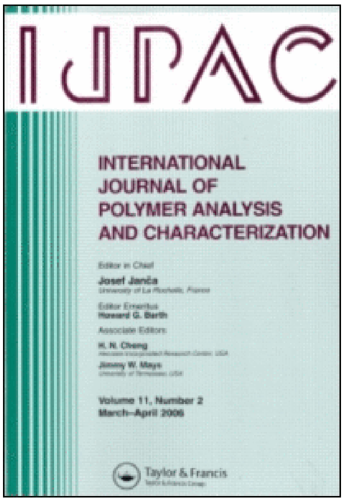

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Use of Flax-g-poly(MMA) as Reinforcing Material for Enhancement of Properties of Phenol Formaldehyde Composites

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Use of Flax-g-poly(MMA) as Reinforcing Material for Enhancement of Properties of Phenol Formaldehyde Composites

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Abstract: The present article deals with synthesis of phenol-formaldehyde (PF) matrix-based composites using raw flax and flax graft copolymers as reinforcing agents. Prior to use of the graft copolymer as reinforcing material, its strength vis-à-vis that of raw flax was studied. Composites thus prepared were subjected to the evaluation of different mechanical properties such as wear test, tensile strength, and compressive strength. It has been observed that the composites reinforced with raw flax were more wear-resistant than the graft copolymer-reinforced composites. In the case of tensile strength, composites reinforced with grafted flax showed more extension, but required higher force (175 N) at break-point than composites reinforced with raw flax, which failed at 150 N. Phenol-formaldehyde composite with grafted fiber reinforcement was found to show more compressive strength (800 N) than flax reinforcement. Moreover, the water-repellency property of the fiber could be improved on grafting with methyl methacrylate (MMA), whereas the raw flax was found to be more vulnerable to moisture.

Keywords: Composites; Fiber strength; Flax; Mechanical behavior; Phenol-formaldehyde

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INTRODUCTION

Graft copolymerization is one of the best techniques to modify the properties of natural fibers. Modifying the properties of natural polymers through graft copolymerization has been reported by various workers,[1–5] but only a few have reported the use of graft copolymers as reinforcing material in the preparation of composites.[6] Kaith and Kalia[7–10] have studied the mechanical properties of polymer composites reinforced with graft copolymers of natural fibers, and an improvement in mechanical strength of composites has been reported. Mechanical properties of composites reinforced with acrylate-grafted henequen cellulosic fibers were studied. They found that the best results could be obtained with poly(MMA)-grafted cellulose fibers because of better fiber-matrix adhesion.[11]

Since phenolic resins are hard, rigid, and strong materials, they have excellent heat, moisture, chemical, and abrasion resistance. It is necessary to increase the hydrophobicity of the natural fibers and to improve the interface between matrix and natural fibers. Graft copolymerization of natural fibers is one of the best methods to attain these improvements. Only a few workers have reported the use of graft copolymers as reinforcing material in the preparation of composites. In the present work, attempts have been made to develop phenol-formaldehyde matrix-based composites using flax-g-poly(MMA) vis-à-vis raw flax as reinforcement materials with better mechanical properties.

EXPERIMENTAL SECTION

Materials

Natural flax fibers (*Linum usitatissimum*) were supplied by the Department of Agronomy, CSK HP Agriculture University, Palampur (India). Phenolic resin (resole) was prepared by the reaction of phenol (SD Fine-Chem Ltd., India) and formaldehyde (CDH, India) in a material science laboratory.[12] The specific absorption bands in the IR spectrum of the phenolic resin confirm the presence of its typical structural components. They are as follows: aromatic ring, 1594–1605 cm^{-1}; hydroxyl groups, 3306 cm^{-1}; hydroxyl groups connected with phenyl ring, 1229.4 cm^{-1}; hydroxymethyl groups, 993–1023 cm^{-1}; methylene linkages, 2873–2959 and 1456–1473 cm^{-1}; and ether linkages, 1069 cm^{-1}. The chemical structure of the phenolic resin (average molecular weight of about 457 g/mol) is also confirmed by ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra, where the chemical shifts corresponding to the protons from relevant structural segments are indicated.[8]

Flax fibers were Soxhlet extracted with acetone for 72 h. Methyl methacrylate (MMA) (Fluka) was washed with 5% sodium hydroxide followed by water and was dried over anhydrous sodium sulfate. The dried monomer was distilled and the middle fraction was used. Strength of fiber was measured with a Stelometer (FO501, MAG). Flow time of resin was measured with a Red Wood Viscometer No. 2.

