EFFECT OF PRESSURE INDUCED GRAFT COPOLYMERIZATION ON THE PHYSICO-CHEMICAL PROPERTIES OF BIO-FIBERS

Amar Singh Singha* and Raj K. Rana

The present study deals with the surface modification of *Agave americana L*. fiber through graft copolymerization of methyl methacrylate under pressure in the presence of ceric ammonium nitrate as redox initiator. The various reaction parameters such as reaction time, pressure, concentration of nitric acid, initiator, and monomer, etc. were optimized to have the maximum graft yield of 13.6%. The grafted fibers were then subjected to the evaluation of different physico-chemical properties such as swelling behavior, solubility, moisture absorption under different humidity levels, resistance to acids and bases, etc. It was observed that swelling behavior, solubility behavior, and moisture absorbance decreased with increase in grafting, whereas resistance to acids and bases increased with grafting. The fibers grafted under the optimized conditions were then characterized by Fourier transform infra-red spectroscopy, scanning electron microscopy, thermogravimetric analysis, and x-ray diffraction techniques.

Keywords: Pressure; Agave; Swelling behavior; Initiator; Methyl methacrylate

Contact information: Applied Chemistry Research Laboratory, Department of Chemistry
National Institute of Technology Hamirpur-177005 Himachal Pradesh, India
E-mail: singhaasnit@gmail.com; rajnitham@gmail.com Phone: +91-1972-304120 Fax: +91-1972-223834

INTRODUCTION

Since the evolution of man on Earth he has always utilized his potential to develop new materials and techniques. During this journey of new developments man entered into the age of polymers, where he utilized the polymeric materials in many applications ranging from building materials, leisure, medical, sports, defence, automobile, to aerospace. During the past decades apart from the conventional building materials such as wood, metals, etc., the role of the polymer composites cannot be ignored. Further, man exploited the resources for his comfort without taking sufficient account of the natural environment.

Most polymer composites utilize synthetic fibers such as glass, carbon, or aramid fibers etc. as reinforcement, which are non-renewable resources and non-biodegradable (Garoushi et al. 2007; Lassila et al. 2002; Pihtili 2009). With increase in the population, the excessive use of synthetic materials has led to many environmental imbalances and health hazards. It has forced researchers and material scientists around the globe to develop eco-friendly materials that are less toxic and pose less threat to human life. Keeping in view the above drawbacks of synthetic materials, the new materials, namely eco-composites, have been advocated which use natural fibers as reinforcement. Natural fibers have a number of advantages over the synthetic fibers, such as low cost, low density, non-abrasive character, biodegradability, high toughness, acceptable specific strength, reduced dermal and respiratory irritation, etc., which make them a potential reinforcement in eco-composites (Baley 2002; Mohanty et al. 2004; Voorn et al. 2001).

However, the major disadvantages of the natural fibers are their poor compatibility with polymeric matrices and high moisture absorption, which results in dimensional changes in the composites reinforced with cellulosic fibers (John and Anandjiwala 2008; Mohd Edeerozey et al. 2007). Before utilizing natural fibers in polymer composites as reinforcement, these limitations need to be overcome. Various chemical treatments such as mercerization (Suizu et. al. 2009), silane treatment (Singha and Thakur 2009), peroxide treatment (Augustine et al. 1997), permanganate treatment (Sreekala et al. 2002), isocyanate treatment (Rozman et al. 2004), acetylation (Khalil et al. 2001), benzoylation (Wang et al. 2007), latex coating (Sreekala and Thomas 2003), and graft copolymerization have been used in the literature for surface modification of natural fibers.

Graft copolymerization is a versatile technique for the modification of lignocellulosic fibers. This technique involves the incorporation of branches of synthetic polymers onto the cellulose macromolecules. It results in the development of copolymers having many desirable and modified physico-chemical properties while retaining the basic properties of the cellulosic fiber. The process of graft copolymerization depends upon the reactivity of the monomer, the type of initiation, and the accessibility of the cellulose molecules by the radiacals. Several redox systems such as ceric ammonium nitrate, ferrous ammonium sulphate, potassium bromate, etc., have been used to generate free radicals on cellulose molecules to initiate graft copolymerization. During the polymerization of the vinyl monomer onto cellulosic fiber in presence of free radical, a hydrogen atom is abstracted from this fiber by the growing chain radical, which leaves a free electron centre on the backbone fiber that is capable of initiating the grafting process.

A survey of the literature reveals that a lot of work has been done on graft copolymerization of natural fibers with a number of vinyl monomers under different reaction conditions such as in air and under the influence of microwave radiations (Arbelaiz et al. 2005; Kaith and Kalia 2008; Pulat and Isacoka 2006). But only very limited work on pressure-induced graft copolymerization of natural fibers appears in the literature (Singha et al. 2008). The important advantage of pressure-induced grafting over the corresponding polymerization in air or under the influence of microwave radiations is that only very little changes take place in the texture of the fiber.

In the present work pressure-induced graft copolymerization of methyl methacrylate onto *Agave americana* L. fiber has been carried out, and graft copolymers thus formed were characterized by Fourier transform infra red spectroscopy, scanning electron microscopy, thermal, and x- ray diffraction studies. Further, the graft copolymers were subjected to the study of various physico-chemical properties to investigate the effect of graft copolymerization. The present research work allows the proper utilization of the waste biomass of Himachal Pradesh, which is traditionally used by the local people for making ropes, mats, etc., However the most of the resource remains unused. Our work will ensure the commercial exploitation of the waste biomass in the preparation of biocomposites, which will find their applications in the area of infrastructure, automobile, and marine industry.

EXPERIMENTAL

Materials

Agave americana is a thick, long-leaved, subtropical plant, which is used for domestic, commercial, ornamental, and medicinal applications. The fibers obtained from the leaves of this plant have fairly good mechanical properties. *Agave americana* L. plants were collected from the vicinity of National Institute of Technology Hamirpur (H.P.) India during the month of September, 2008. Agave fiber bundles were extracted after the treatment of the leaves.

Fiber Bundle Extraction

Freshly cut leaves of *Agave americana* plant were kept in air at room temperature for about 48 hours and then immersed in continuously flowing fresh water for about 30 days at a temperature ranging between 22°C -28°C. The leaves were then taken out of water and beaten gently in order to partially remove the waxes from the outer layer and cementing materials such as hemicellulose present between the cellulose fibers. Like most of the cellulosic fibers, agave fiber bundles are composed mainly of cellulose, hemicellulose, and lignin, plus a low content of waxes (Li et al. 2000). The fibers thus extracted were washed with fresh water several times and finally with distilled water.

The washed fibers were then dried in a vacuum oven for 12 hours at 60 °C in order to remove moisture under soft conditions. The fiber bundles were thoroughly combed in order to remove any impurities. The combed fiber bundles were soxhlet extracted with acetone for 72 hours in order to remove waxes and other impurities.

