

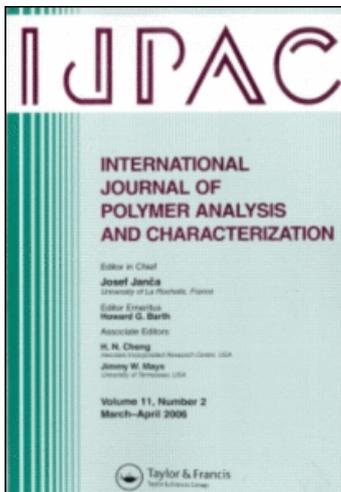
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GRAFT COPOLYMERIZATION OF METHYL METHACRYLATE (MMA) ONTO AGAVE AMERICANA FIBERS AND EVALUATION OF THEIR PHYSICOCHEMICAL PROPERTIES

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In the present article graft copolymerization of methyl methacrylate (MMA) onto Agave americana fiber has been carried out in air in the presence of ceric ammonium nitrate (CAN) as redox initiator. The various reaction parameters such as reaction time, temperature, and concentration of initiator, nitric acid, and monomer were optimized to get the maximum graft yield (43.5%). The graft copolymers thus synthesized were evaluated for their physicochemical properties such as swelling behavior in different solvents, water uptake behavior, moisture absorbance at different humidity levels, and resistance to chemicals. The graft copolymers were subsequently characterized by infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), and thermal analysis (TG/DTA).

Keywords: Agave; CAN; Graft copolymerization; Water uptake; XRD

INTRODUCTION

Polymers have become an important part of human life and are encountered in many daily life activities in one or other way. These polymers are generally synthetic materials such as polyethylene, polypropylene, polystyrene, polyesters, and polyamides, which are widely used in industry for making commercial as well as household goods. Human use of polymers has traveled a long journey of thousands of years, and they have served mankind in every possible way from food and medicine to structural materials.

Among structural materials, composites, the latest engineering materials, play an important role in different fields. Traditional fiber-reinforced composites use various types of reinforcements such as glass fibers, carbon fibers, and aluminum oxide. However, due to increased environmental awareness, the use of synthetic fibers has been discouraged. Moreover, biopolymers, as renewable raw materials, are gaining considerable importance because of recent environmental regulations.^[1] Natural fibers such as flax, jute, hemp, sisal, henequen, saccharum, grewia, and many others were used by some researchers as reinforcements for composites.^[2–4] These reinforcements are inexpensive and are obtained from renewable resources.

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Advantages of natural fibers over synthetic fibers include their low density, biodegradability, ease of processing, low cost, nonabrasive nature, recyclability, and less wear to equipment during their processing.^[5-7] Keeping in view the above advantages, natural fibers are considered the best replacement for glass fibers in composite materials.^[8] As the mechanical properties of natural fibers are comparable to those of man-made fibers, natural fiber-reinforced composites can be used in plastics, packaging, and the automobile industry to reduce material cost.^[9]

However the hydrophilic nature of natural fibers restricts their application as reinforcement in polymer composites. The poor moisture resistance of natural fibers results in incompatibility and reduced bonding at the fiber/matrix interface.^[10,11] Therefore, in order to incorporate natural fibers as reinforcement into polymer matrices, the interfacial incompatibilities must be overcome. This can be achieved by surface treatments of fibers. Chemical treatments such as use of compatibilizers,^[12] alkali treatment,^[13] acetylation,^[14] silane treatment,^[15] ethylenediamine tetraacetic acid (EDTA) treatment, lime water treatment,^[16] maleic anhydride treatment, and graft copolymerization^[17,18] have been reported by researchers.

In the present communication grafting of methyl methacrylate onto *Agave americana* fiber extracted from the wild-growing perennial plant is reported under different conditions of reaction time, temperature, and initiator and monomer concentrations. The graft copolymers obtained under optimum reaction conditions were then characterized with the help of Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), thermal analysis (TGA/DTA), and X-ray diffraction (XRD) techniques. The graft copolymers were further evaluated for swelling behavior in different solvents, water uptake behavior, moisture absorbance behavior under different humidity levels, and chemical resistance behavior for acids and bases of different strengths.

EXPERIMENTAL SECTION

Materials

Agave americana fibers were extracted from 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 poly(methyl methacrylate) (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.

