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Studies on *Bamboosa Balcooa* bamboo fibre for green composites with polyurethane and polyurethane/poly(methyl methacrylate) semi-interpenetrating polymer network

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Abstract—The poly(ethylene glycol) (PEG)-based polyurethane (PU) and its semi-interpenetrating polymer network (SIPN) with poly(methyl methacrylate) (PMMA) have been coated on the surface of alkali-treated and untreated bamboo fibres (*Bambusa balcooa*). The mechanical properties, like tensile strength and tensile modulus, and the chemical resistance of bamboo fibres before and after coating with PU and PU/PMMA SIPN have been studied. Improvement in tensile strength, tensile modulus and chemical resistance of bamboo fibres were observed after coating with polymers. The PU/PMMA-coated system showed better performance as compared to PU-coated bamboo fibre composite.

Key words: PU/PMMA; bamboo fibres; composites; tensile behaviour; chemical resistance.

INTRODUCTION

In recent years there has been a considerable demand for the development of composites made out of renewable fibres as reinforcement. The composites made with natural fibres as reinforcement are known as 'green composites'. The green composites made from cellulose materials as reinforcements are low cost, lightweight, have enhanced mechanical properties and they are biodegradable [1]. Studies on the performance of polymer coated natural fibres have been made by many scientists [2–9]. Compared to studies on other natural fibre reinforced composites, less effort have been made on bamboo fibre reinforced plastics. Bamboo is one of nature's most valuable gifts to mankind. Its remarkable growth rate and versatile properties

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have made it one of the most sought after materials, especially in tropical countries. A major drawback with bamboo is that it is not durable against wood-degrading organisms. Thus, most bamboos used for structural purposes deteriorate in a couple of years. Jain *et al*. studied the mechanical properties of bamboo-reinforced polyester composites [10]. The microstructure and mechanical properties of bamboo reinforced epoxy composites have been studied by Shin *et al*. [11]. The majority of scientists have studied the behaviour of bamboo composites with thermoset. Chen *et al*. [12] have studied the mechanical properties of bamboo reinforced polypropylene (PP) composites. Wiggins *et al*. [13] have successfully studied the biodegradation of polyether polyurethane. The biodegradation of starch and PMMA-grafted starch by *Aspergillus niger* was successfully established by Canche-Escamilla *et al*. [14]. The selections of polymer systems are very vital in determining the property of the end-product. Both PU and PMMA show excellent mechanical and optical properties, and good solvent and oil resistance. Thus, an IPN of these two polymers is likely to produce an excellent application-oriented material. A thorough literature survey has revealed a lack of literature on PU- and IPN-coated natural fibre systems. In our previous communication [15], we have reported the effect of unsaturated polyester resin and its IPN with polyacrylonitrile. In the present research article the authors report the effect of PU and PU/PMMA coating on tensile and chemical properties of bamboo fibres with an objective of finding suitable matrix for making coated bamboo fibres.

EXPERIMENTAL SET-UP

Materials

Bamboo fibres (*Bamboosa balcooa*) were procured from a local market and used in the dried form. The greasy material and lignin were removed from the fibres by soaking them in 2% NaOH solution for 30 min as described [16]. These fibres were then washed thoroughly with distilled water and dried under the sun for two weeks. The fibre cross section was rectangular with breadth and thickness varying from 0.71 to 2.27 mm. For tensile properties and chemical resistance studies, the fibres were cut to 12 and 6 cm length, respectively. Methyl methacrylate (Aldrich, USA), benzoyl peroxide (Aldrich), 4,4′-diphenyl methane diisocyanate (MDI) (Merck, India), polyethylene glycol-400 (Ranbaxy, India) and new catalyst (Merck) were used. Methyl methacrylate was used after removing inhibitors.

Sample preparation

Benzoyl peroxide (0.5%) and new catalyst (0.05%) were made to dissolve in methyl methacrylate monomer. To the above solution a mixture of polyethylene glycol-400 (PEG) and 4,4′-diphenyl methane diisocyanate (MDI) (1 : 1.5, mol/mol) was added to prepare the PU/PMMA (50 : 50) IPN. The mixture was constantly stirred at room

Table 1.
Tensile behaviour of coated and uncoated bamboo fibre with and without alkali treatment