Chemicals and Instruments

All the chemicals used were of analytical grade. Methyl methacrylate of 99.5% purity supplied by CDH India was used as vinyl monomer. MMA was purified by initial washing with 5% sodium hydroxide and then drying over anhydrous Na_2SO_4 followed by distillation. The middle fraction of the distillate was used for further studies. Ceric ammonium nitrate (CAN) supplied by E. Merck was used as initiator. Acetone of 99% purity supplied by Rankem India was used for removal of homopolymer, and nitric acid supplied by CDH was used to dissolve CAN.

A digital balance of Shimadzu Libror AEG-220 make was used for weighing. An autoclave supplied by Secor India was used to maintain the pressure, and a humidity chamber supplied by Swastika India was used to maintain the relative humidity during moisture absorbance studies.

Chemical treatment of Agave fibers

Graft copolymerization

0.5g of Agave fibers were immersed in 100ml distilled water for 24 hours prior to the graft copolymerization reaction in order to swell the fibers and activate the reactive sites on the fiber surface. The swelling of the fibers facilitates the movement of radicals onto the cellulose microfibrills. The calculated amount of initiator dissolved in optimized amount of nitric acid was added to the reaction mixture. It was followed by the addition of a definite amount of monomer in small fractions with constant stirring. The polymerization reaction was carried out in a 250 ml reaction flask, which was transferred to an autoclave maintained at a definite pressure.

The various reaction parameters such as reaction time, pressure, concentration of nitric acid, initiator, and monomer were optimized to obtain the maximum graft yield. The graft copolymerized product thus formed was washed thoroughly with distilled water, and then homopolymer was separated by extraction with acetone in a soxhlet apparatus (sec. 2.3.1). The grafted product was then dried at 60°C in an oven until constant weight. Percent graft yield and percent efficiency were calculated according to the following relations (Sakia and Ali 1998),

$$\%\ Grafting\left(P_g\right) = \frac{W_g - W}{W} \times 100 \tag{1}$$

$$\%\ Efficiency\left(P_e\right) = \frac{W_g - W}{W_m} \times 100 \tag{2}$$

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

Homopolymer extraction

After completion of the graft copolymerization reaction, the fibers were taken out of the reaction flask and transferred to a beaker containing acetone. The contents of the reaction flask left after the removal of fibers were allowed to stand undisturbed until the homopolymer had settled down at the bottom. The transparent liquor of the reaction flask was carefully decanted off, and the remaining contents were filtered using Whatmann filter paper. The residue left on the filter paper was collected (W_1).

The homopolymer associated with the grafted sample was dissolved in acetone, which was then recovered by distillation (W_2). The residue left on the filter paper (W_1) and homopolymer recovered from acetone (W_2) gave the total amount of homopolymer formed during the graft copolymerization reaction (W_H). The percent homopolymer was calculated according to the following relation (Sakia and Ali 1998),

$$\%\ Homopolymer\ (H_p) = \frac{W_H}{W_m} \times 100 \tag{3}$$

where W_m and W_H are the weights of monomer and homopolymer, respectively.

Evaluation of Physical Properties

Swelling behavior

The swelling behavior of grafted and raw fibers was studied in water, ethanol, DMF, and CCl_4 solvents. The grafted as well as ungrafted fibers were subjected to the evaluation of swelling behavior by immersing the known weights of fibers in known amounts of different solvents for 24 hours. Before taking the initial weights of the fiber, they were completely dried to constant weight. The samples were taken out, and the excess of solvent was removed by putting them in the folds of filter paper. The samples were again weighed to obtain the final weight, and percent swelling was calculated using the following relationship,

$$\%\ Swelling = \frac{W_f - W_i}{W_i} \times 100 \qquad (4)$$

where W_f = final weight after swelling and W_i = initial weight of fiber.

Solubility Studies

The solubility of the graft copolymers in different solvents was investigated as a function of weight loss. The samples taken out of the solvents after the swelling studies were dried to constant weight at 60°C and then the final weight was noted. The percent solubility was calculated according to the following relationship,

$$\%\ So\mathrm{lub}ility = \frac{W_1 - W_2}{W_1} \times 100 \qquad (5)$$

where W_1 = Initial weight of grafted fiber (before immersing in the solvent for swelling studies), and W_2 = Final weight of grafted fiber (after heating to constant weight).

Moisture Absorption Studies

The moisture absorption studies were performed under different humidity levels ranging from 20% to 85% in humidity chamber. Each sample was subjected to a particular humidity level for a fixed time interval of 2 hours. The percent moisture absorption was studied as a function of weight gain and was calculated using the following formula,

$$\%\ Mabs = \frac{W_2 - W_1}{W_1} \times 100 \qquad (6)$$

where W_1 = weight of dry fiber sample, and W_2 = final weight of sample taken out from humidity chamber.

Evaluation of Chemical Properties

Chemical resistance

The chemical resistance of the graft copolymers was studied as a function of percent weight loss. Known amounts (W_1) of graft copolymers were subjected to the effect of hydrochloric acid and sodium hydroxide of different strengths ranging from 0.5 N to 2.0N for a time interval of 24 hours in order to evaluate their chemical resistance. The samples were weighed again to get the final weights (W_2). The percent weight loss was determined using the following formula:

$$\%\ Wt.loss\ =\ \frac{W_1 - W_2}{W_1} \times 100 \tag{7}$$

Characterization of Graft Copolymerized Natural Fibers

Fourier Transform Infra-Red Spectroscopy (FT-IR)

Fourier transform infra-red studies were carried out in order to confirm the synthesis of graft copolymers Agave-g-poly-(MMA). This spectroscopic technique was used in order to obtain the evidence of grafting MMA chains onto the surface of backbone polymer. IR spectra were recorded on a Perkin-Elmer spectrophotometer using KBr pellets, from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}.

Study of Surface Morphology

The surface morphology of raw and grafted fibers was studied using a Leo scanning electron microscopy (SEM) machine (435 VP). Fibers were mounted on the specimen holders with the help of electro conductive tape. In order to conduct the SEM studies, all the samples were gold plated in order to make them conducting. Scanning was synchronized with the microscopic beam for the maintenance of small size over large distance relative to the specimen. All of the images were taken at a resolution of 500 X.

X-Ray Diffraction Studies (X-RD)

X-ray diffraction studies were perfomed on a X-ray diffractometer (Brucker D8 Advance). X-RD studies were carried out using Cu Kα (1.5418Å) radiation, a Ni- filter and a scintillation counter as a detector at 40 KV and 40 mA on rotation from 5° to 50° at 2θ scale.

