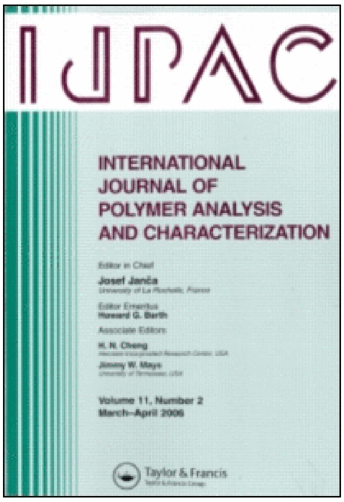

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Microwave Induced Graft Copolymerization of Methyl Methacrylate onto Lignocellulosic Fibers

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MICROWAVE INDUCED GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE ONTO LIGNOCELLULOSIC FIBERS

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Surface modification of natural fibers helps to improve their existing properties such as swelling behavior, water uptake, moisture absorbance, resistance to chemicals, and thermal behavior. In the present communication, surface modification of* Agave americana *fiber through graft copolymerization under the influence of microwave radiation has been reported. Grafting of methyl methacrylate onto the fiber was done using ceric ammonium nitrate as redox initiator under different conditions of reaction time, temperature, and nitric acid, initiator, and monomer concentration. The optimized reaction conditions resulted in maximum graft yield of 10.4%. The graft copolymers obtained under optimum conditions were subsequently subjected to evaluation of various physicochemical properties such as swelling behavior in different solvents, solubility behavior, moisture absorbance behavior, and resistance to acids and bases. The graft copolymers were further characterized with the help of Fourier transform-infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermogravimetric analysis, and X-ray diffraction studies.

Keywords: Grafting; Natural fibers; Redox initiator; SEM; Swelling behavior

INTRODUCTION

Plant fibers are renewable, cheap, and easily available materials that can be obtained from agricultural and forest crops. These materials can be used for various domestic applications and industrial purposes. They have applications in textiles, insulating materials, and pulps and increasingly as reinforcements in polymer matrix–based eco-friendly composites.[1] Moreover, due to increasing environmental and health concerns, emphasis is being placed on the synthesis of polymeric materials that are biodegradable and pose the least threat to the environment.[2,3] The use of natural fibers as reinforcement in biocomposites has a number of advantages, including biodegradability, low cost, easy availability, low density, nonabrasive nature,

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recyclability, no health hazards, and high specific properties. Moreover, natural fibers exhibit good thermal and acoustic insulation.[4,5]

However, there are certain limitations that discourage the use of natural fibers in the above-mentioned applications, especially in biocomposites. One of the major drawbacks of natural fibers is their hydrophilic nature, which leads to poor compatibility with hydrophobic polymer matrices. Another major disadvantage of cellulosic fibers is their moisture sensitivity, which can cause the degradation of the fiber as well as dimensional variation. A number of surface modification techniques such as alkali treatment,[6,7] acetylation,[8] isocyanate treatment,[9] and graft copolymerization[10] have been reported to overcome the incompatibility between fibers and polymer matrix. Graft copolymerization is one of the best and most convenient methods to modify the properties of cellulosic fibers. The resulting copolymer exhibits the properties of both fibrous cellulose and grafted polymer.[11] Many workers have modified natural fibers through the grafting technique by using different initiating systems.[12,13] Chauhan et al. graft copolymerized a binary monomer mixture of styrene and maleic anhydride onto cellulose extracted from pine needles through gamma radiation.[14] Okieimen and Ogbeifun graft copolymerized methacrylate (MA), ethyl acrylate (EA), and ethyl methacrylate on carboxymethyl cellulose by using ceric ions as initiator.[15] Many desirable properties such as water repellency and resistance to chemicals, moisture and swelling in different solvents can be incorporated through graft copolymerization.[16]

The grafting process involves the polymerization of the vinyl monomers onto the cellulose initiated by the free radicals, which depends upon the reactivity and the type of initiation. Free radicals may be produced either by the radiation method or by the use of chemical initiators. The irradiation of the macromolecules can cause homolytic cleavage, which forms free radicals on the backbone polymer. In this technique, the presence of initiator is not essential. In the chemical process, the presence of initiator is very important as it determines the path of the grafting process. In this process, the free radicals are produced from initiators and transferred to the substrate to react with monomers to produce graft copolymers.[17]

A number of graft copolymerization studies have been carried out in air by varying the temperature of the reaction medium.[18] In the present communication, we have reported the ceric ion–initiated graft copolymerization of MMA onto *Agave americana* fibers under the influence of microwave radiation. The advantage of graft copolymerization under the influence of microwave radiation has been that it leads to little change in the texture of the fiber because the grafting reaction lasts only for a few minutes as compared to longer time in air.[19] Moreover, the properties of the fibers treated under microwave-assisted techniques are the same or better than those of fibers modified by other conventional techniques.[20]