Composites were prepared in a compression molding machine (Santec, India). Mechanical studies such as wear resistance of the composites were carried out on a wear and friction monitor (20LE, DUCOM) and tensile strength and compressive strength of PF composites were carried on a H25KS Universal Testing Machine (Hounsfield).

Methods

Graft Copolymerization of MMA onto Flax Fiber

Flax fiber (0.5 g) was activated by immersion in 100 mL of distilled water for 12 h. Known amounts of Ferrous ammonium sulfate–Hydrogen peroxide (FAS–H_2O_2) as an initiator was added to the reaction medium, followed by addition of MMA in small quantities while stirring the reaction mixture constantly for 120 min. Optimization of different reaction parameters was carried out so as to obtain the maximum graft yield. The homopolymer formed was removed by Soxhlet extraction with acetone, and the graft copolymers were dried at 50°C until a constant weight was obtained. The results are depicted in Table I. The percent grafting (P_g) and percent efficiency (P_e) were calculated as follows:

$$P_g = \frac{W_g - W}{W} \times 100 \qquad P_e = \frac{W_g - W}{W_m} \times 100$$

where W, W_g, and W_m are the weights of ungrafted, grafted, and monomer samples, respectively.

Fiber Strength, Water Uptake Behavior, and Characterization of Resin

Fiber strength was measured with a fiber bundle strength tester (Stelometer) as per ASTM D-1445-95 (Flat Bundle Method). A definite number of fibers (five) were taken in a bundle and put in the Stelometer. Total strength (g/tex) required to break the fiber bundle was measured and calculated as follows:

$$\text{Strength (Kg/mg)} = \frac{\text{Total strength of fiber in Kg}}{\text{Total weight of fiber in mg}}$$

Table I. Effect of monomer concentration, reaction time, temperature, initiator concentration, and pH on graft copolymerization of MMA onto flax

Sample no	Temp (°C)	Time (min)	$[MMA] \times 10^{-3}$ mol/L	Molar ratio FAS:H_2O_2	pH	Pg	Pe
1.	35	120	1.96	1:6	7.0	08.20	02.09
2.	45	120	1.96	1:6	7.0	20.28	05.17
3.	55	120	1.96	1:6	7.0	41.74	10.64
4.	65	120	1.96	1:6	7.0	21.40	05.45
5.	75	120	1.96	1:6	7.0	10.20	02.60
6.	55	60	1.96	1:6	7.0	04.28	01.09
7.	55	90	1.96	1:6	7.0	34.16	08.71
8.	55	150	1.96	1:6	7.0	25.90	06.60
9.	55	180	1.96	1:6	7.0	12.70	03.23
10.	55	210	1.96	1:6	7.0	00.00	00.00
11.	55	120	1.47	1:6	7.0	15.40	05.23
12.	55	120	2.45	1:6	7.0	14.56	02.97
13.	55	120	2.94	1:6	7.0	11.96	02.03
14.	55	120	3.43	1:6	7.0	09.32	01.35
15.	55	120	3.92	1:6	7.0	09.20	01.17
16.	55	120	1.96	1:4	7.0	08.56	02.18
17.	55	120	1.96	1:5	7.0	22.40	05.71
18.	55	120	1.96	1:7	7.0	14.66	03.73
19.	55	120	1.96	1:8	7.0	09.40	02.39
20.	55	120	1.96	1:9	7.0	02.10	00.53
21.	55	120	1.96	1:6	4.0	10.32	02.63
22.	55	120	1.96	1:6	5.0	19.36	04.93
23.	55	120	1.96	1:6	6.0	33.48	08.54
24.	55	120	1.96	1:6	8.0	34.56	08.81
25.	55	120	1.96	1:6	9.0	26.86	06.85

$$\text{Strength (g/tex)} = \text{Strength (Kg/mg)} \times 15.0 \text{ (constant factor)}$$

$$\text{Actual strength (g/tex)} = \text{Strength (g/tex)} \times \text{Humidity correction factor}$$

where humidity correction factor at RH 53% is 1.0756.

Water uptake behavior of the grafted and ungrafted samples was carried out by suspending the wicks of the samples of a particular diameter in water for a particular time interval and noting the distance covered by water in cm. Water travels up by capillary action of the fiber.

The pH value of synthesized resin was measured with a digital pH meter (Ri make, India).

Flow time of resin was measured with a Red Wood Viscometer No. 2 for a definite volume of resin at different temperatures.