Each sample was finely powdered into small particle size and homogeneously mixed before being subjected to X- ray exposure. The finely powdered sample was evenly distributed in the cavity of the sample holder with the help of a glass slide. The glass slide was carefully removed without disturbing the surface of sample. The randomly oriented powdered sample with uniform surface was exposed to X- rays from all possible planes. The angle of scattering of diffracted beam was measured with respect to the incident beam of X- rays, and the relative intensity was obtained.

Crystallinity index (*C.I.*) was determined by using the wide angle X-ray diffraction counts at 2θ angle close to 22° and 18°. The counter reading of peak intensity close to 22° and 18° is said to represent the crystalline material and amorphous material in cellulose, respectively. Percent crystallinity and crystallinity index (*C.I.*) were calculated using the following equations (Mwaikambo and Ansell 2002),

$$\%\ C_r\ =\ \frac{I_C}{I_C + I_A} \times 100 \tag{8}$$

$$C.I.\ =\ \frac{I_C - I_A}{I_C} \tag{9}$$

where I_C and I_A are the crystalline and amorphous intensities at 2θ scale close to 22° and 18° angles.

TGA and DTA Analysis of Raw and Grafted Fibers

Thermal studies of graft copolymers were conducted on a Perkin Elmer thermal analyzer (Pyris Diamond make) at a heating rate of 10°C/min. The sample weights of raw and grafted fibers used for TGA/DTA studies were 7.79 mg and 9.35 mg, respectively. Thermograms were recorded over a temperature range of 25°C to 800°C in the presence of air with the flow rate of 200 ml/min.

RESULTS AND DISCUSSION

An initiator plays an important role in the grafting reactions initiated by chemical means. The initiator generates free radicals, which are transferred to the backbone to react with monomers and form graft copolymers. The free radicals may be generated through direct or indirect methods. By indirect method free radicals are generated through redox reactions.

Ceric ammonium nitrate is a redox initiator that forms a complex with the cellulose molecules through hydroxyl groups at C_2 and C_3 of the glucose units (eq.10). Ce (IV) ions are reduced to Ce (III) ions by the transfer of electron from the glucose unit of cellulose molecule, and therefore free radical sites are generated on the polymer backbone. Also ceric ions form free radicals in the monomer chains, which are bonded at the reactive sites on the polymer backbone to form graft copolymers eq.16 (Mino and Kaizerman 1958). Also monomer free radicals combine with each other to form homopolymer $[(M)_{n+1} - M]$(eq. 18).

$$R + Ce^{4+} \rightarrow [C] \rightarrow R^{*} + Ce^{3+} + H^{+} \qquad (10)$$

$$M + Ce^{4+} \rightarrow [D] \rightarrow M^{*} + Ce^{3+} \ H^{+} \qquad (11)$$

$$M^{*} + nM \rightarrow (M)^{*}_{n+1} \qquad (12)$$

$$(M)^{*}_{n+1} + R \rightarrow (M)_{n+1} - H + R^{*} \qquad (13)$$

$$R^{*} + M \quad \rightarrow RM^{*} \qquad (14)$$

$$RM^{*} + nM \rightarrow R(M)^{*}_{n+1} \qquad (15)$$

$$R(M)^{*}_{n+1} + Ce^{4+} \rightarrow \underset{(Graft\ copolymer)}{R(M)_{n+1}} + Ce^{3+} \qquad (16)$$

$$(M)^{*}_{n+1} + Ce^{4+} \rightarrow (M)_{n+1} + R(M)_{n+1} + Ce^{3+} \qquad (17)$$

$$(M)^{*}_{n+1} + M^{*} \rightarrow \underset{(Homopolymer)}{(M)_{n+1} - M} \qquad (18)$$

In the above equations, R= -C-CH_2OH of *Agave americana* fiber, M = monomer (MMA), C = fiber and ceric ion complex, and D = monomer and the ceric ion complex.

Optimization of the Reaction Variables for Graft Copolymerization

The extent of grafting on the natural fiber mainly depended upon the availability of the active sites on the polymeric backbone. However the reaction variables such as reaction time, pressure, concentration of initiator, nitric acid, and monomer had a pronounced effect on the graft yield. The optimum values of above parameters were determined by varying one parameter within certain limits while keeping the values of the other parameters constant. Table 1 represents the results of the experimental studies that were performed to optimize various reaction parameters to obtain the maximum graft yield of 13.6 %.

Table 1. Evaluation of Optimum Reaction Parameters for Pressure Induced Grafting of MMA onto *Agave americana* fiber

Sr. No.	Time (Min.)	Pressure (Kg/cm^2)	Initiator (Mol/Lx 10^{-3})	Nitric Acid (Mol/Lx 10^{-1})	Monomer (Mol/Lx 10^{-1})	P_g	P_e	H_p (%)
1.	30	2.0	8.77	2.77	1.81	5.2	1.36	16.27
2.	60	2.0	8.77	2.77	1.81	6.4	1.70	16.43
3.	90	2.0	8.77	2.77	1.81	9.6	2.55	28.60
4.	120	2.0	8.77	2.77	1.81	6.5	1.73	28.41
5.	150	2.0	8.77	2.77	1.81	4.2	1.09	25.33
6.	90	0.5	8.77	2.77	1.81	5.7	1.52	25.80
7.	90	1.0	8.77	2.77	1.81	10.6	2.82	28.67
8.	90	1.5	8.77	2.77	1.81	11.7	3.11	28.98
9.	90	2.5	8.77	2.77	1.81	7.2	1.74	25.42
10.	90	1.5	2.19	2.77	1.81	5.5	1.45	13.48
11	90	1.5	4.38	2.77	1.81	6.9	1.83	15.33
12.	**90**	**1.5**	**6.58**	**2.77**	**1.81**	**13.6**	**3.61**	**30.98**
13.	90	1.5	10.96	2.77	1.81	10.9	2.89	25.12
14.	90	1.5	6.58	0.69	1.81	6.8	1.82	18.93
15.	90	1.5	6.58	1.38	1.81	8.9	2.37	25.59
16.	90	1.5	6.58	2.07	1.81	9.7	2.57	28.65
17.	90	1.5	6.58	3.46	1.81	7.8	2.07	16.95
18.	90	1.5	6.58	2.77	0.45	6.7	7.11	5.66
19.	90	1.5	6.58	2.77	0.91	7.8	4.12	21.31
20.	90	1.5	6.58	2.77	1.36	8.8	3.11	16.76
21.	90	1.5	6.58	2.77	2.26	7.6	1.61	20.66

Effect of Reaction Time

Reaction time has a significant effect on grafting, as it determines the extent to which the free radicals move onto the reactive sites of the polymer backbone. The effect of reaction time on grafting was studied in terms of weight gain of the polymer backbone, which may probably be due to the incorporation of the monomer chains onto the fiber backbone.

