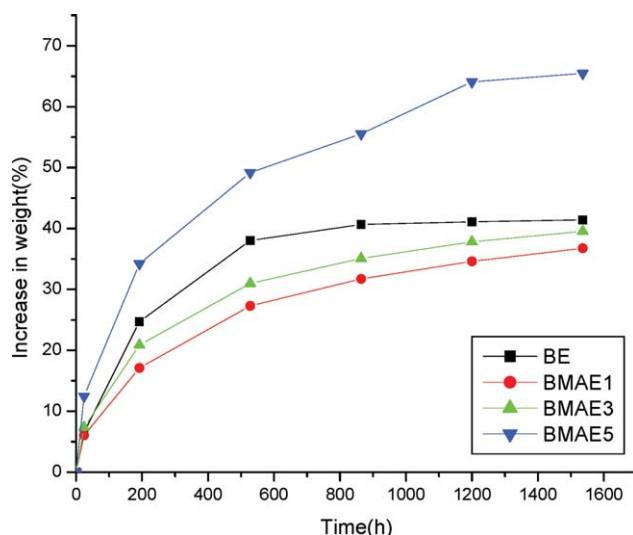


Figure 6 Water absorption curve for bamboo–epoxy composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

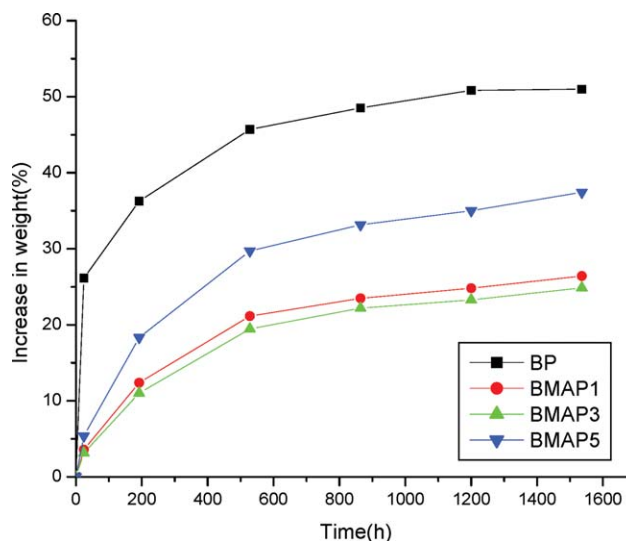


Figure 7 Water absorption curve for bamboo–polyester composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

14%. Composites BMAE1, BMAE3, and BMAE5 absorb lower percent of water than the untreated fiber composite i.e., 9.07, 8.2 and 13%, respectively. Percent water absorb by untreated bamboo–polyester composite is 60.5%. There is drastic reduction in water absorption by bamboo–polyester composites after MAA treatment. Water absorption is reduced to 8.91, 10.12, and 12.31% for BMAP1, BMAP3, and BMAP5, respectively.

Water absorption in polymers is often analyzed in terms of Fickian diffusion, which requires that the results are plotted as weight gain (as a percentage of dry weight) versus square root of time.²⁵ As shown in Figure 9, where percentage moisture absorption

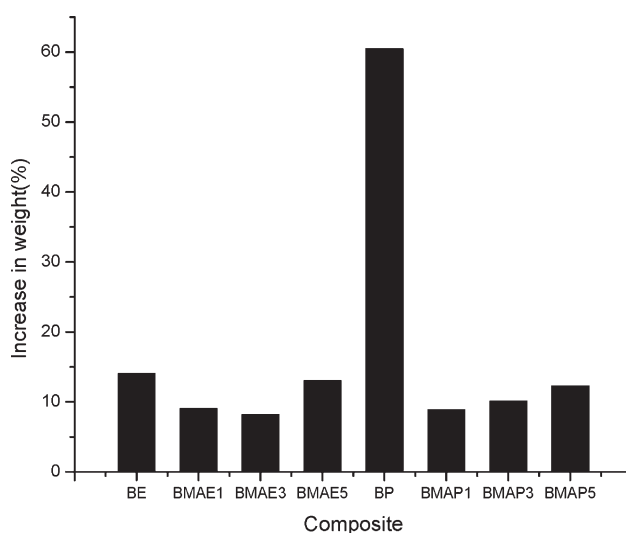


Figure 8 Percent increase in water absorption after 2 h boiling.

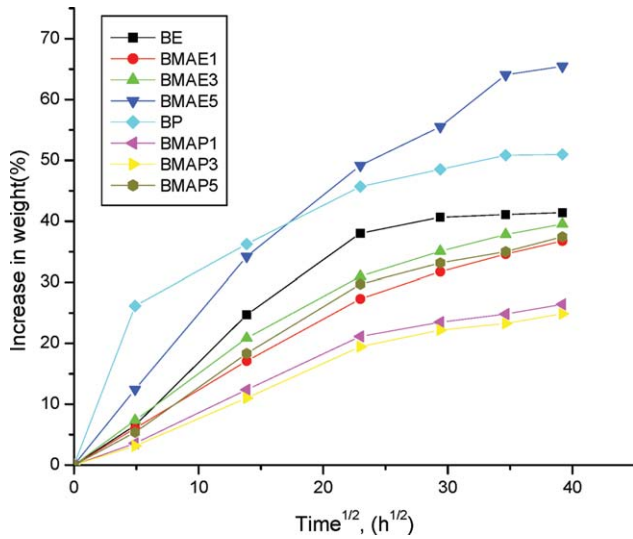


Figure 9 Water absorption curve indicating Fickian diffusion. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increases steadily with $t^{1/2}$ in the initial stage and then tends to level off following the saturation point, indicating a Fickian mode of diffusion.