Water tolerance of resin was measured by adding the water from a burette to 5 mL of resin taken in a conical flask until the appearance of turbidity. The amount of water required in proportion to the amount of resin taken gave the water tolerance of resin.

Preparation of Composites

A definite amount of phenol-formaldehyde resin with fibers (10:0.5 w/w) was thoroughly mixed. The mixture was then poured in molds. The surfaces of the molds were coated on the inside with oleic acid to avoid adhesion of the mixture to the mold and to allow easy removal of the composites after their production. The whole assembly was then placed inside a hot press and cured at 90°C and a pressure of 10 $\mathrm{Kg/cm^2}$ for 5 h. Composites thus prepared were subjected to evaluation of different mechanical properties such as wear resistance, tensile strength, and compressive strength. Three specimens were used for the determination of mechanical properties, and tests were conducted at ambient laboratory conditions.

Wear Test

Wear testing was carried out on DUCOM machine as per ASTM D 3702 standard. Wear resistance was conducted against a hardened steel disc having a hardness of 60 HRC and a roughness Ra of 0.5 μm. The counter surface was polished using emery paper and cleaned with acetone before each sliding test. Samples for the wear test (3 cm) were held against a rotating counter surface at different speeds (100–600 RPM) and normal loads (2–8 kg). Each test was conducted for 5 min of sliding. Loss of weight was used as a measure of wear.

Tensile Strength Test

Tensile strength testing was done as per ASTM D 3039. A composite sample of 8 cm length was clamped between two jaws of the Universal Testing Machine. Each end of the jaws covered 2 cm of the sample. The rest of the 4 cm sample was used to study the tensile behavior. Readings for force and extension were set at zero. The test was conducted at a constant strain rate of the order of 5 mm/min. Tensile stress was applied until the failure of the sample and the load-extension curve were obtained.

Compressive Strength Test

Compressive strength of the samples was studied by using the procedure described in ASTM D 3410. A composite sample of 4 cm was held between two platforms, and the strain rate was fixed at 2 mm per min. The compression stress was applied until the failure of the sample. Total compression per unit force was noted.

RESULTS AND DISCUSSION

Very few investigations have been reported on the use of this versatile redox system for the preparation of graft copolymers. During grafting, an initiator helps in generating the free radicals that are responsible for creating active sites on the polymeric backbone. Along with graft copolymerization, homopolymerization and various other side reactions also take place. In order to minimize such undesirable side reactions and homopolymerization, the FAS-H_2O_2 system has been used for the generation of active sites onto the polymeric backbone. In the case of flax cellulose, C_2, C_3, and C_6 are the most active sites for grafting of vinyl monomer on the backbone. The proposed mechanism for the grafting of methyl methacrylate in the presence of Fenton's reagent onto flax is as follows:

$$Fe^{2+} + H-O-O-H \longrightarrow OH^* + Fe^{3+} + OH^- \tag{1}$$

$$OH^* + M \longrightarrow OH-M^* \xrightarrow{nM} OH-(M)^*_{n+1} \tag{2}$$

$$OH^* + Flax-H \longrightarrow Flax^* + H_2O \tag{3}$$

$$OH-(M)^*_{(n+1)} + Flax-H \longrightarrow Flax^* + OH-(M)_{n+1}-H \tag{4}$$

$$Flax^* + M \longrightarrow Flax-M^* \xrightarrow{nM} Flax-(M)^*_{n+1} \tag{5}$$

$$Flax-(M)^*_{n+1} + OH^* \longrightarrow Flax-M_{n+1}-OH \tag{6}$$

$$Flax-(M)^*_{n+1} + Fe^{3+} \longrightarrow Flax-(M)_{n+1} + Fe^{2+} \tag{7}$$

where M denotes the monomer.

It is evident from the above mechanism that grafting initiation takes place by processes (3) and (4). The abstraction of hydrogen atom from the main backbone through process (3) is unlikely, as the concentration of Fenton's reagent is very small. Therefore, OH^* will prefer to interact with vinyl monomer, thereby leading to a growing polymeric chain, which in turn will create active sites on flax-H by the hydrogen abstraction process (4). However, the concentration of Fe^{3+} plays an important role in getting the percent graft, as it is directly involved in the termination of the reaction.

Optimization of Various Reaction Parameters

Effect of Monomer Concentration

As is evident from Table I, P_g increases with increase in monomer concentration and after reaching the maximum value (41.74%, $1.96 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$), further increase in monomer concentration decreases the graft yield, which may be due to the predomination of homo-polymerization over graft copolymerization.