Agave americana fiber is a wild perennial plant that is found abundantly in Himachal Pradesh, a hilly state of northern India. The fibers extracted from leaves of this plant have good mechanical strength and have been used for domestic purposes like making ropes, mats, and bags by the native people of the region. Literature review reveals that no work has been done on the graft copolymerization of this fiber under the influence of microwave radiation. Therefore, exhaustive work has been initiated in our Applied Chemistry Laboratory in order to ensure the effective and economic use of this fiber.

EXPERIMENTAL SECTION

Materials

Agave americana fibers were extracted from leaves of the wild growing perennial plant by immersing them under water for 28 days. Fibers were washed with detergent in order to remove impurities and then Soxhlet extracted with acetone for 72 h in order to remove waxes, lignin, and other impurities. Methyl methacrylate (MMA) of 99.5% purity supplied by CDH was used as vinyl monomer. Acetone of 99% purity supplied by Rankem was used for removal of homopolymer (PMMA).

Ceric ammonium nitrate (CAN) (E. Merck) was used as initiator. All the other chemicals used were of AR grade and were used as such without any further purification. A Shimadzu Libror-220 digital balance was used for weighing the samples.

Grafting of MMA onto *Agave americana* Fiber

First, 0.5 g of agave fiber was immersed in 100 mL distilled water in a 250 mL reaction flask for 24 h prior to graft copolymerization reaction in order to activate the reactive sites on the fiber surface. The calculated amount of CAN dissolved in an optimized amount of HNO_3 was added to the reaction mixture. It was followed by addition of a known amount of monomer (MMA) to the reaction mixture in small fractions with constant stirring. The reaction flask containing the reaction mixture was placed in a microwave reactor operated at 70 watt power for a definite interval of time. Various reaction parameters such as reaction time and concentrations of HNO_3, monomer, and initiator were optimized to get the maximum graft yield (Table I). The graft copolymerized product was then thoroughly washed with distilled water, and homopolymer was removed by extraction with acetone in a Soxhlet apparatus. The homopolymer formed during the grafting was also separated.

Graft copolymer thus obtained was dried at 60°C to a constant weight. Percent graft yield, grafting efficiency, and percent homopolymer were calculated as per the formulas given below:[21]

$$\%\ \mathit{Grafting}\ (P_g) = \frac{W_g - W}{W} \times 100$$

$$\%\ \mathit{Efficiency}\ (P_e) = \frac{W_g - W}{W_m} \times 100$$

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

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

Swelling Behavior

The swelling behavior of the fibers was studied as a function of weight. First, 100 mg of grafted and raw fibers were immersed in 100 mL each of water, ethanol,

Table I. Evaluation of optimum reaction parameters for grafting of MMA onto *Agave americana* fiber under the influence of microwave radiation

Sr. no.	Time (min)	Initiator (mol/L × 10^{-3})	Monomer (mol/L × 10^{-1})	Nitric acid (mol/L × 10^{-1})	P_g	P_e	H_p (%)
1	5	8.77	1.81	2.77	0.5	0.13	7.4
2	10	8.77	1.81	2.77	7.2	1.91	9.6
3	20	8.77	1.81	2.77	8.1	2.15	35.04
4	30	8.77	1.81	2.77	6.7	1.78	25.19
5	40	8.77	1.81	2.77	5.8	1.54	20.83
6	50	8.77	1.81	2.77	1.6	0.42	7.95
7	20	2.19	1.81	2.77	4.1	1.09	6.29
8	20	4.38	1.81	2.77	4.9	1.30	20.19
9	**20**	**6.58**	**1.81**	**2.77**	**10.4**	**2.76**	**35.66**
10	20	10.96	1.81	2.77	7.2	1.90	28.62
11	20	13.15	1.81	2.77	5.3	1.41	15.33
12	20	6.58	0.45	2.77	3.3	0.88	22.89
13	20	6.58	0.91	2.77	5.9	1.58	31.99
14	20	6.58	1.36	2.77	7.3	1.94	38.82
15	20	6.58	2.26	2.77	6.9	1.84	50.33
16	20	6.58	2.72	2.77	5.7	1.50	81.13
17	20	6.58	1.81	0.69	4.4	1.17	8.42
18	20	6.58	1.81	1.38	6.3	1.67	18.66
19	20	6.58	1.81	2.07	7.8	2.08	23.72
20	20	6.58	1.81	3.46	9.3	2.47	28.13
21	20	6.58	1.81	4.15	4.8	1.27	16.24