Grafting of MMA onto *Agave americana* Fiber

A 0.5 g amount of agave fiber was immersed in 100 mL distilled water for 24 h prior to graft copolymerization reaction in order to activate the reactive sites on the fiber surface. The grafting reaction was carried out in a 250 mL reaction flask kept in a water bath over a hot plate cum magnetic stirrer. 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 with constant stirring for a definite time interval, at a definite temperature. Various reaction parameters such as reaction time, temperature, and concentration of HNO_3 , monomer, and initiator were optimized to get the maximum graft yield. The graft copolymerized product was then thoroughly washed with distilled water, and the homopolymer was removed by extraction with acetone in a Soxhlet apparatus.

The graft copolymer thus obtained was dried at 50°C to a constant weight. Percent graft yield and grafting efficiency was calculated on the basis of dry weight of fiber^[19]:

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

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

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

Swelling Behavior

A 100 mg amount of grafted and raw fibers was immersed in 100 mL each of water, n-butanol, dimethyl formamide (DMF), and carbon tetrachloride (CCl_4) for 24 h. The samples were then taken out of 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:

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

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

Moisture Absorbance Studies

Moisture absorbance studies were made in a humidity chamber supplied by Swastika India. Known weights (W_1) of dry grafted and raw fibers were placed in the humidity chamber for 2 h under different humidity levels ranging from 20% to 100%. Final weights (W_2) of the samples exposed to different humidity levels were then noted. The percent moisture absorbance (% Mabs) was calculated by using the following formula:

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

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 ink mark was drawn at one end. The wicks were then dipped into beakers containing water for 24h. The rise of water in each wick was noted with the help of the ink mark.

Chemical Resistance Studies

Chemical resistance studies were carried out for grafted as well as raw fibers using acids (HCl) and bases (NaOH) of different strengths. These studies were carried out in terms of weight loss. Known weights (W_1) of both grafted and raw fibers were immersed in acids and bases of known strengths for 24h. 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:

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

FT-IR and Scanning Electron Microscopy

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.

XRD Studies

X-ray diffraction studies were performed on a Bruker D8 Advance X-ray diffractometer, using Cu $K\alpha$ (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 the sample holder with the help of a glass slide. The glass slide was carefully removed without disturbing the surface of the 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 (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.^[23] Percent crystallinity and crystallinity index (C.I.) were calculated using the following formulas:

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

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

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

Thermal Analysis

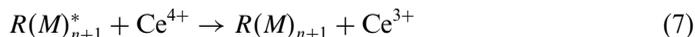
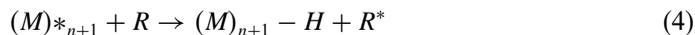
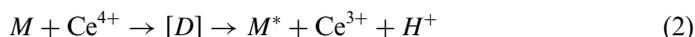
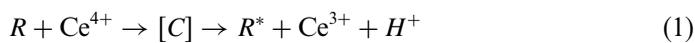
Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of both raw and grafted fibers were performed as a function of percent weight loss versus temperature. Thermal studies were carried out in air at a heating rate of $10^\circ\text{C}/\text{min}$ using a PerkinElmer (Pyris Diamond)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

RESULTS AND DISCUSSION

Mechanism

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

Ceric ions form the chelate complex with the cellulose molecule through C_2 and C_3 hydroxyl ($-\text{OH}$) of glucose unit. $\text{Ce}(\text{IV})$ is reduced to $\text{Ce}(\text{III})$ 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 following mechanism^[20]:



(Graft copolymer)

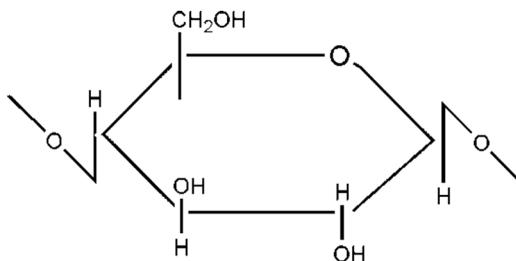
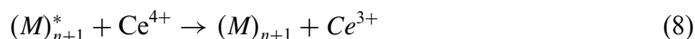


Figure 1. Structure of cellulose.



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 monomer chain (Equations (2) and (3)), which is attached 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 temperature, reaction time, and concentration of HNO_3 , initiator, and monomer. Table I shows different values of graft yields during optimization of the reaction parameters.