Effect of Redox Initiator Concentration

The molar ratio of FAS-H_2O_2 plays an important role in deciding the graft yield. Maximum grafting has been observed at a molar ratio of 1:6. However, further increase in molar ratio resulted in decreased P_g, which probably is due to the fact that at higher concentrations, more Fe^{3+} ions are produced, which may cause chain termination.

Effect of Reaction Temperature and Time

With increase in reaction temperature and time, P_g has been found to increase, but after 55°C and 120 min, a decline in P_g has been observed (Table I). This may occur due to the setting up of various hydrogen abstraction reactions and increase in viscosity of the medium, coupled with dissolution of water-soluble components of the fiber.

Effect of pH of the Reaction Medium

Grafting has been found to increase with increase in pH of the reaction medium up to 7.0 pH. However, further increase in pH resulted in decreased P_g. The increased OH ion concentration in the solution results in the premature termination of the grafted chain:

$$\mathrm{Flax}-(\mathrm{M})_{n+1}^{*}+\mathrm{OH}^{*}\longrightarrow\mathrm{Flax}-(\mathrm{M})_{n+1}-\mathrm{OH}$$

Effect of Grafting on Fiber Strength and Water Repellency

It is quite evident from Figure 1 that with increase in percent grafting, there is a decrease in fiber strength. This is due to the fact that on grafting, the crystal lattice of the fiber was disturbed, which leads to decrease in fiber strength.

Water repellency of the fiber has been found to increase on grafting (Figure 2). This was due to blocking of active sites by poly(MMA) on

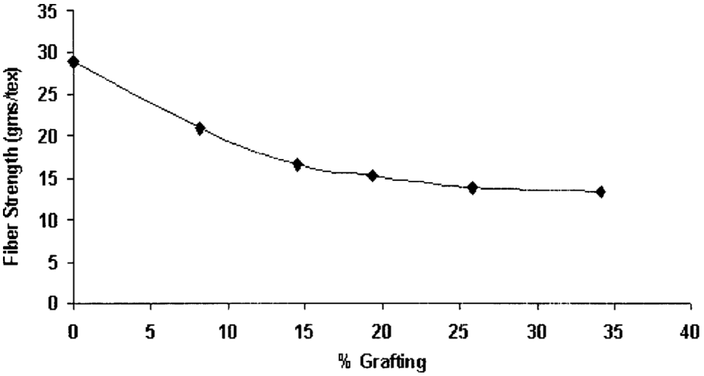

Figure 1. Effect of % grafting on fiber strength.

the polymeric backbone, which were vulnerable to water, thereby resulting in water repellency with increase in grafting.

Physical Parameters of Phenol-Formaldehyde Resin

The pH value and water tolerance of the phenol-formaldehyde resin has been found to be 9.0 and 1:3.6 (resin:water), respectively. It has been observed that with increase in temperature there is a decrease in flow time (seconds) of the resin (Table II). This was due to decrease in secondary bonding forces between different layers of the resin with increase in temperature.

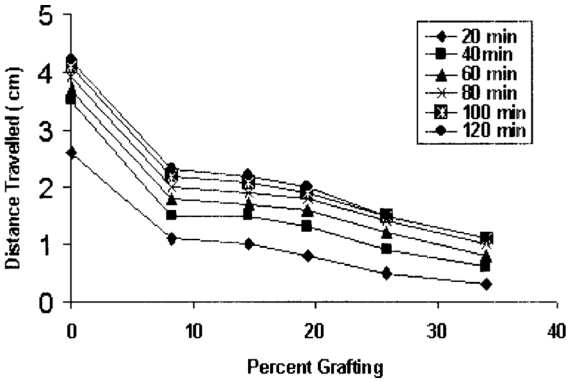

Figure 2. Effect of % grafting on water repellency.

Table II. Flow time of phenol-formaldehyde resin at different temperatures

Sample no.	Amount of resin (mL)	Temperature (°C)	Flow time (s)
1	20.0	30	45
2	20.0	40	26
3	20.0	50	12
4	20.0	60	10

Mechanical Properties of Phenol-Formaldehyde Composites Using Raw Flax and Flax-g-poly(MMA) as Reinforcement

Wear Test

It has been found that wear resistance is maximum with raw flax reinforcement followed by flax-g-poly(MMA) reinforcement and phenol-formaldehyde matrix. Loss of material in this case is due to abrasion and frictional heat effects, which enhances further on increasing the load (Figure 3). In the case of reinforcement of the phenol-formaldehyde matrix with graft copolymer, a reduced wear rate has been obtained. Maximum weight loss was found in the case of phenol-formaldehyde matrix, followed by reinforcement with graft copolymer and original flax.

