

Modifications of jute by grafting for use in composites

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Jute fibres were modified by treatment with sodium hydroxide and graft copolymerization with methyl methacrylate (MMA). The conditions for grafting of MMA onto jute fibres were optimized. Hybrid composites were fabricated using glass fabric, modified jute fibres and unsaturated polyester resins. Grafted jute fibres based composites had better tensile, flexural and interlaminar shear strength than those composites fabricated using untreated jute fibres.

Keywords: Composites, Grafting, Jute fibre, Methyl methacrylate, Unsaturated polyester resin

1 Introduction

Amongst the naturally occurring lignocellulosic fibres, jute contains a high proportion of natural cellulose. In the textile industry, the high stiffness of jute is often a limitation because of difficulties in fine spinning, thus leading to only harsh and coarse fabrics. However, in fibrous composites, stiffness of fibres is an important basis of design criteria. Although the tensile strength and Young's modulus of jute are lower than those of glass, the specific modulus of jute is superior to that of glass. Therefore, jute may be used to replace, fully or partially, glass fibres in those application areas where high strength is not a priority.

However, to develop jute composites with better mechanical properties and environmental performance, it is necessary to impart hydrophobicity to jute fibres. A decrease in moisture regain has been observed for several naturally occurring lignocellulosic fibres by grafting with vinyl monomers such as methyl methacrylate, ethyl acrylate, styrene, vinyl acetate, acrylonitrile etc¹⁻⁸. Fabrication of composites using such modified jute fibres and evaluation of their properties has not been carried out.

In the present work, graft copolymerization of jute fibres with methyl methacrylate was carried out using ceric ammonium nitrate in nitric acid as an initiator. The conditions of grafting were optimized in terms of pH, monomer and initiator concentration and duration of polymerization reaction. Hybrid composites were fabricated using jute fibres (2 cm long) as core, faced on either side with one layer of glass fibre mat and the mechanical properties of the composites were evaluated.

2 Materials and Methods

2.1 Materials

Jute fibres were obtained from Jute Technological Research Laboratories, Calcutta. Baker analyzed reagent grade ceric ammonium nitrate (CAN) and conc. nitric acid were used as such. Methyl methacrylate (BDH) was purified by washing with 5% NaOH and then dried before use. Unsaturated polyester resin—Acrolite (grade 404, Acropolymers Pvt. Ltd, Faridabad), methyl ethyl ketone peroxide and cobalt naphthenate (A.G. Fluka) were used as such. Polyester compatible glass fabric RP-10 (Fibre Glass Pilkington) weighing 360 g m⁻² was used.

2.2 Chemical Treatment of Jute Fibres

Jute fibres were treated with 10% NaOH solution for 2h at room temperature (31 ± 2°C). After the treatment, the fibres were thoroughly washed with water to remove alkali.

2.3 Grafting Procedure

The grafting procedure was similar to that reported earlier for coir fibres⁷. Alkali-treated jute fibres (5 g) were immersed in a solution of nitric acid (0.025-0.5N) and CAN (0.005-0.02N) in a two-necked flask maintained at the desired temperature. Nitrogen was allowed to bubble through the solution and the required amount of MMA was added to the contents of the flask. The reaction was carried out in the N₂ atmosphere with continuous stirring. A material-to-liquor ratio of 1:100 was used for the graft copolymerization reaction. After the reaction was allowed to proceed for the desired interval of time, the fibre bundle was taken out, washed with water and

dried. The grafted material was then subjected to soxhlet extraction with acetone for 12 h and then dried at 80°C. Graft add-on was calculated as percentage increase over the original weight of the sample.

2.4 Test Methods

The denier of different fibre samples was measured at 65% RH and $32 \pm 2^\circ\text{C}$. Fibres of 5 cm length were exactly weighed to calculate the value of denier. The average weight of 100 fibres was taken to calculate the denier.

FT-IR spectra of various jute samples in KBr pellets were recorded using Nicolet MX-5-FT-IR spectrophotometer.

The density of the fibres was determined at 24°C using a density gradient column, which was prepared using xylene ($\rho = 0.865 \text{ g cm}^{-3}$) and carbon tetrachloride ($\rho = 1.595$). The column was left undisturbed for 24 h to stabilize and then it was calibrated using standard hollow glass floats. The fibres were pressed into thick balls and dropped into the gradient column. The heights at which the samples floated were noted down after 24 h from which the density was calculated.