Table I. Evaluation of optimum reaction parameters for grafting of MMA onto *Agave americana* fiber

Sr. no.	Monomer (mol/L $\times 10^{-1}$)	CAN (mol/L $\times 10^{-3}$)	Nitric acid (mol/L $\times 10^{-1}$)	Time (min)	Temp. ($^{\circ}C$)	Pg	Pe
1	1.81	8.77	2.77	120	25	13.00	3.45
2	1.81	8.77	2.77	120	35	21.20	5.62
3	1.81	8.77	2.77	120	45	26.44	7.01
4	1.81	8.77	2.77	120	55	15.00	3.98
5	1.81	8.77	2.77	120	65	14.20	3.93
6	1.81	8.77	2.77	30	45	8.40	2.23
7	1.81	8.77	2.77	60	45	15.20	4.03
8	1.81	8.77	2.77	90	45	24.40	6.48
9	1.81	8.77	2.77	150	45	18.30	4.86
10	1.81	2.19	2.77	120	45	3.80	1.01
11	1.81	4.38	2.77	120	45	17.00	4.51
12	1.81	6.58	2.77	120	45	43.50	11.54
13	1.81	10.96	2.77	120	45	25.40	6.74
14	1.81	13.15	2.77	120	45	23.50	6.24
15	1.81	6.58	0.69	120	45	15.82	4.19
16	1.81	6.58	1.38	120	45	19.08	5.06
17	1.81	6.58	2.07	120	45	27.40	7.27
18	1.81	6.58	3.46	120	45	23.66	6.28
19	1.81	6.58	4.15	120	45	19.80	5.25
20	0.45	6.58	2.77	120	45	6.60	7.00
21	0.91	6.58	2.77	120	45	8.30	4.41
22	1.36	6.58	2.77	120	45	16.68	5.90
23	2.26	6.58	2.77	120	45	9.44	2.00
24	2.72	6.58	2.77	120	45	10.72	1.89

Effect of Reaction Temperature

The graft yield increases with the initial increase in temperature, reaches the optimum value at 45°C, and then decreases with further rise in temperature. The effect of reaction temperature on percent grafting of MMA onto *Agave americana* fiber has been represented in Figure 2.

The above behavior of variation of percent grafting with temperature can be attributed to fact that with the initial rise in temperature, as the kinetic energy of the molecules increases more and more radicals drifted at faster rate onto the backbone, resulting in the increase in graft yield. However, after reaching the optimum temperature, with further increase in temperature a considerable amount of homopolymer is formed, which results in increase in the viscosity of the reaction mixture. It provides a hindrance for the radicals to move towards the active sites of the polymeric backbone, resulting in the decrease in percent grafting.

Effect of Reaction Time

With the initial increase in time graft yield increases, reaches an optimum value at 120 min, and decreases with further increase in reaction time (Figure 3).

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 the increased graft yield. After reaching the optimum value with further increase in reaction time, most of the active sites on the backbone are occupied by the radicals and the formation of the homopolymer dominates the graft copolymerization. Also, viscosity of the reaction medium increases with time, which provides hindrance for radicals to move onto active sites of the backbone, resulting in the 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 the concentration of initiator increases, more and

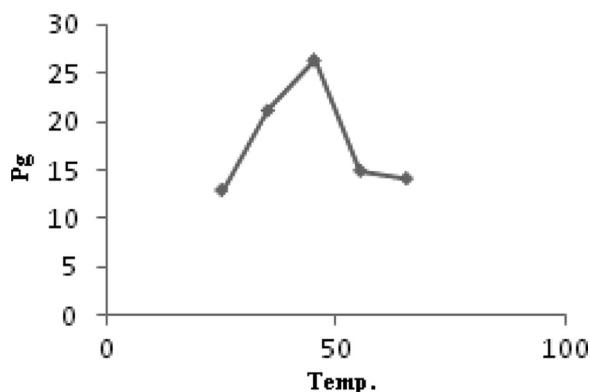


Figure 2. Effect of reaction temperature on percent grafting.