The effect of reaction time is shown in Fig. 1. From the figure it is clear that initially graft yield increased with increase in reaction time, it achieved a maximum at 90 minutes, and it decreased with further increase in the reaction time. This may be explained by the fact that with increase in the reaction time, interactions between Ce (IV) ions and fiber backbone increased, resulting in the generation of the reactive sites on the backbone as well as monomer radicals therefore increasing the graft yield.

However graft yield decreased with increase in reaction time beyond the optimum value. This could be due to the increase in the viscosity of the reaction medium, which offers hindrance for the movement of radicals onto the backbone. Also with the passage of the time the reactive sites available on the polymer backbone decrease.

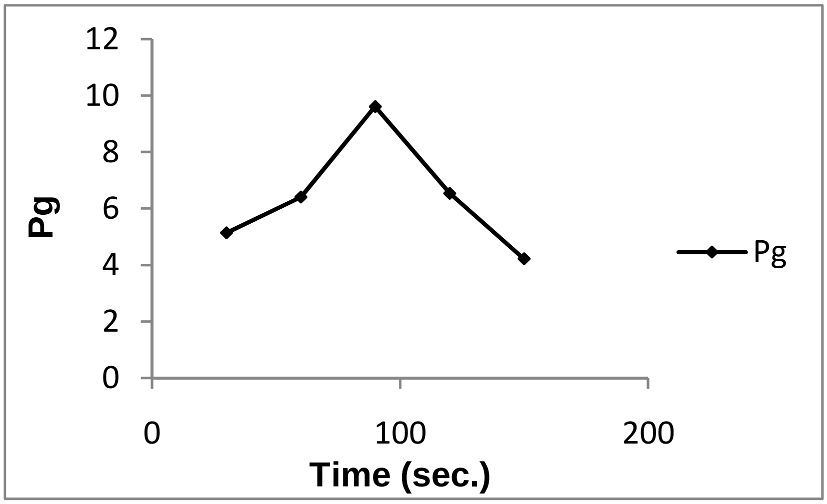

Figure 1. Effect of reaction time on percent grafting (Pressure = 1.5 kg/cm^2, Initiator = 6.58 x 10^{-3} mol/lt, Nitric Acid = 2.77 x 10^{-1} mol/lt, Monomer = 1.81 x 10^{-1}mol/lt)

Effect of Pressure

During the experimental studies it was observed that pressure affected the graft yield. Initially when the pressure on the reaction medium was increased, graft yield also increased. After reaching the optimum value (1.5 Kg/cm^2), graft yield decreased with further increase in pressure (Fig. 2). This could be explained on the basis that an initial increase in pressure drifts the radicals onto the fiber backbone, hence increasing the graft yield. With further increase in the pressure after reaching the optimum value, the movement of the radicals through the reaction mixture is slowed down at high pressure.

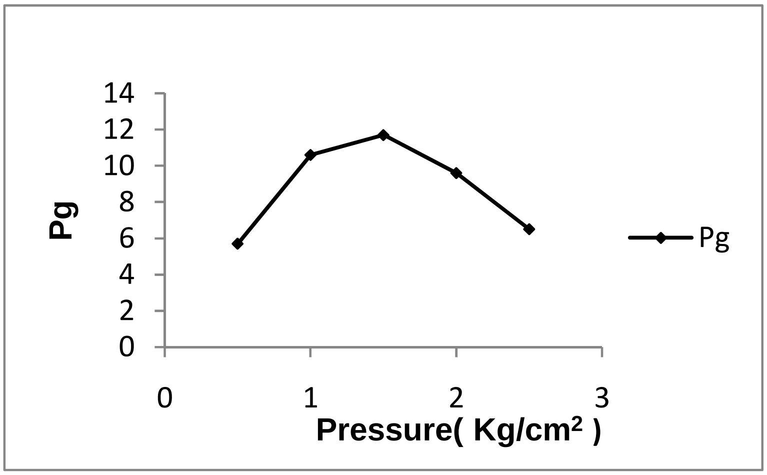

Figure 2. Effect of pressure on percent grafting (Time = 90 Min., Initiator = 6.58 x 10^{-3} mol/lt, Nitric Acid = 2.77 x 10^{-1} mol/lt, Monomer = 1.81 x 10^{-1}mol/lt)

Effect of Initiator

The effect of initiator is shown in Fig. 3. With the initial increase in the initiator concentration, more Ce (IV) ions are available in the reaction medium to initiate the reaction and generate the reactive sites on the cellulosic backbone, which results in an increase in percent graft yield. However, after attaining the optimum value, when further concentration of initiator is increased, the presence of excess of Ce (IV) ions terminates free radical chain reaction by accepting electrons from the monomer radicals.

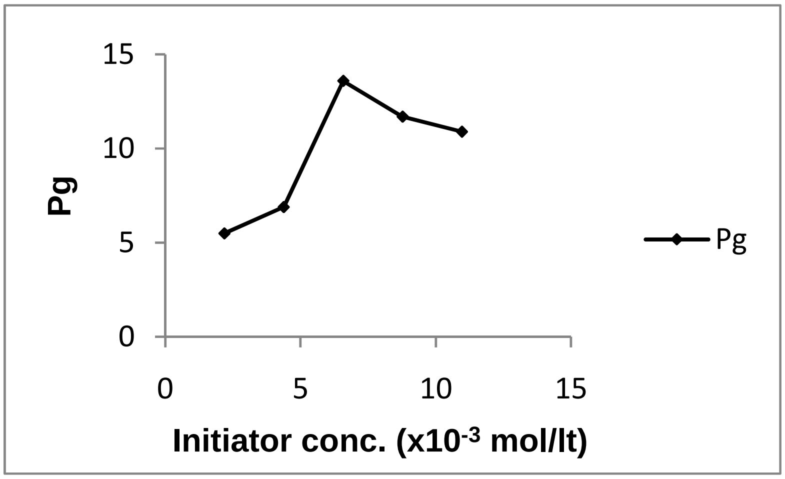

Figure 3. Effect of initiator conc. on percent grafting (Time = 90 Min., Pressure = 1.5 kg/cm^2, Nitric Acid = 2.77 x 10^{-1} mol/lt, Monomer = 1.81 x 10^{-1}mol/lt)

Effect of Nitric Acid

In aqueous medium CAN exists as Ce^{4+}, $[Ce (OH)]^{3+}$, and $[Ce\text{-}O\text{-}Ce]^{6+}$ ions (eqs.10 and 11). Due to their large size these ions are not able to form a complex with carbon chains on the backbone. However in presence of HNO_3 the equilibrium shifts more and more towards Ce^{4+} ions, therefore graft yield increases with increase in the nitric acid concentration.