Wide angle X-ray photographs were recorded with Norelco type 120-101-85 Philips electronic instrument employing nickel filtered CuK_α radiation. The generator was operated at 40 kV and 30 mA. The sample-to-film distance was kept at 3.5 cm with an exposure time of 4 h. Crystallinity measurements were done at 30°C and 65% RH by taking finely powdered fibre samples to randomise the orientation effects. The integrated intensity due to crystalline reflection and amorphous scatter was found by measuring the area between the peaks and the background line of I vs. 2θ scans. The height of the background line below the minimum, between the (002) and the composite (101) and (101) peaks, was taken as a measure of the content alone. The degree of crystallinity was determined by comparing the crystalline areas of the samples with that of ramie^{9,10}.

The tensile properties of the fibres were evaluated using an Instron tensile testing machine (Model-1112). From each sample, 50 fibres were tested using the following specifications: gauge length (5 cm), cross-head speed (0.5 cm/min), chart speed (100 cm/min), full-scale load (100 g) and 'B' load cell. Fibres were tested under constant strain rate. From the load-elongation curves an average stress-strain curve was plotted. Initial modulus, tensile strength and elongation-at-break were calculated from the stress-strain curves.

Moisture regain of different samples was determined using vacuum desiccator method. The sam-

ples, conditioned at 65% RH and 20°C , were accurately weighed and kept over P_2O_5 in a desiccator under vacuum for 72 h and then weighed again to get the bone dry weights of the samples. Moisture regain (R) was evaluated as percentage of bone dry weight of the sample using the following expression:

$$R = \frac{100 M}{D}$$

where R is the moisture regain; M , the weight of water desorbed; and D , the bone dry weight of the sample.

2.5 Fabrication of Composite

A mild steel mould of $22.5 \text{ cm} \times 15.3 \text{ cm}$ was used for making the composites. Hybrid composites were fabricated with grafted and ungrafted jute fibres (2 cm long) and polyester compatible glass fabric using compression moulding. Silicone mould releasing agent was sprayed on the surface of two mild steel mould. A $18 \text{ cm} \times 14.5 \text{ cm}$ glass mat was uniformly coated with the resin solution containing 3% methyl ethyl ketone and 0.5% cobalt naphthenate and placed on the female tool of the mould. The jute fibres were uniformly spread above the glass mat and then impregnated with the resin solution. The second glass mat, which was similarly coated with the resin, was then put on the chopped jute fibres. The male tool of the mould was then placed on this assembly and composite was compression moulded at 100°C for 1 h at a pressure of 160 psi using Carver Laboratory Press.

The resin content of the composites was determined by pyrolysis in a muffle furnace. A known weight of the sample was heated in a silica crucible at 500°C for 4.5 h. The residual glass fibres were weighed. From the weight of jute fibres taken, the weight fraction of the resin was calculated.

The density of the composites was determined according to ASTM D792-66. The flexural strength of different composites was determined according to ASTM D790-71 using a span-to-depth ratio of 32:1, cross-head speed of 5 mm/min, full-scale load of 100 kg and chart speed of 50 mm/min. The average of 4-5 specimens tested was taken. The interlaminar shear strength of composites was determined according to ASTM D2344-76 using a span-to-depth ratio of 5:1, length-to-depth ratio of 7:1, cross-head speed of 1 mm/min and full-scale load of 100 kg. The tensile strength was determined according to ASTM D638-72 specification.

3 Results and Discussion

The structural changes in jute fibres on treatment with alkali and graft copolymerization were studied

by FT-IR spectroscopy. In the IR spectra of jute fibres, a broad and strong peak due to O–H stretch ($3200\text{--}3400\text{ cm}^{-1}$), absorption bands due to C–H stretch (2925 cm^{-1}), C=O stretch (1740 cm^{-1}), aromatic skeletal vibrations (1600 cm^{-1}) and CH_3 and CH_2 bands were observed. Similar bands have been reported earlier^{11,12}. The medium intensity peak at 1740 cm^{-1} disappeared on treatment with alkali. The existence of an alkali sensitive ester linkage between lignin and hemicellulose was indicated. These results indicate partial loss of lignin from jute on treatment with alkali. A reduction in weight of the fibre was also observed on treatment with alkali. In grafted jute samples, the absorption peak at 1740 cm^{-1} due to C=O of methyl methacrylate reappeared. The intensity of this absorption peak increased with an increase in % graft add-on.

3.1 Optimization of Conditions for Grafting of MMA on Jute Fibres

The effect of concentration of nitric acid, initiator and monomer on the % graft add-on of alkali-treated jute fibres was investigated to optimize the conditions of graft copolymerization. For studying the effect of these variables the temperature and duration of graft copolymerization were kept constant at 50°C and 180 min respectively.