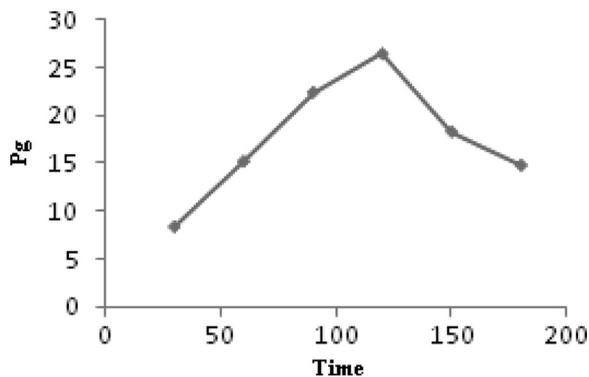


Figure 3. Effect of reaction time on percent grafting.

more radicals are generated, which results in the increase in graft yield. After reaching the optimum value, graft yield decreases with further increase in initiator concentration (Figure 4). It may be due to the fact that with further increase in the initiator concentration chain termination reactions dominate the graft copolymerization, which leads to premature decay of the monomer radicals.

Effect of Nitric Acid Concentration

In aqueous medium CAN exists as Ce^{4+} , $[\text{Ce}(\text{OH})]^{3+}$, and $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$ 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 the presence of HNO_3 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 the oxidation of the fiber. Moreover, increased concentration of

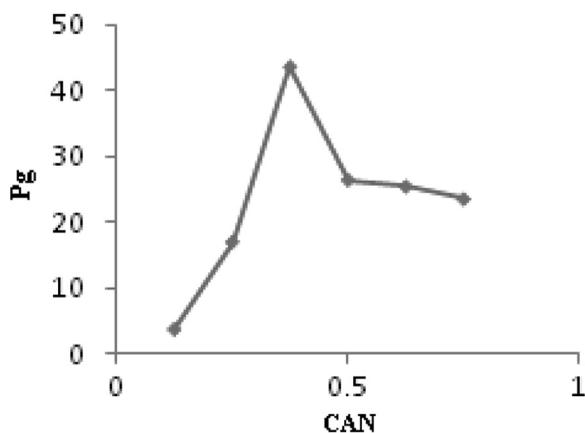


Figure 4. Effect of initiator concentration on percent grafting.

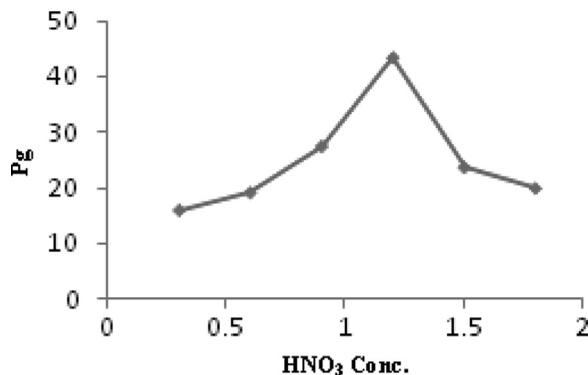
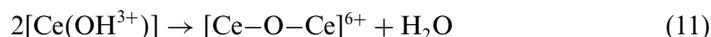
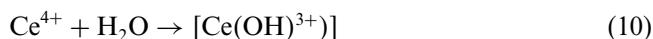


Figure 5. Effect of concentration of nitric acid on percent grafting.

nitric acid leads to early degeneration of the radicals (Figure 5).



Effect of Monomer Concentration

The graft yield increase with the initial increase in monomer concentration reaches the optimum value and then decreases with further increase in the monomer concentration (Figure 6). The above behavior of the 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 further increase in the monomer concentration, homopolymerization dominates over graft copolymerization, leading to decreased graft yield.

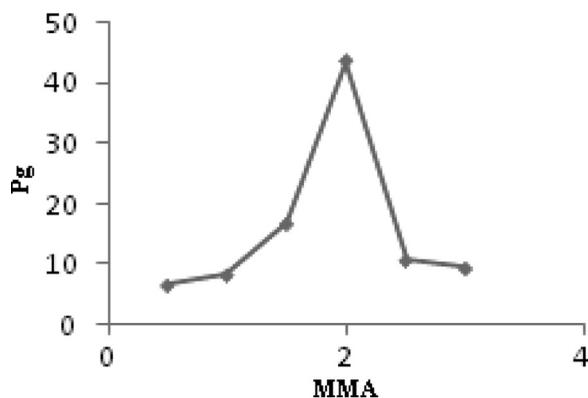


Figure 6. Effect of monomer concentration on percent grafting.