However, with further increase in the concentration of nitric acid, graft yield decreases due to hydrolysis of the fiber. Moreover, increased concentration of nitric acid leads to early degeneration of the radicals. Figure 4 represents the variation of percent graft with the concentration of nitric acid.

$$Ce^{4+} + H_2O \rightarrow [Ce(OH)^{3+}] \qquad (10)$$

$$2[Ce(OH)^{3+}] \rightarrow [Ce-O-Ce]^{6+} + H_2O \qquad (11)$$

Effect of Monomer

The effect of the monomer concentration on grafting is shown in Fig. 5. As shown, the percent graft yield increased with initial rise in the monomer concentration. This increase in the graft yield may be attributed to the generation of more monomer radicals to reach onto the reactive sites on fiber backbone. However, after reaching to the optimum value, the graft yield decreased, which could be due to the predominance of homopolymer formation over graft copolymerization and other side chain reactions such as hydrogen abstraction reactions on the polymer backbone.

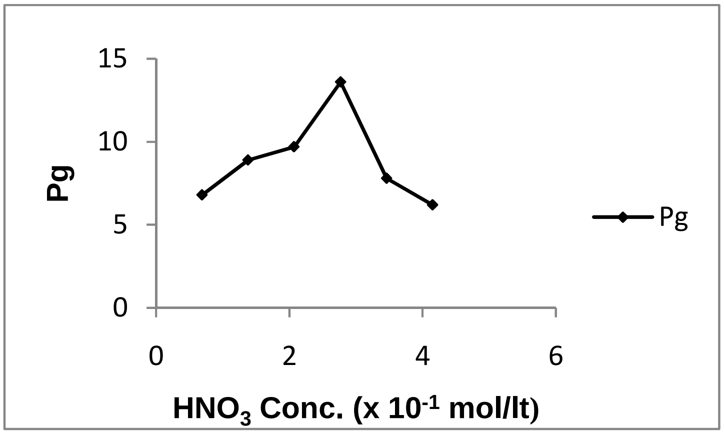

Figure 4. Effect of concentration of nitric acid on percent grafting (Time = 90 Min., Pressure = 1.5 Kg/Cm^2, Initiator = 6.58 x 10^{-3} mol/lt, Monomer = 1.81 x 10^{-1}mol/lt)

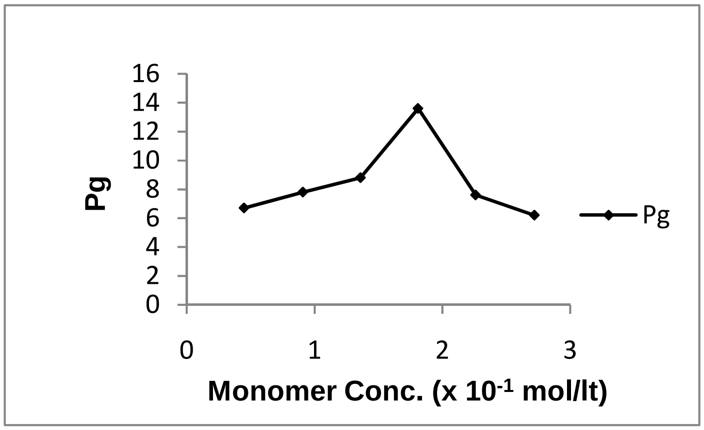

Figure 5. Effect of monomer conc. on percent grafting (Time = 90 Min., Pressure = 1.5 Kg/cm^2, Initiator = 6.58 x 10^{-3} mol/lt, Nitric Acid = 2.77 x 10^{-1} mol/lt)

Evidence of Grafting

Fourier-Transform Infra Red spectra

The FT-IR spectrum of raw *Agave americana* L. fiber showed a broad peak at 603 cm^{-1} (due to out of plane –OH bending), 898 cm^{-1} (due to β-glycosidic linkage), 1257.9 cm^{-1} (due to -C-O-C and –C=O stretching in xylan side substituent and lignin aromatic C=O stretching), milder peaks at 1381.2- 1432.0 cm^{-1} (due to -CH, -CH_2 and –CH_3 bending), 1505.8 cm^{-1} (lignin aromatic ring vibration and stretching), 1652.7 cm^{-1} (due to H-O-H bending of absorbed water and for lignin C-H deformation), 2138.7 cm^{-1} (due to O-H stretching of absorbed moisture), 2368.5 cm^{-1} (due to C-H stretching in polysaccharide chains), 2918.1cm^{-1} (for C-H stretching vibration of aliphatic methylene groups), and 3397.1 cm^{-1} (due to bonded -OH group). However in the case of Agave-g-poly-(MMA) an additional peak at 1735.3 cm^{-1} was observed, which is peculiar to the carbonyl group (>C=O) of ester stretching vibrations. The above results suggest that MMA has been grafted onto the agave fiber through covalent linkages.

Scanning Electron Microscopy

The change in the morphology of the *Agave americana* L. fibers is quite clear from SEM images. The scanning electron micrographs of raw (Fig. 6) and grafted fibers (Fig. 7) were taken at 350 X-500 X magnification. From study of the SEM micrographs it was observed that upon graft copolymerization the surface of fiber became rough as compared to raw fibers. This may probably be due to the deposition of poly-(MMA) chains on the surface of raw fibers upon grafting.

X-Ray diffraction studies

The raw fiber at 2θ scale gave peaks at 22.03° and 14.22° with relative intensities of 97.6 and 46.1, respectively. Similarly Agave-g-poly-(MMA) showed peaks at 22.38° and 14.11° with relative intensities of 100 and 60.0, respectively. The percent crystallinity of raw and grafted fibers came out to be 67.92 and 62.5, respectively, whereas crystallinity index was 0.53 and 0.40, respectively. It is clear that grafted fiber showed lower percent crystallinity (%Cr) as well as crystallinity index (*C.I.*). Crystallinity index gives the quantitative measure of the orientation of the cellulose crystals in the fibers with respect to the fiber axis. Lower crystallinity index of the grafted fiber indicates that there may be disorientation of the cellulose crystals when poly-(MMA) chains are incorporated in the fiber.

Thermal studies

In case of raw fiber two-stage decomposition was observed, with the maximum weight loss between 240°C - 346°C (50.6 %) and 346°C - 432°C (32.3 %). The first stage of decomposition may be due to cellulosic decomposition, and the second stage may be due to the degradation of lignin and oxidation of char. The initial and final decomposition temperatures of raw fiber were 240°C and 432°C, respectively.