dimethyl formamide (DMF), and carbon tetrachloride (CCl_4) for 24 h. The samples were then taken out from the solvents and excess of solvent was removed with the help of filter paper. The final weights of samples were noted and percent swelling was calculated according to the following relationship:

$$\%\ Swelling = \frac{W_f - W_i}{W_i} \times 100$$

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

Solubility in Different Solvents

The solubility of the graft copolymers was studied as a function of weight loss of the grafted fiber. Definite weights (W_1) of the grafted fibers were immersed in different solvents for 24 h. The fibers were then taken out of the solvent and dried to constant weight in an oven at 50°C. The dried fibers were weighed (W_2) immediately after being taken out of the oven, and percent solubility was calculated using the following formula:

$$\%\ Solubility = \frac{W_1 - W_2}{W_1} \times 100$$

where W_1 = initial weight of grafted fiber (before being immersed in the solvent) and W_2 = final weight of grafted fiber (after being heated to constant weight).

Moisture Absorbance Studies

Moisture absorbance studies were made in a humidity chamber supplied by Swastika India. Known weights (W_1) of dried grafted and raw fibers were placed in humidity chamber for 2 h under different humidity levels ranging from 25% to 85%. Final weights (W_2) of the samples exposed to different humidity levels were then noted. The percent moisture absorbance (% Mab) was calculated by using the following formula:

$$\%\, Mabs = \frac{W_2 - W_1}{W_1} \times 100$$

Water Uptake Study

Water uptake studies of the grafted as well as ungrafted fibers were carried out using the concept of capillary action. Wicks of fibers of 0.5 mm diameter were prepared and an initial mark in ink was drawn at one end. The wicks were then dipped into the beakers containing water up to the initial mark for 24 h. The rise of water in each wick was noted with the help of the final position of the ink mark.

Chemical Resistance Studies

Chemical resistance studies were carried out for grafted as well as raw fibers using an acid (HCl) and a base (NaOH) of different strengths. The results were determined by weight loss. Known weights (W_1) of both grafted and raw fibers were immersed in acids and bases of known strengths for 24 h. Final weights (W_2) of the samples subjected to the action of acids and bases were noted. Percent weight loss was then calculated using the following formula:

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

Fourier Transform-Infrared (FT-IR) Spectroscopy and Scanning Electron Microscopy (SEM)

IR spectra of raw and grafted fibers were recorded on a PerkinElmer spectrophotometer using KBr pellets, from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}.

The scanning electron microscopic analysis of raw and grafted fiber was performed on a Leo Electron Microscopy Machine (No. 435-25-20). Fibers were mounted on the specimen holders with the help of electro-conductive tape.

X-ray Diffraction Studies

X-ray diffraction (XRD) studies were performed on an X-ray diffractometer (Brucker D8 Advance). XRD studies were carried out using Cu Kα (1.5418 Å) 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 a 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 the diffracted beam was measured with respect to the incident beam of X-rays and relative intensity was obtained.

Crystallinity index was determined by using 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 formulas:

$$\%\,Cr = \frac{I_C}{I_C + I_A} \times 100$$

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

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

Thermal Analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of both raw and grafted fibers were performed as a function of percent weight loss versus temperature. Thermal studies were carried out in air at a heating rate of 10°C/min using a PerkinElmer (Pyris Diamond) thermal analyzer.

RESULTS AND DISCUSSION

Mechanism

From Figure 1 it is clear that C_2, C_3, and C_6 hydroxyl groups (–OH) and C–H are active sites on the cellulosic fibers at which the polymeric chains can be incorporated through grafting.

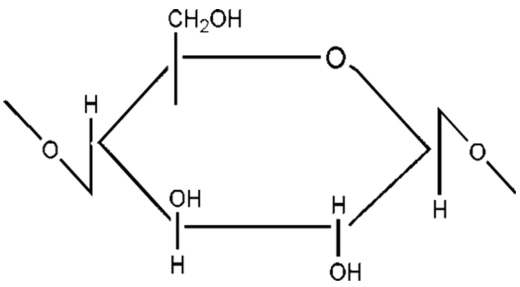

Figure 1. Structure of cellulose.