Swelling Behavior of Raw Fibers and Their Graft Copolymers

Raw and grafted fibers show different swelling behaviors in different solvents. The variation of percent swelling as a function of P_g for raw as well as for agave-g-poly (MMA) is shown in Figure 7. The swelling behavior of ungrafted fiber in different solvents follows the trend: $H_2O > CH_3OH > C_2H_5OH > CCl_4$. On the other hand, in the case of grafted fiber the percent swelling varies as a function of P_g according to the following trend: $CCl_4 > C_2H_5OH > H_2O > CH_3OH$.

The swelling behavior of raw fibers may be explained on the basis that in case of raw fibers due to the presence of $-OH$ groups, H_2O has more affinity for these groups, so that water can penetrate more easily and deeply into the fiber, resulting in maximum percent swelling. However, between CH_3OH and C_2H_5OH , raw fiber shows more swelling in methanol, which may probably be due to the presence of the bulkier $-C_2H_5$ group in ethanol providing hindrance to sorption.

In the case of grafted fibers, the active sites on the fiber surface are blocked by hydrophobic poly (MMA) chains, as a result of which water and methanol could not interact to the same extent as with raw fiber. Moreover, poly (MMA) chains on grafted fiber are more solvated by nonpolar solvents like CCl_4 ; hence, grafted fiber shows more percent swelling in CCl_4 .

Moisture Absorbance Behavior

The moisture absorbance behavior of raw as well as grafted fibers as a function of P_g at different humidity levels is represented in Figure 8. The percent of Mabs decreases with increase in graft yield, which can be due to the fact that on grafting, active sites on the fiber surface are blocked by poly (MMA) chains. As poly (MMA) chains are hydrophobic in nature, they have less affinity towards water, therefore the percent of Mabs decreases with increase in P_g . In the case of raw fiber, the percent of Mabs is maximum due to the presence of hydrophilic $-OH$ groups.

Moreover, for a particular value of P_g , the percent of Mabs increases with increase in humidity level. It may be due to the fact that with increase in the humidity level, moisture content increases, and more and more moisture is absorbed.

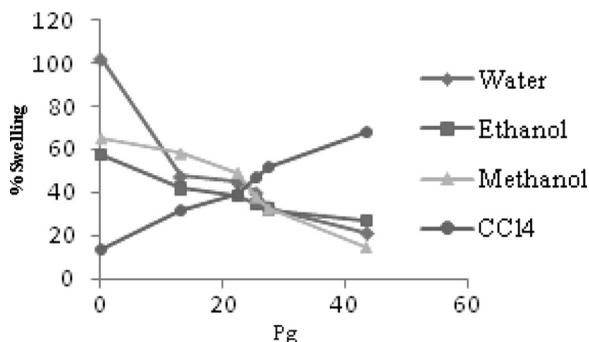


Figure 7. Effect of grafting on swelling behavior in different solvents.

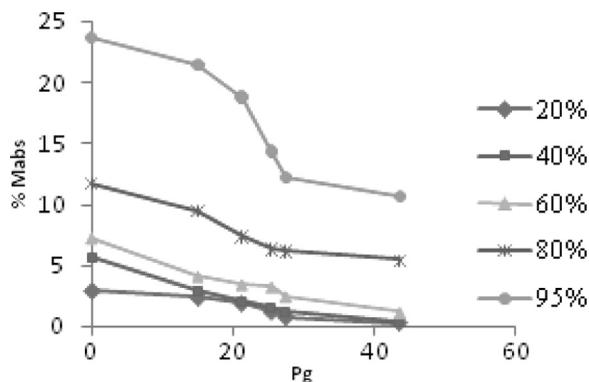


Figure 8. Effect of grafting on moisture absorbance behavior at different humidity levels.

Water Uptake Behavior

Water uptake studies of the raw and grafted fibers have been made by capillary action. It has been observed that water uptake decreases with increase in percent graft (Figure 9). This behavior of grafted fibers may be attributed to the hydrophobicity of poly (MMA) chains that are incorporated at active sites on the fiber surface as a result of graft copolymerization.

Chemical Resistance Studies

The chemical resistance of the raw as well of the grafted fibers has been studied in terms of percent weight loss. Chemical resistance of grafted fibers increases with increase in percent grafting (Figures 10 and 11). This behavior is observed due to the deactivation of the active sites on the polymer backbone by the poly (MMA) chains.