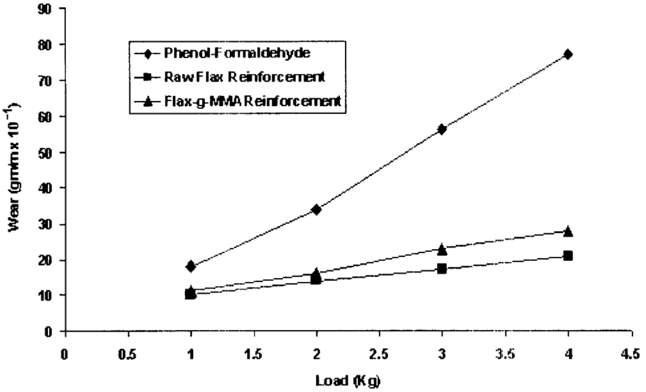

Figure 3. Effect of raw flax and flax-g-poly(MMA) reinforcement on wear rate of the phenol-formaldehyde composites.

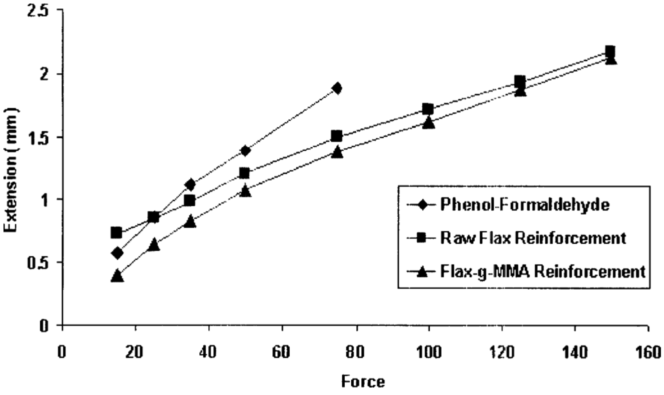

Figure 4. Effect of raw flax and flax-g-poly(MMA) reinforcement on tensile strength of the phenol-formaldehyde composites.

Tensile Strength

It is evident from Figure 4 that at a particular applied load, composites reinforced with grafted flax showed more extension than those reinforced with raw flax. However, in the case of reinforcement with flax-g-poly (MMA), with further extension beyond 2.52 mm at load >175 N the composite breaks, whereas reinforcement with raw flax showed less extension (2.17 mm) but failure at 150 N.

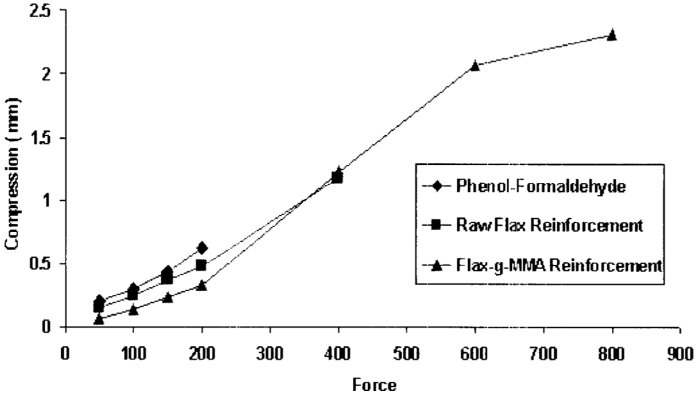

Figure 5. Effect of raw flax and flax-g-poly(MMA) reinforcement on compressive strength of the phenol-formaldehyde composites.

Compressive Strength

It has been found that the composite reinforced with raw flax fiber initially showed more compression than the composite reinforced with grafted fiber but on applying higher force, the graft copolymer-reinforced composite was found to show more compressive strength (Figure 5). Composites reinforced with flax-g-poly(MMA) can bear loads up to 800 N with compression of 2.32 mm, in contrast to composites reinforced with raw flax fibers, which fail at 400 N with a compression of 1.18 mm.

Mechanical properties of phenolic composites were enhanced on reinforcement with flax-g-poly(MMA) because of better interaction of fiber and matrix. Moreover, water repellency of flax was also increased on graft copolymerization.

CONCLUSIONS

Through graft copolymerization, water repellency of flax fibers was increased and the reinforcement of the phenol-formaldehyde resin with flax-g-poly(MMA) improved the tensile strength as well as the compressive strength of the composites in comparison to reinforcement with raw flax.

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