Ceric ions form the chelate complex with the cellulose molecule through C_2 and C_3 hydroxyl (–OH) of glucose unit. Ce (IV) is reduced to Ce (III) by the transfer of an electron from the cellulose molecule. The breaking of bonds at C_2 and C_3 of the cellulose molecule results in the formation of free radical sites (R^*). The grafting of methyl methacrylate onto the backbone is supposed to follow the mechanism:[22]

$$R + Ce^{4+} \rightarrow [C] \rightarrow R^* + Ce^{3+} + H^+ \tag{1}$$

$$M + Ce^{4+} \rightarrow [D] \rightarrow M^* + Ce^{3+} + H^+ \tag{2}$$

$$M^* + nM \rightarrow (M)^*_{n+1} \tag{3}$$

$$(M)^*_{n+1} + R \rightarrow (M)_{n+1} - H + R^* \tag{4}$$

$$R^* - M \rightarrow RM^* \tag{5}$$

$$RM^* + nM \rightarrow R(M)^*_{n+1} \tag{6}$$

$$R(M)^*_{n+1} + Ce^{4+} \rightarrow R(M)_{n+1} + Ce^{3+} \tag{7}$$

Graft copolymer

$$(M)^*_{n+1} + Ce^{4+} \rightarrow (M)_{n+1} + Ce^{3+} \tag{8}$$

$$(M)^*_{n+1} + M^* \rightarrow (M)_{n+1} - M \tag{9}$$

Homopolymer

where R = –C–CH_2OH of *Agave americana* fiber, M = monomer (MMA), C = fiber and ceric ion complex, and D = monomer and ceric ion complex.

Ceric ions from CAN form complexes with carbon chains of the polymer backbone and generate free radicals (Equation (1)). Also, ceric ions form free radicals in the monomer chain (Equations (2) and (3)), which attach at the reactive site on the polymer backbone to form graft copolymer [$R(M)_{n+1}$] (Equation (7)). Different monomer free radicals combine with each other to form homopolymer [$(M)_{n+1}$–M] (Equation (9)).

Optimization of Reaction Parameters for Graft Copolymerization of MMA onto *Agave americana* Fiber

The various reaction parameters that have been optimized to get the maximum graft yield are reaction time and concentrations of HNO_3, initiator, and monomer. Table I shows different values of graft yields during optimization of the reaction parameters.

Effect of Reaction Time

With the initial increase in time graft yield increases, reaches an optimum value at 20 min, and decreases with further increase in reaction time (see Figure 2).

This variation of percent graft yield with time can be explained on the basis that as the reaction time increases more and more radicals move onto the backbone, resulting in increased graft yield. After yield reaches an optimum value with further increase in reaction time, most of the active sites on the backbone are occupied by the radicals. Also, viscosity of the reaction medium increases with time, which provides hindrance for radicals to move onto active sites of the backbone, resulting in decrease in graft yield.

Effect of Initiator Concentration

Ceric ions from CAN form complexes with carbon chains on the backbone and generate active sites. Also, ceric ions generate free radicals in the monomer chains (Equations (1)–(3)). As concentration of initiator increases, more and more radicals are generated, which results in increase in graft yield. After reaching the optimum value, graft yield decreases with further increase in initiator concentration (see Figure 3). This may be due to the fact that with further increase in initiator concentration, chain termination reactions dominate the graft copolymerization (Equation (7)), which leads to premature decay of the monomer radicals.

Effect of Nitric Acid Concentration

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

However, with further increase in the concentration of nitric acid, graft yield decreases due to oxidation of the fiber. Moreover, increased concentration of nitric

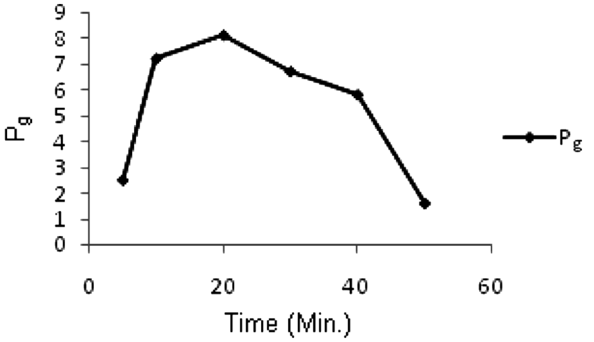

Figure 2. Effect of reaction time on percent grafting.

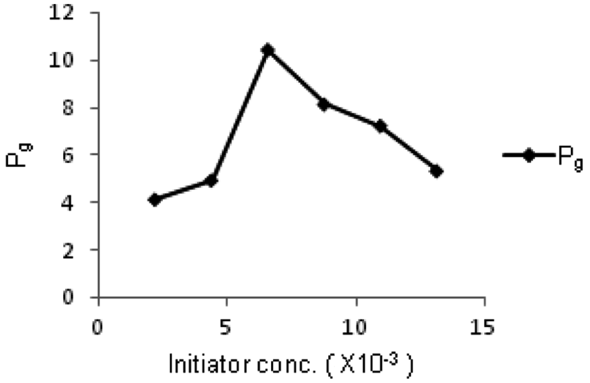

Figure 3. Effect of initiator concentration on percent grafting.

acid leads to early degeneration of the radicals (see Figure 4).