The effect of nitric acid concentration was studied by varying the concentration from 0.025 to 0.5 *N* and using 5% monomer and 0.01 mol/l ceric ammonium nitrate. The lowest graft add-on of 2.3% was obtained at 0.5 *N* acid concentration and the highest graft add-on of 13.2% was obtained at 0.1 *N* acid concentration. The % graft add-on was found to be 9.0, 11.8 and 7.0 for acid concentrations 0.025, 0.05 and 0.25 *N* respectively.

By using 0.1 *N* HNO_3 and keeping 5% monomer concentration the influence of ceric ammonium nitrate on % graft add-on was determined. The optimum grafting (13.2%) was observed when 0.01 *M* initiator concentration was used. The % graft add-on was found to be 5.6, 11.9, 11.5 and 9.6 for 0.005, 0.0075, 0.015 and 0.02 *M* initiator concentrations respectively.

Grafting studies were also carried out at four different monomer concentrations (2.5–10.0%). Up to 5% monomer concentration, a rapid increase in % graft add-on was observed. However, further increase in monomer concentration did not result in any significant increase in % graft add-on. For example at 0.1 *N* HNO_3 conc. and 0.01 *M* initiator conc., the % graft add-on was found to be 8, 13.2, 13.5 and 13.7 for 2.5, 5.0, 7.5 and 10.0% monomer concentrations respectively.

The effect of temperature and duration of graft

copolymerization on % graft add-on was evaluated by keeping the concentrations of initiator (0.01 *M*), acid (0.1 *N*) and monomer (5%) constant. The temperature was varied from 30 to 70°C keeping the duration of polymerization 3 h. The maximum grafting (15%) was observed at low temp. (30°C) and increase in temperature to 70°C resulted in a decrease in graft add-on (10.6%). At 40, 50 and 60°C the % graft add-on was found to be 14.5, 13.2 and 12.1 respectively.

The % graft add-on increased with the increase in the duration of polymerization from 30 min to 180 min. Further increase in the duration of graft copolymerization did not increase the % graft add-on.

The % graft add-on in jute and coir fibres has been found to be lower than that in cotton fibres. This can be attributed to the presence of lignin in these fibres. The % graft add-on in coir fibre was lower than that in jute⁷. Coir has higher % of lignin than jute.

3.2 Moisture Regain

The adsorption-desorption hysteresis cycles were obtained gravimetrically. For adsorption regain measurements (AR), known weights of dry samples (0.3–0.5 g) were successively kept in desiccators having relative vapour pressure (RVP) in ascending order for 2 days each. The desorption regain (DR) measurements were made in a similar manner keeping the sample in desiccators having RVP in the descending order for 2 days each. The RVP in each desiccator was monitored by Huger hygrometer (model 3123). At all RVP's, the AR and DR values of untreated jute fibres were higher than those of MMA-grafted jute fibres (Fig. 1). The magnitude of reduction increased with the increase in % graft add-on.

The relative hysteresis (RH) which gives a quantitative measure of the amount of hysteresis at a particular temperature and RVP was also determined as follows:

$$\text{RH} = \frac{\text{DR} - \text{AR}}{\text{AR}} \times 100$$

The RH data for jute fibres and MMA-grafted jute fibres are plotted as a function of RVP in Fig. 2. The relative hysteresis for both treated and untreated fibres decreased with an increase in RVP.

3.3 Tensile Behaviour

The stress-strain diagram of jute fibres shows an almost linear relationship with little or no plastic deformation. The tenacity, elongation-at-break and modulus values for the untreated, alkali-treated and grafted jute fibres are given in Table 1. While the tenacity and elongation-at-break reduced for the grafted samples to the extent of $\sim 27\%$, the initial modu-

lus increased considerably. The observed decrease in tenacity on grafting may be either due to partial oxidation of cellulose by Ce^{4+} ion or due to non-uniform distribution of stress in the fibres. MMA, being a glassy polymer at room temperature, increases the rigidity of the fibre.

3.4 X-ray Crystallinity

An increase of 6% in degree of crystallinity was observed on treatment of jute with alkali (Table 1). The degree of crystallinity decreased with increase in % graft add-on. This indicates an increase in am-

orphous content in grafted fibres. The density of jute fibres was found to be 1.283.

3.5 Properties of Hybrid Composites

The mechanical properties of 3 composite samples based on untreated, alkali-treated and MMA-grafted jute fibres are given in Table 2. The composites based on alkali-treated jute fibres showed better mechanical properties than the composites based on untreated jute fibres. The best results were obtained with MMA-grafted jute fibres. Similar results were obtained when modified coir fibres were used instead of jute fibres as a reinforcement⁷.