Bamboo + coating	Untreated			Alkali treated		
	Tensile strength (MPa)	Tensile modulus (MPa)	Improvement in tensile modulus compared to bare fibre (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Improvement in tensile modulus compared to bare fibre (%)
Uncoated	132.0	4779	1.0	117.2	5346	11.9
PU-coated	182.8	4844	1.4	243.5	5575	16.7
PU/PMMA-coated	234.8	5003	4.7	249.4	5655	18.3

temperature for 30 min to obtain a viscous reaction mixture. The PEG combined with MDI in presence of new catalyst should give PU as reported elsewhere [17]. Then, the fibres were soaked for 30 min in the viscous reaction mixture containing methyl methacrylate monomer embedded in PU. The excess resins from the fibres were removed by hanging them in vertical position in a closed chamber. The fibres were kept in closed chamber for 12 h for the complete polymerisation of PU. The temperature of the system was then slowly raised to 80°C to initiate the polymerisation of methyl methacrylate in presence of benzoyl peroxide and maintained at this temperature for 12 h to complete the polymerisation. To get a PU coat on fibres, new catalyst (0.05%) was dissolved in PEG. The required amount of MDI was added to the reaction mixture, stirred and poured on to the fibres. When the reaction mixture becomes viscous, the excess pre-polymer was removed by hanging them in vertical position in a closed chamber. The coated fibres were kept in a closed chamber for 12 h to complete the polymerisation of PU. The polymer-coated bamboo fibres were stored in air tight polyethylene bags.

Tensile strength measurements

The tensile strength of the coated and uncoated bamboo fibres were determined using Lloyds instruments. Ten samples were tested in each case and the average tensile strength was determined by dividing the tensile load at break by the cross-sectional area of the fibres (Table 1).

Chemical resistance measurements

The chemical resistance of the PU and PU/PMMA-coated and uncoated bamboo fibres were studied according to the ASTM D 543-87 method with 40% nitric acid, 10% hydrochloric acid, 8% acetic acid, 10% sodium hydroxide, 20% sodium carbonate, 10% ammonium hydroxide, toluene, carbon tetrachloride and distilled water. In each case, six previously dried and weighed coated samples were immersed in the chemical reagents for 24 h at room temperature. After 24 h they were removed, washed with water and dried by pressing them between filter papers. The changes in the surface characteristics and percentage weight are given in Table 2.

Table 2.
Chemical resistance of PU, PU/PMMA (50/50) coated and uncoated bamboo fibres

Chemical reagents	Percent change in weight after 24 h					
	Untreated and uncoated	Alkali-treated and uncoated	Untreated and PU/PMMA-coated	Alkali-treated and PU/PMMA-coated	Untreated and PU-coated	Alkali-treated and PU-coated
40% Nitric acid	−24.1	−11.7	−20.9	−20.6	−5.1	−15.0
10% Hydro-chloric acid	41.5	38.4	31.0	19.5	29.5	29.9
8% Acetic acid	45.7	32.5	36.8	11.6	31.1	16.4
10% Sodium hydroxide	57.5	44.2	54.4	48.2	35.4	32.7
20% Sodium carbonate	71.8	56.2	9.4	10.8	8.8	22.6
10%Ammonium hydroxide	108.8	31.8	26.2	2.8	28.4	20.9
Toluene	7.3	3.0	2.8	2.6	3.1	5.0
Carbon tetra chloride	16.4	5.2	3.1	2.5	4.2	5.6
Water	90.8	30.9	31.0	12.3	20.0	15.1

RESULTS AND DISCUSSION

The appearance of PU- and PU/PMMA-(50 : 50)-coated fibres were yellow to light brown, transparent with glossy surface [18]. The tensile behaviour has been measured for untreated and alkali-treated fibres with and without PU and PU/PMMA coat and it is given in Table 1. The tensile properties of coated and treated fibres have been compared with untreated bare fibres. The strength of uncoated fibre after alkali treatment has come down by 11.2%, this is probably due to the removal of hemi-cellulose and lignin by alkali treatment, but modulus has increased by 11.9%. The polymer coatings on untreated and alkali treated bamboo fibres have increased the tensile behaviour. The PU and PU/PMMA coating on alkali-treated bamboo fibres have increased the tensile property considerably. This is due to removal of hemicelluloses and lignin by alkali treatment, thereby increasing the surface area on the bamboo fibres. The increased surface area facilitates the adherence or interaction of polymer system on to the fibres, thus there will be increase in the tensile behaviour. High tensile behaviour was noticed for PU/PMMA-coated fibres compared to PU-coated fibres. This is due to combined effect of PU and PMMA on the fibre.