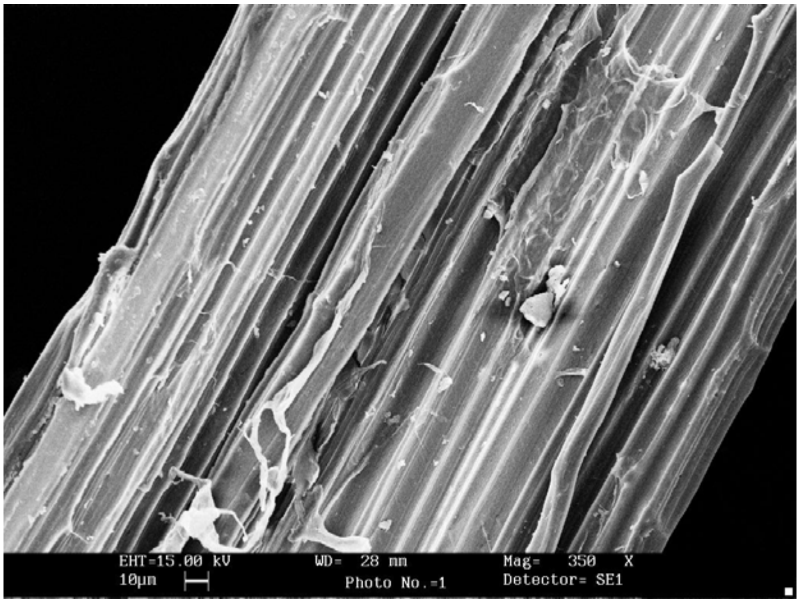

Figure 6. Scanning electron micrograph of raw fiber

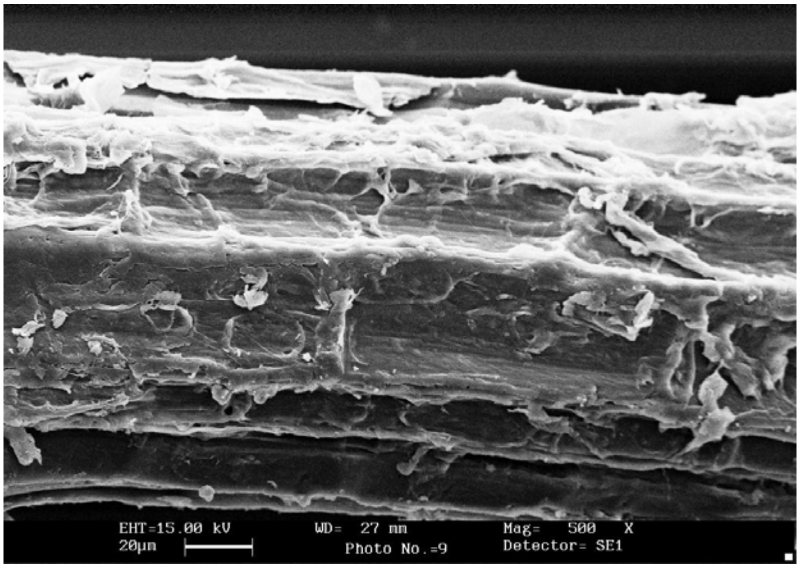

Figure 7. Scanning electron micrograph of Agave-g-Poly-(MMA)

The thermogram of grafted fiber also showed two-stage decomposition. The first stage decomposition took place at 260°C to 350°C with weight loss of 60.6%. This can be attributed to the breakdown of hemicellulose and glycosidic linkages of cellulose, whereas the second stage of decomposition occurred between 350°C to 461°C with weight loss of 24.5%. This may be related to the degradation of grafted poly-(MMA) chains onto the fiber surface. In case of Agave-g-poly-(MMA) the initial and final decomposition temperatures were 260°C and 461°C, respectively. From the above results it is clear that there was an increase in the thermal stability of fiber upon grafting, which may be due to the development of more covalent bonds between the poly-(MMA) chains and the fiber.

The TGA studies were further supported by the results of DTA evaluation. The exothermic peak at 439°C (237.2 µv) in case of raw fiber corresponds to the 346°C to 432°C decomposition stage in the TGA curve. However, in the case of Agave-g-poly-(MMA), the exothermic peak was observed at elevated temperature along with higher energy release, which supports the higher thermal stability of the graft copolymers than raw fibers.

Studies on Physical Properties

Swelling behavior

Figure 8 shows the percent swelling of raw and grafted fiber in different solvents. The trend of percent swelling of grafted fibers is just the reverse of the raw fibers. Raw fibers have hydrophilic hydroxyl (-OH) groups at C_2, C_3, and C_6 of glucose units, which have strong affinity with water. Therefore, raw fibers show maximum swelling (97.6%) in water, whereas raw fibers show least swelling in CCl_4, which is a nonpolar solvent having little affinity with hydrophilic groups on the fiber surface.

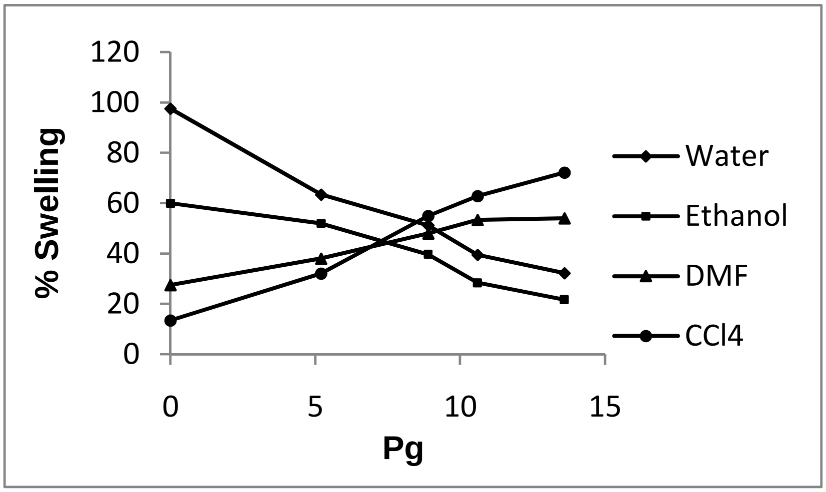

Figure 8. Effect of grafting on swelling behavior in different solvents

Due to the presence of polar –OH groups in ethanol the raw fibers are more solvolysed and hence show more swelling than in DMF. The trend in the swelling behavior of raw fibers may be given as:

$$H_2O > C_2H_5OH > DMF > CCl_4$$

The grafted fibers have hydrophobic poly-(MMA) chains incorporated in them, because of which these are solvolysed by nonpolar solvents such as CCl_4 to a maximum extent and hence show maximum percent swelling in CCl_4. The grafted fibers exhibit least swelling in C_2H_5OH due to the presence of a bulkier alkyl group in ethanol, which leads to less solvolyzation of polymeric chains on grafted fibers. The order of percent swelling of grafted fibers in different solvents is given as:

$$CCl_4 > DMF > H_2O > C_2H_5OH$$

Solubility studies

The graft copolymers showed maximum percent solubility in CCl_4 (7.53%). The solubility of the graft copolymers decreased in DMF, followed by ethanol, and was least in water (0.36 %). This solubility behavior of graft copolymers could be attributed to the affinity of poly-(MMA) chains with different solvents. CCl_4 is a nonpolar solvent, which has a strong affinity with hydrophobic poly-(MMA) chains, hence the solubility of graft copolymers is maximum. On the other hand, water, being a highly polar solvent, has the least affinity with poly-(MMA) chains. Further, the solubility of graft copolymers in CCl_4 decreased with decrease in percent graft yield, whereas it increased in water. The solubility behavior of raw and grafted fibers is shown in Fig. 9.