The analysis of the diffusion mechanism and kinetics was performed based on the Fick's theory. It is considered that the change of weight gain for all samples is a typical Fickian diffusion behavior. The mechanism of water uptake and hence the study of the kinetic parameters n and k , the data were analyzed by adjusting the experimental values to the following equation, which is derived from the eq. (1).

$$\log M_t/M_s = \log(k) + n \log(t) \quad (3)$$

Figure 10 show examples of the fitting of the experimental data to eq. (3). The values of the

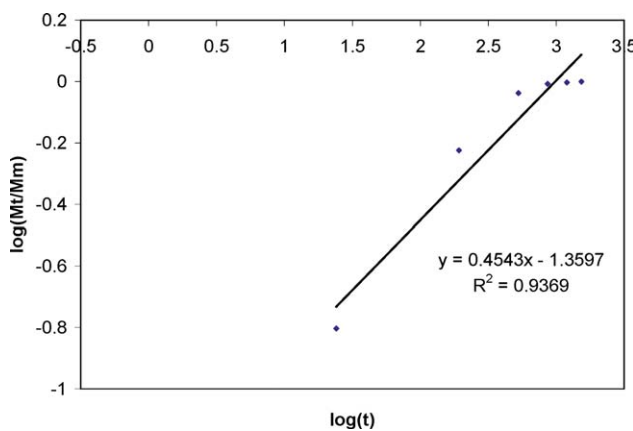


Figure 10 Diffusion curve fitting plots for BE to determine constants n and k . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

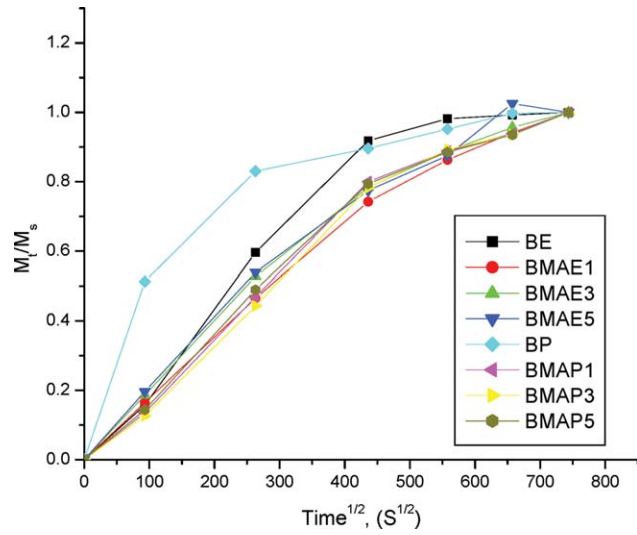


Figure 11 Diffusion curve fitting plots for composites for diffusion coefficient. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

parameters n and k obtained from the fitting curves of the water absorption of the composites are summarized in Table II. As the value of the parameter n approach to 0.5 the composites show a tendency to approach Fickian behavior. An increase in the k value is observed for some silane treated composites, indicating increase in the moisture interaction with the composite material.

The diffusion coefficient (D) is the most important parameter of the Fick's model, which shows the ability of the water molecules to penetrate inside the composites, was calculated using the following equation from the initial slope of the plot of M_t/M_m against $(t)^{1/2}$ shown in Figure 11²⁶:

$$M_t/M_s = (4/h)(D/\pi)^{1/2}t^{1/2}.$$

The values of D are also summarized in Table III. Because of the hydrophilic character of natural fibers, the inclusion of water molecules inside the composite material is favored as demonstrated by the kinetics of the diffusion processes. The values

TABLE III
Moisture Sorption Constants and Diffusion Coefficient of Composites

Samples	n	k	$D \times 10^{-12} \text{ m}^2/\text{s}$
BE	0.4543	0.0437	11.36
BMAE1	0.4408	0.0429	14.73
BMAE3	0.4093	0.0548	16.24
BMAE5	0.4006	0.0589	204.21
BP	0.1687	0.300	180.11
BMAP1	0.4889	0.0316	12.91
BMAP3	0.5071	0.0277	10.47
BMAP5	0.4714	0.0357	15.63

obtained for diffusion coefficients are in agreement with the range of values reported by other authors.²⁷⁻²⁹ According to these reports the values for diffusion coefficient for natural fiber reinforced composites fall in the order of $10^{-12} - 10^{-13} \text{ m}^2/\text{s}$.

CONCLUSION

MAA grafted bamboo reinforced epoxy and polyester matrix composites were fabricated. One percent treatment of bamboo with MAA gives optimum results with epoxy resin. Three percent treatment of bamboo with MAA gives optimum results with polyester resin. Both the mechanical and water resistance properties were improved at lower graft yield. The graft yield was observed to increase with the monomer concentration. Grafting of MAA improved the thermal stability. The decomposition temperature and the weight retention value of MAA grafted bamboo composite was observed to increase. Clearly grafting increases the thermal stability of bamboo composite. Grafting also affected the fiber morphology.

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