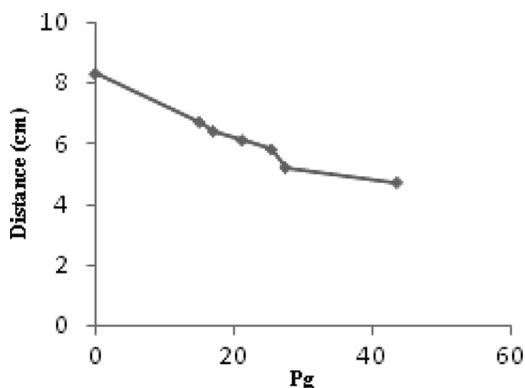


Figure 9. Effect of grafting on water uptake behavior.

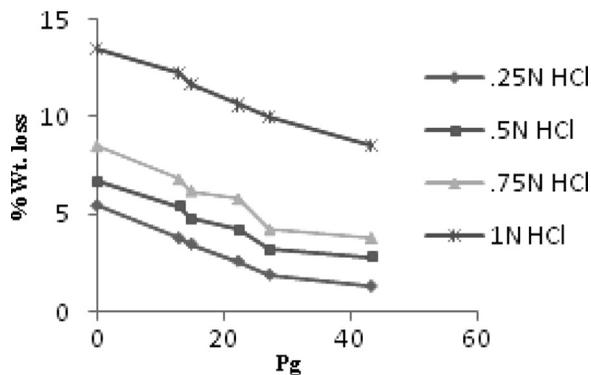


Figure 10. Effect of grafting on acid resistance behavior.

EVIDENCE OF GRAFTING

Characterization by FT-IR Spectroscopy

The FT-IR spectrum of raw the *Agave americana* fiber showed a broad peak at 3397.1 cm^{-1} due to bonded $-\text{OH}$ group and peaks at 2918.1 cm^{-1} , 1432 cm^{-1} , and 1054.9 cm^{-1} due to $-\text{CH}_2$, $\text{C}-\text{C}$, and $\text{C}-\text{O}$ stretching respectively. However, in the case of agave-g-poly (MMA) an additional peak at 1735.2 cm^{-1} was observed, which can be attributed to the carbonyl group ($>\text{C}=\text{O}$) of ester stretching vibrations. The above results suggest that MMA has been grafted onto the agave fiber through covalent bonds.

Characterization by Scanning Electron Microscopy

The scanning electron micrographs of raw fibers and agave-g-poly (MMA) show a clear distinction between ungrafted and grafted fibers (Figures 12–13), which is evidence for the change in morphology of the fiber surface on grafting.

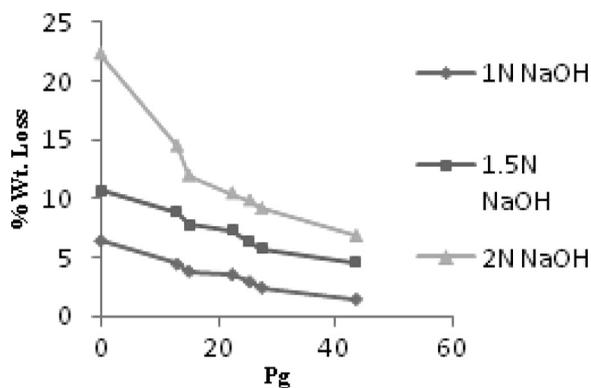


Figure 11. Effect of grafting on resistance to base.

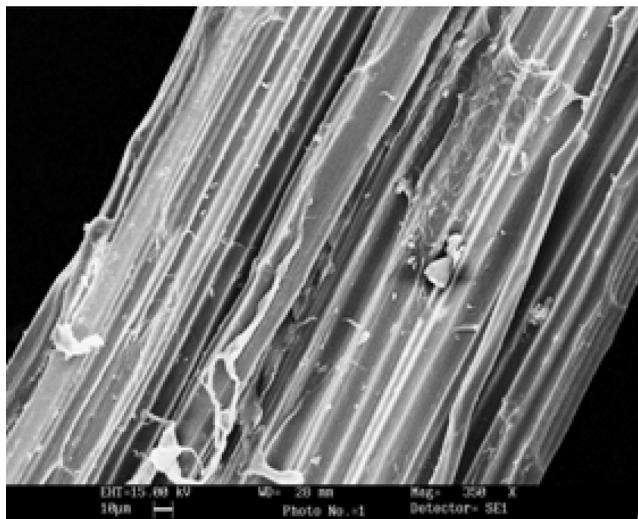


Figure 12. Scanning electron micrographs of raw fiber.