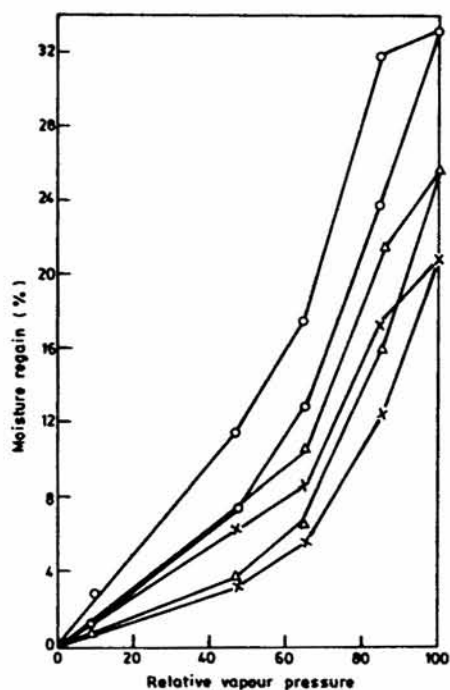


Fig. 1—MR-RVP hysteresis loops of (—○—) jute fibres, (—△—) NaOH-treated jute fibres, and (—×—) MMA-grafted jute fibres having 15.4% graft add-on

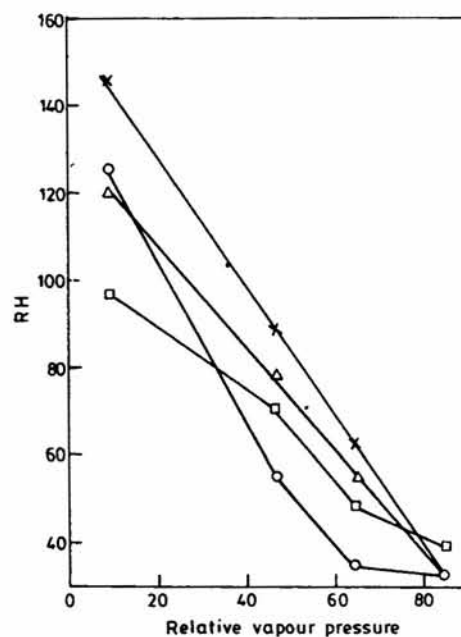


Fig. 2—RH-RVP plots of (—○—) jute fibres, (—×—) NaOH-treated jute fibres, (—△—) MMA-grafted jute fibres having 10.5% graft add-on, and (—□—) MMA-grafted jute fibres having 15.4% graft add-on

Table 1—Effect of MMA grafting on tensile properties and crystallinity of jute fibres

Jute fibre	Graft add-on %	Initial modulus g/den	Tenacity g/den	Elongation-at-break %	Degree of crystallinity %
Untreated	—	258.4	4.832	1.87	58.7
Alkali-treated	—	285.7	4.613	1.64	64.5
Grafted	6.42	301.3 (16.6%)	4.438 (- 8.1%)	1.60 (- 14.0%)	61.93
	10.46	328.7 (27.21%)	3.903 (- 19.2%)	1.49 (- 20.3%)	55.42
	13.2	340.2 (31.66%)	3.659 (- 24.3%)	1.40 (- 25.1%)	52.00
	15.39	351.1 (35.87%)	3.508 (- 27.4%)	1.35 (- 27.8%)	50.13

Figures in parentheses indicate the % changes in properties with respect to untreated jute fibres.

Table 2—Properties of hybrid composites fabricated using glass/jute as reinforcement and USP resin as matrix

Measured property	Sample		
	A	B	C
Jute fibre content, wt %	24	23.5	24.5
Glass fibre content, wt %	12.5	12.0	12.0
Resin content, wt %	63.5	64.5	63.5
Density, g cm ⁻³	1.38	1.41	1.43
Flexural strength, MN/m ²	203.7	220	240
Flexural modulus, GN/m ²	9.6	10.8	11.8
Interlaminar shear strength, MN/m ²	7.5	8.9	9.3
Tensile strength, MN/m ²	177	190	194
Tensile modulus, GN/m ²	7.9	8.8	10.0

Sample A—Composite fabricated using untreated jute fibres

Sample B—Composite fabricated using alkali-treated jute fibres

Sample C—Composite fabricated using grafted jute fibres

4 Conclusions

Moisture absorption of jute fibres could be reduced significantly by treatment with alkali and graft copolymerization with methyl methacrylate. The tenacity and elongation-at-break of jute fibres dec-

reased on grafting whereas the initial modulus increased with increase in % graft add-on. Thus, jute fibres can be made more hydrophobic and rigid by graft copolymerization. An improvement in the mechanical properties of the hybrid composites fabricated from MMA-g-jute fibres was observed.

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