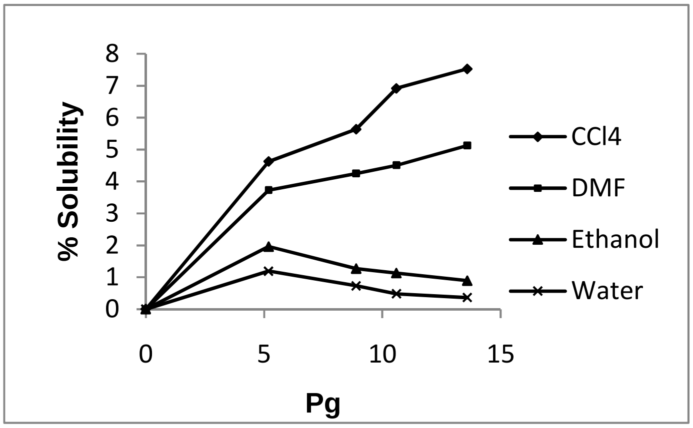

Figure 9. Solubility behavior of graft copolymers in different solvents

Moisture Absorbance Studies

At a particular humidity level raw fibers absorb maximum moisture (21% Mab at 85% humidity), which may be due to the strong affinity of the –OH groups on the cellulosic backbone with water. Further, moisture absorbance decreased with increase in percent graft yield, and was minimum (6.6% Mab) for graft copolymers (13.6% graft yield) at 85 % humidity level. This moisture absorbance behavior is clear from the decline in the curve with increase in % graft yield (Fig. 10).

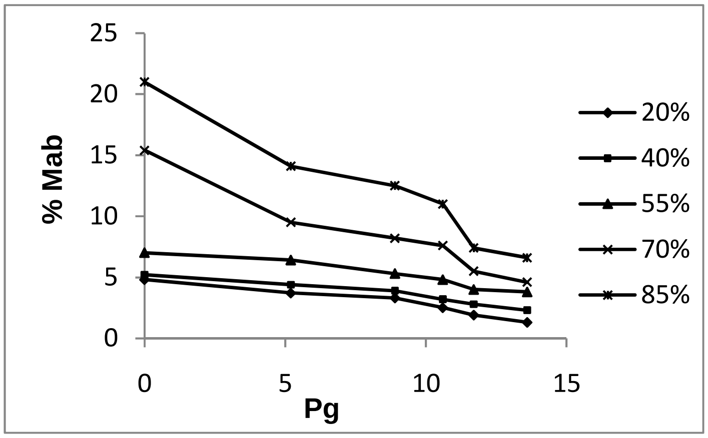

Figure 10. Effect of grafting on moisture absorbance behavior at different humidity levels

Studies on Chemical Properties

Acid and Base resistance behavior

The effect of acid (HCl) and base (NaOH) was studied by keeping both raw and grafted fibers in acid or base for a period of 24 hours. For a given strength of acid (1.0 N HCl), raw fibers showed maximum weight loss (19 %). The weight loss decreased with the increase in percent graft yield, reaching a minimum (8%) for graft copolymers having 13.6 % graft yield, as is clear from Fig. 11. This greater resistance of graft copolymers towards acids could be due to the blocking of reactive sites on the cellulosic backbone by poly-(MMA) chains that are incorporated as a result of graft copolymerization.

As raw fibers have all the reactive sites exposed, which are prone to be attacked by base, therefore these fibers showed a maximum weight loss (25 %) when subjected to the action of 1.0 N NaOH. However percent weight loss decreased (7.8 %) with the increase in the percent graft yield (13.6 %). The decrease in the percent weight loss of graft copolymers is due to the reduction in the number of reactive sites as a result of graft copolymerization which could be attacked by NaOH molecules. The behavior of raw and grafted fibers towards resistance to NaOH is shown in Fig. 12.

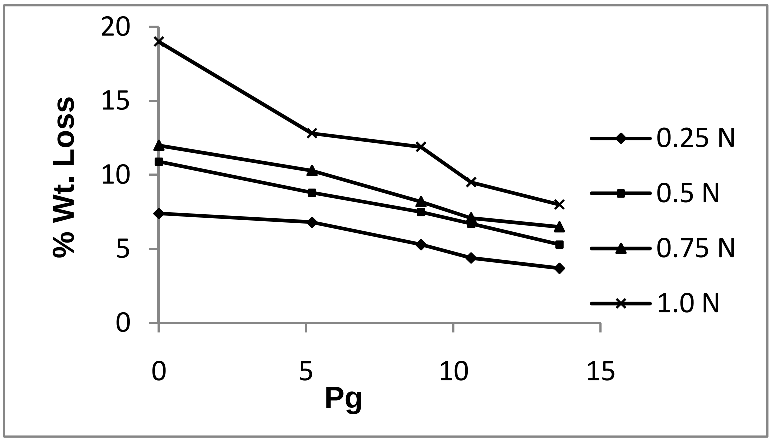

Figure 11. Effect of grafting on Acid resistance behavior

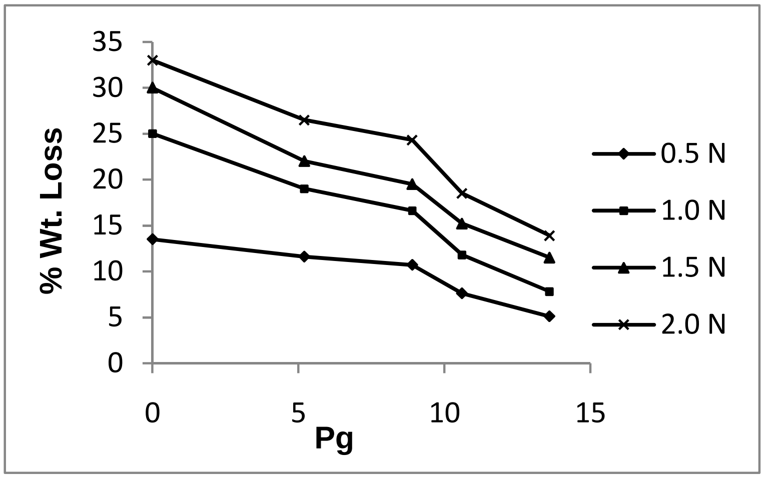

Figure 12. Effect of grafting on resistance to base

CONCLUSIONS

1. It is concluded from the evaluation of physical properties that incorporation of poly-(MMA) chains on the surface of cellulosic fiber through graft copolymerization reduces the affinity of lignocellulosic fiber with water. Thus when grafted fibers are used as reinforcement in composite materials, the chances of composite failure due to moisture absorption are reduced to a great extent
2. The blockage of reactive sites on the polymer backbone by poly-(MMA) chains leads to increased resistance to acids and bases. TGA/DTA studies indicate that grafted fiber exhibited greater thermal stability as compared to raw fiber. Therefore the grafted fibers can be used for the fabrication of fiber-reinforced polymer composites, which in turn can be used for high temperature applications in various fields.