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

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

Effect of Monomer Concentration

The graft yield increase with initial increase in monomer concentration reaches the optimum value and then decreases with further increase in the monomer concentration (see Figure 5). The above behavior of monomer concentration may be explained on the basis that initially more and more radicals reach onto the backbone, resulting in the increase in graft yield. However, with the further increase in monomer concentration, graft yield decreases due to increase in the viscosity of the reaction medium.

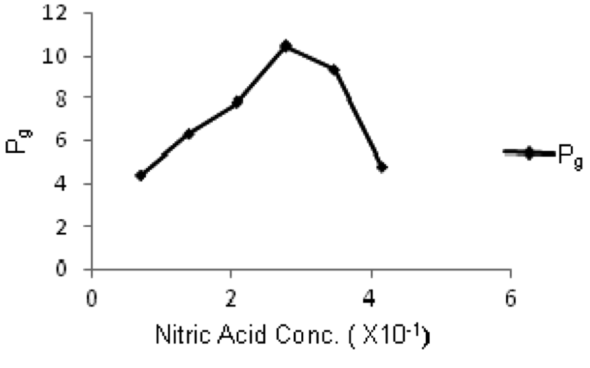

Figure 4. Effect of concentration of nitric acid on percent grafting.

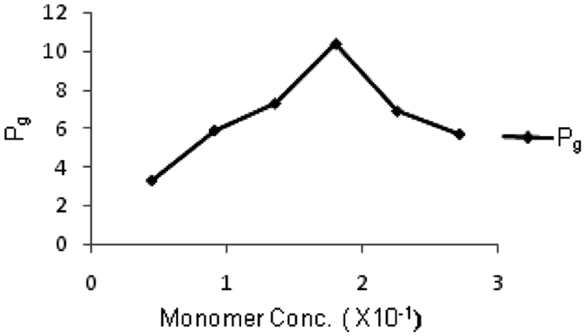

Figure 5. Effect of monomer concentration on percent grafting.

Swelling Behavior of Raw Fiber and Its Graft Copolymers

The swelling behavior of raw fiber in different solvents follows the trend:

$$H_2O > C_2H_5OH > DMF > CCl_4$$

Whereas the swelling behavior of grafted fibers follows the reverse order:

$$CCl_4 > DMF > H_2O > C_2H_5OH$$

The raw fibers show the maximum swelling in water, which may be due to more affinity of water molecules with hydrophilic –OH groups on the cellulosic fibers, whereas raw fibers show least swelling in CCl_4, which is a nonpolar solvent having little affinity with the hydrophilic groups on the fiber surface. These fibers show more swelling in C_2H_5OH than in DMF due to the presence of polar –OH group in ethanol, which has greater affinity with the polar groups on the fiber surface.

The order of swelling is just the reverse in the case of grafted fibers. The grafted fibers show maximum swelling in CCl_4, which may be attributed to the incorporation of hydrophobic poly(MMA) chains in the fiber. The grafted fibers exhibit least swelling in C_2H_5OH due to the presence of bulkier alkyl group in ethanol, which leads to less solvolyzation of polymeric chains on grafted fibers. The swelling behavior of both raw and grafted fibers is represented in Figure 6.

Solubility Behavior of Graft Copolymers

From the solubility behavior studies it may be concluded that graft copolymer exhibits maximum solubility in CCl_4. This may be due to more solvolyzation of the poly(MMA) chains on the fiber surface by nonpolar CCl_4. Further, the solubility is minimum in water, which may be due to the least affinity of the polar water molecules toward nonpolar poly(MMA) chains. The solubility behavior of graft copolymers is depicted in Figure 7.

Moisture Absorbance Behavior

At a particular humidity level percent moisture absorbance (% Mab) is maximum for the raw fibers, and it further decreases with increase in graft yield.