The chemical resistivities of bamboo fibres before and after coating have been measured by gravimetric method. The effects of alkali treatment and coating on the chemical resistivity of the fibres have been studied. The variations in surface characteristics of test specimens after exposure to chemical environments are also

Table 3.
The percent change in weight of PU and PU/PMMA (50 : 50) systems

Chemical reagents	Percent change in weight after 24 h	
	PU	PU/PMMA
40% Nitric acid	Degenerated as sticky mass	Degenerated as sticky mass
10% Hydrochloric acid	8.0	18.8
8% Acetic acid	16.7	17.6
10% Sodium hydroxide	4.2	2.8
20% Sodium carbonate	6.9	5.4
10% Ammonium hydroxide	9.3	16.5
Toluene	3.3	13.3
Carbon tetrachloride	3.7	3.5
Water	8.6	9.6

been studied. The measured percentage weight changes for bamboo fibres, polymer-coated bamboo fibres and polymers (PU and PU/PMMA) are given in Tables 2 and 3, respectively. The surface of coated samples exposed to oxidative HNO_3 environment was sticky. This is due to chemical degradation of superficial layers; hence, there was loss of materials [16]. The same trend was observed with bare fibres, polymers (Table 3) and coated fibres indicating that all materials are sensitive to HNO_3. Coating of fibres with polymers has reduced the chemical degradation but change is marginal. In alkaline medium PU/PMMA-coated fibres had a dull grey look after the said period. This is probably due to interaction of alkali with ester group present in IPN. In acidic, organic and aqueous media no surface changes of coated fibres were observed.

With higher weight gain, the interaction increases: more interaction leads to a decrease in chemical resistance. This is the general guiding principle for the gravimetric method of analysis. From Table 2 it was noticed that the weight gained by the polymer-coated fibres is more than the corresponding polymer, but less than that of bare fibres. There is no much difference in chemical resistance between untreated fibres with PU and PU/PMMA coating. The considerable improvement in chemical resistance was observed with alkali-treated and polymer-coated fibres. The removal of lignin and hemicelluloses by alkali treatment increases the surface area of the fibres and, thus, there will be an increase in interaction between polymer and fibres. Higher chemical resistance was noticed for alkali-treated and PU/PMMA-coated fibres compared to PU coated fibres. This is due to combined effect of PU and PMMA in IPNs on bamboo fibres. The same trend was not followed for untreated and polymer coated systems. Similar anomalies were reported elsewhere [8, 16]. The improvements of chemical resistance of treated and coated fibres over bare fibres have been shown in the form of a bar graph in Fig. 1.

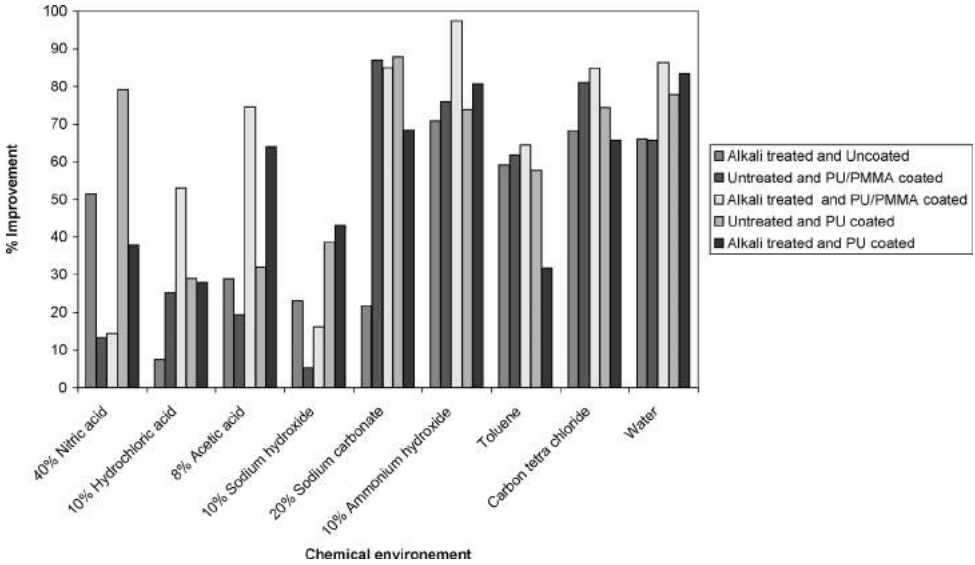

Figure 1. Improvement in Chemical resistance of treated and coated fibres over bare fibres.

CONCLUSIONS

(1) Enhancement in tensile strength and tensile modulus was observed after coating with PU and PU/PMMA systems. Higher tensile strength and modulus was noticed for the PU/PMMA-coated system compared to PU.

(2) Chemical resistivity was improved after PU and PU/PMMA coating on both alkali-treated and untreated bamboo fibres.

(3) The obtained results revealed that PU/PMMA is a favourable matrix for making green composites of bamboo.

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