From the electron micrograph it is clear that surface of raw fiber is smoother than that of the grafted fiber. This difference is due to the deposition of poly (MMA) chains on the surface of raw fiber through graft copolymerization.^[22]

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 22.18° and 16.95° with relative intensities of 100.0 and 48.9

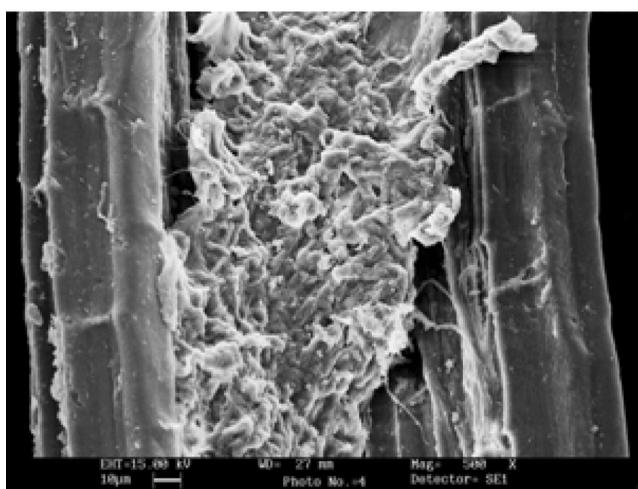


Figure 13. Scanning electron micrograph of agave-g-poly (MMA).

Table II. Percentage crystallinity and crystallinity index (C.I.) of raw fiber and agave-g-poly (MMA)

Sample	$I_{C22.03^\circ}$	$I_{A14.22^\circ}$	% Cr	C.I.
Raw fiber	97.6	46.1	67.92	0.53
Sample	$I_{C22.18^\circ}$	$I_{A16.95^\circ}$	% Cr	C.I.
Agave-g-poly (MMA)	100	48.9	67.16	0.51

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

respectively. Percent crystallinity of raw and grafted fibers is 67.92% and 67.16%, respectively, which shows that there is no significant change in the morphology of the fiber upon grafting. It may be due to the small amount of disturbance in the crystal lattice of raw fiber, due to the 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° and 346°C (50.6%) and 346° 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 may be attributed to breakdown of hemicellulose and glycosidic linkages of cellulose, and the second stage of decomposition may be related to the degradation of grafted poly (MMA) chains onto the fiber surface. In the case of a-g-poly (MMA), the initial and final decomposition temperatures are 280°C and 465°C respectively. From the above results it is clear that there has been 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 have been further supported by DTA evaluation. The exothermic peak at 439°C ($237.2\mu\text{v}$) in the case of raw fiber corresponds to the 346° to 432°C decomposition stage in the TGA curve. The sharp exothermic peak at 467°C ($109.9\mu\text{v}$) in the case of grafted fiber corresponds to 355° to 465°C

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

Sample	TGA					DTA	
	1st stage decomp. ($^\circ\text{C}$)	% Wt. loss	2nd stage decomp. ($^\circ\text{C}$)	% Wt. loss	Total % wt. loss	% Residue	Observed peaks in $^\circ\text{C}$ [μv]
Raw fiber	240–346	50.6	346–432	32.3	95.9	4.1	439 ($237.2\mu\text{v}$)
Agave-g-poly (MMA)	281–355	68.9	355–465	20.1	100	–	467 ($109.9\mu\text{v}$)

decomposition stage in the TGA curve and may be due to the combustion of poly (MMA) chains. The results of TGA/DTA studies are depicted in Table III.

CONCLUSION

The graft copolymerization of MMA onto *Agave americana* in air carried out in the present work has a significant effect on the physicochemical properties of agave fibers. The swelling behavior of grafted copolymers is in accordance with the affinity of different solvents towards poly (MMA) chains.

Upon graft copolymerization poly (MMA) chains are incorporated on the surface of fibers, therefore grafted fibers become more resistant to moisture absorbance and attack by chemicals. Agave-g-poly (MMA) shows good thermal stability as compared to raw fibers. There has been little decrease in the crystallinity of fibers on grafting.

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