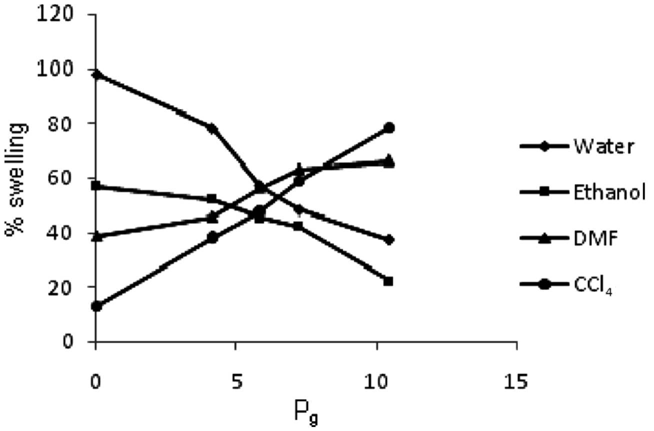

Figure 6. Effect of grafting on swelling behavior in different solvents.

Due to the presence of hydrophilic –OH groups on the raw fibers, they have more affinity for water and hence exhibit greater % Mab. On the other hand, due to incorporation of hydrophobic poly(MMA) chains in grafted fibers, these are less solvolyzed by water molecules. Therefore, grafted fibers exhibit less % Mab. The variation of % Mab with P_g is shown in Figure 8.

Water Uptake Behavior

Water uptake behavior of raw and grafted fibers is shown in Figure 9. From the figure it is found that the raw fibers exhibit more water uptake than the grafted fibers. This is probably due to the greater affinity of water molecules with hydrophilic –OH groups of raw fibers.

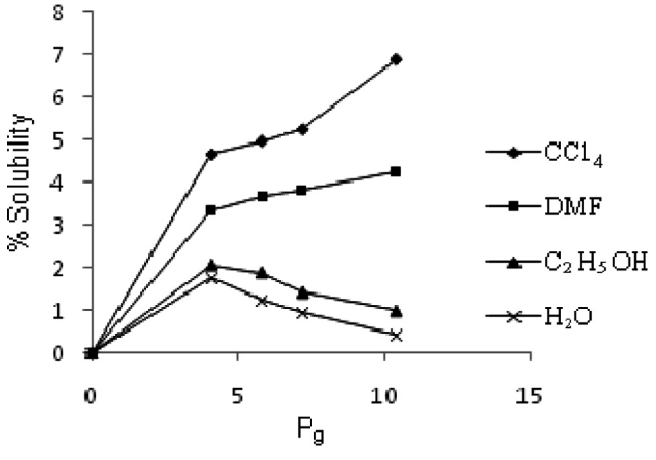

Figure 7. Solubility behavior of graft copolymers in different solvents.

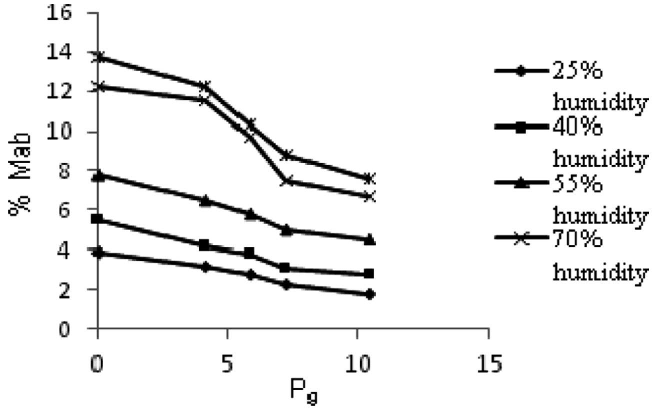

Figure 8. Effect of grafting on moisture absorbance behavior at different humidity levels.

Chemical Resistance Studies

The active sites on the surface of raw fibers are more prone to the attack of chemicals. The chemical resistance of raw and grafted fibers has been studied with an acid (HCl) and a base (NaOH) of different strengths and is shown in Figures 10 and 11. From the figures it can be seen that grafted fibers exhibit better chemical resistance than raw fibers. As a result of graft copolymerization, the active sites of the fibers are blocked by poly(MMA) chains, therefore the possibility of chemical attack on the grafted fibers is reduced to a greater extent than the possibility on the raw fibers where the active sites are more exposed to the attack of chemicals.

Evidences of Grafting

Characterization by FT-IR spectroscopy. The FT-IR spectrum of raw *Agave americana* fiber showed a broad peak at 3397.1 cm^{-1} due to bonded –OH

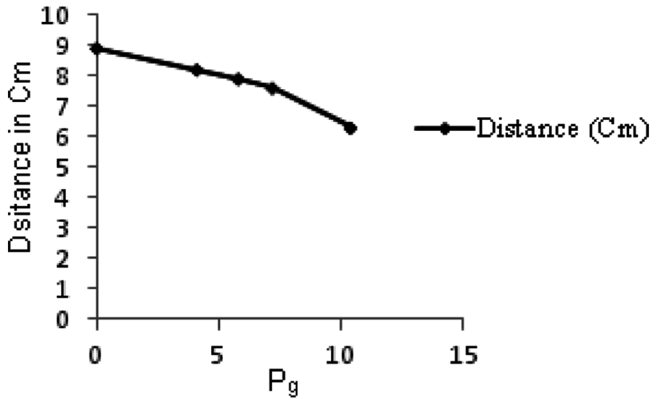

Figure 9. Effect of grafting on water uptake behavior.