ACKNOWLEDGEMENTS

The authors wish to thank the Director, National Institute of Technology Hamirpur (H.P.) India for providing laboratory facility to complete this work and MHRD (New Delhi) for the financial assistance.

REFERENCES CITED

Augustine, P., Kuruvilla, K., and Sabu, T. (1997). "Effect of surface treatments on the electrical properties of low-density polyethylene composites reinforced with short sisal fibers," *Compos. Sci. and Technol*. 57(1), 67-79.

Arbelaiz, A., Fernández, B., Cantero, G., Llano-Ponte, R., Valea, A., and Mondragon, I. (2005). "Mechanical properties of flax fibre/polypropylene composites. Influence of fibre/matrix modification and glass fibre hybridization," *Compos Part A: Appl. Sci. and Manuf*. 36 (12), 1637-1644.

Baley, C. (2002). "Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase," *Compos. Part A: Appl. Sci. Manuf*. 33 (7), 939-948.

Garoushi, S., Vallittu, P. K., and Lassila, L. V. J. (2007). "Short glass fiber reinforced restorative composite resin with semi-inter penetrating polymer network matrix," *Dental Materials* 23(11), 1356-1362.

John, M. J., and Anandjiwala, R. D. (2008). "Recent developments in chemical modification and characterization of natural fiber-reinforced composites," *Polym. Compos*. 29, 187-207.

Kaith, B. S., and Kalia, S. (2008). "Preparation of microwave radiation induced graft copolymers and their applications as reinforcing material in phenolic composites," *Polym. Compos*. 29 (7), 791-797.

Khalil, H. P. S. A., Ismail, H., Rozman, H. D., and Ahmad, M. N. (2001). "The effect of acetylation on interfacial shear strength between plant fibres and various matrices," *Europ. Polym. J*. 37(5), 1037-1045.

Lassila, L. V. J., Nohrström, T., and Vallittu, P. K. (2002). "The influence of short-term water storage on the flexural properties of unidirectional glass fiber-reinforced composites," *Biomaterials* 23 (10), 2221-2229.

Li, Y., Mai, Y. W., and Ye, L. (2000). "Sisal fiber and its composites: A review of recent developments," *Compos. Sci. Technol* 60, 2037-2055.

Mino, G., and Kaizerman, S. (1958). "A new method for the preparation of graft copolymers – Polymerization initiated by ceric ion redox systems," *J. Polym. Sci*. 31, 242-243.

Mohanty, A. K., Wibowo, A., Misra, M., and Drzal, L. T. (2004). "Effect of process engineering on the performance of natural fiber reinforced cellulose acetate biocomposites," *Compos, Part A: Appl. Sci. Manuf.* 35A(3), 363-370.

Mohd Edeerozey, A. M., Akil, H. Md., Azhar, B., and Ariffin, M. I. Z. (2007). "Chemical modification of kenaf fibers," *Material Letters* 61(10), 2023-2025.

Mwaikambo, L. Y., and Ansell, M. P. (2002). "Chemical modification of hemp, sisal, jute and kapok fibers by alkalization," *J. Appl. Polym. Sci*. 84, 2222-2234.

Pihtili, H. (2009). "An experimental investigation of wear of glass fibre–epoxy resin and glass fibre–polyester resin composite materials," *European Polymer Journal* 45(1), 149-154.

Pulat, M., and Isakoca, C. (2006). "Chemically induced graft copolymerization of vinyl monomers onto cotton fibers," *J. Appl. Polym. Sci*. 100(3), 2343-2347.

Rozman, H. D., Ahmadhilmi, K. R., and Abubakar, A. (2004). "Polyurethane (PU)-oil palm empty fruit bunch (EFB) composites: Effect of EFBG reinforcement in mat form and isocyanate treatment on the mechanical properties," *Polym. Test*. 23, 559-565.

Sakia, C. N., and Ali, F. (1998). "Graft copolymerization of methyl methacrylate onto high α-cellulose pulp extracted from *Hibiscus sabdariffa* and *Gmellina arborea*," *Bioresource Technol.* 68, 165-171.

Singha, A. S., Shama, A., and Thakur, V. K. (2008). "Pressure induced graft-co-polymerization of acrylonitrile onto Saccharum cilliare fiber and evaluation of some properties of grafted fiber," *Bull. Mater. Sci*. 31(1), 7-13.

Singha, A. S., and Thakur, V. K. (2009). "Synthesis and characterization of silane treated *Grewia optiva* fibers," *Int. J. Polym. Anal. Charac*. 14, 301-321.

Sreekala, M. S., Kumaran, M. G., and Thomas, S. (2002). "Water sorption in oil palm fiber reinforced phenol formaldehyde composites," *Compos Part A: App. Sci. and Manuf.* 33(6), 763-777.

Sreekala, M. S., and Thomas, S. (2003). "Effect of fibre surface modification on water-sorption characteristics of oil palm fibres," *Compos Sci. Tech*. 63, 861.

Suizu, N., Uno, T., Goda, K., and Ohgi, J. (2009). "Tensile and impact properties of fully green composites reinforced with mercerized ramie fibers," *J. Mater. Sci.* 44, 2477-2482.

Voorn, B. V., Smit, H. H. G., Sinke, R. J., and de Klerk, B. (2001). "Natural fibre reinforced sheet moulding compound," *Composites Part A: Appl. Sci. and Manuf.* 32(9), 1271-1279.

Wang, B., Panigrahi, S., Tabil, L., and Crerar, W. (2007). "Pre-treatment of flax fibers for use in rotationally molded biocomposites," *Journal of Reinforced Plastics and Composites* 26(5), 447-463.

Article submitted: Nov. 14, 2009; Peer review done: Feb. 22, 2010; Revised: March 3, 2010; Revision accepted: April 6, 2010; Published: April 9, 2010.