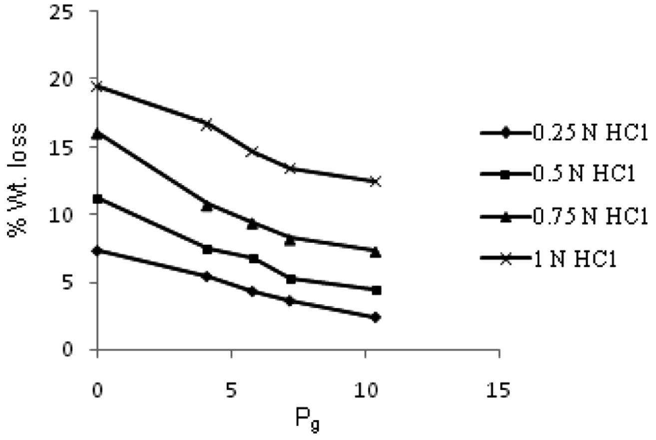

Figure 10. Effect of grafting on acid-resistance behavior.

group and at 2918.1 cm^{-1}, 1432 cm^{-1}, and 1054.9 cm^{-1} due to $-CH_2$, C−C, and C−O stretching respectively. 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.

Characterization by scanning electron microscopy. The scanning electron micrographs of raw and grafted fibers were taken at 500 × magnification. From the study of SEM, it has been observed that upon graft copolymerization the surface of the fiber becomes rough as compared to the raw fiber. This may be due to the deposition of poly(MMA) chains on the surface of raw fibers upon grafting.

Figures 12 and 13 depict the clear change in the morphology of raw fibers upon grafting.

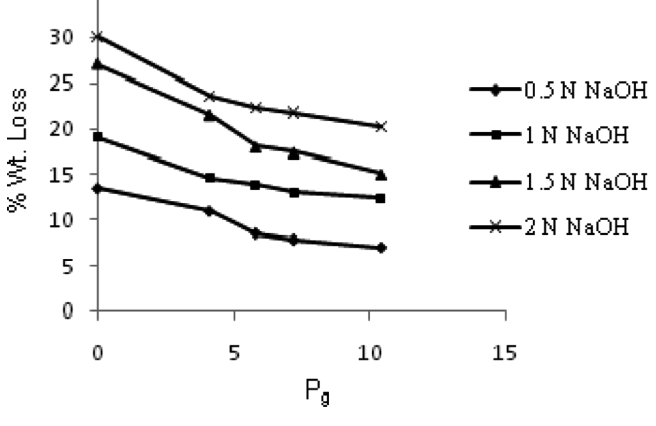

Figure 11. Effect of grafting on resistance to base.

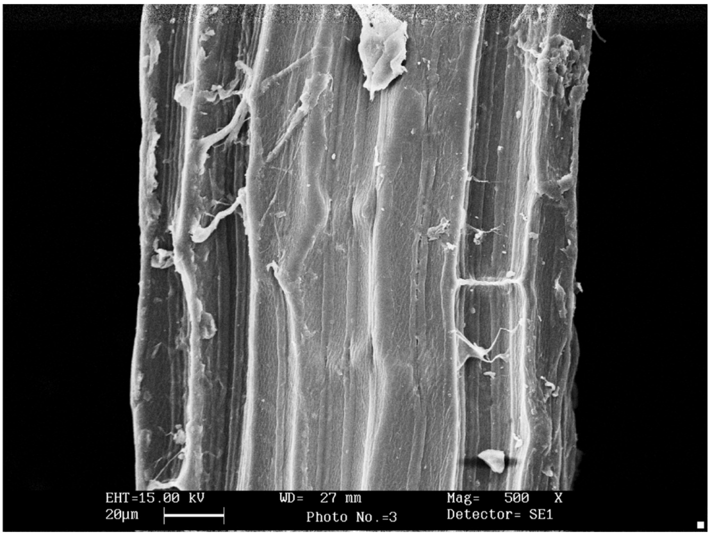

Figure 12. Scanning electron micrograph of raw fiber.

Characterization by XRD. From Table II it is evident that 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) shows peaks at 21.65° and 16.57° with relative intensities of 93.7 and 55.0 respectively. Percent crystallinity of raw and grafted fibers is 67.92% and 63.01% respectively, which shows that there is a slight decrease in the percent crystallinity of the fiber upon graft copolymerization. This decrease in the percent crystallinity may be attributed to the disturbance in the

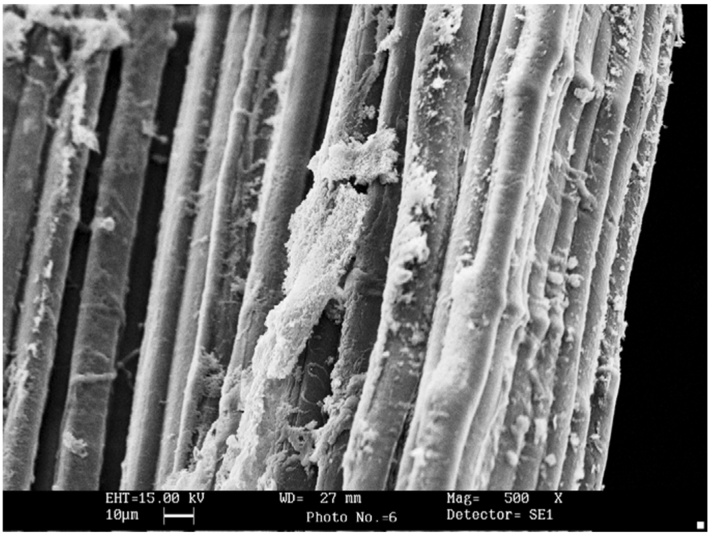

Figure 13. Scanning electron micrograph of agave-g-poly(MMA).

Table II. Percentage crystallinity and crystallinity index (C.I.) of raw fiber and agave-g-poly(MMA) under the influence of microwave radiation

Sample	$I_{C22.03}^{\circ}$	$I_{A14.22}^{\circ}$	% Cr	C.I.
Raw fiber	97.6	46.1	67.92	0.53
Sample	$I_{C21.66}^{\circ}$	$I_{A16.57}^{\circ}$	% Cr	C.I.
Agave-g-poly(MMA)	97.3	55.0	63.01	0.41

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

crystal lattice of the raw fiber, due to incorporation of poly(MMA) chains on the active sites of the backbone during grafting.

Characterization by thermal analysis. In the case of raw fiber two-stage decomposition has been observed, with the maximum weight loss between 240°C and 346°C (50.6%) and 346°C and 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 are 240°C and 432°C respectively.

The thermogram of grafted fiber also shows two-stage decomposition. The first stage, at 251°C to 349°C, may be attributed to breakdown of hemicellulose and glycosidic linkages of cellulose, whereas the second stage of decomposition, at 349°C to 489°C, may be related to the degradation of grafted poly(MMA) chains onto the fiber surface. In case of agave-g-poly(MMA), initial and final decomposition temperatures are 251°C and 489°C respectively. From the above results it is clear that there has been 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.

TGA studies have been further supported by 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. The exothermic peak at 357°C (72.8 μv) in the case of grafted fiber corresponds to 251°C to 349°C decomposition stage in the TGA curve and the peak at 470°C (57.1 μv) corresponds to 349°C to 489°C decomposition stage in the TGA curve, which may be due to the combustion of poly(MMA) chains. The results of TGA/DTA studies are depicted in Table III.

Table III. Thermogravimetric/differential thermal analysis of raw fiber and agave-g-poly(MMA)

	TGA						DTA
Sample	1st Stage decomp. (°C)	% Wt. loss	2nd Stage decomp. (°C)	% Wt. loss	Total % wt. loss	% Residue	Observed peaks in °C [μv]
Raw fiber	240–346	50.6	346–432	32.3	95.9	4.1	439 (237.2 μv)
Agave-g-poly (MMA)	251–349	66	349–489	24.2	99.8	0.2	357 (72.8 μv) 470 (57.1 μv)

CONCLUSION

In the present communication, the effect of graft copolymerization of MMA onto *Agave americana* fiber under the influence of microwave radiation on various physicochemical properties has been investigated. Due to incorporation of poly(MMA) chains the active sites on the fiber surface are blocked, which increases the resistance of the fibers to the attack of acids and bases. Moreover, the grafted fibers exhibited comparatively less swelling in water and are more resistant to moisture absorption, and hence can be used as a reinforcement in polymer-based eco-composites superior to raw fibers.

Further, the incorporation of poly(MMA) chains on the surface of *Agave americana* fiber through graft copolymerization under the influence of microwave radiation disturbs the crystal lattice of the cellulose, which results in a decrease in the percent crystallinity of the fiber.

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