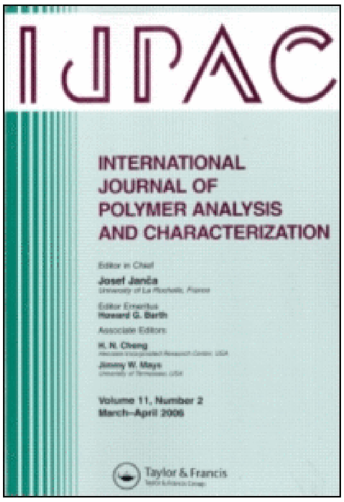

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

X-Ray Diffraction, Morphological, and Thermal Studies on Methylmethacrylate Graft Copolymerized *Saccharum ciliare* Fiber

Amar Singh Singha[a]; Anjali Shama[a]; Vijay Kumar Thakur[a]
[a] Applied Chemistry Research Laboratory, Department of Chemistry, National Institute of Technology Hamirpur, Himachal Pradesh, India

To cite this Article Singha, Amar Singh , Shama, Anjali and Thakur, Vijay Kumar(2008) 'X-Ray Diffraction, Morphological, and Thermal Studies on Methylmethacrylate Graft Copolymerized *Saccharum ciliare* Fiber', International Journal of Polymer Analysis and Characterization, 13: 6, 447 — 462

To link to this Article: DOI: 10.1080/10236660802399747

URL: http://dx.doi.org/10.1080/10236660802399747

International Journal of Polymer Anal. Charact., 13: 447–462, 2008

ISSN: 1023-666X print
DOI: 10.1080/10236660802399747

X-Ray Diffraction, Morphological, and Thermal Studies on Methylmethacrylate Graft Copolymerized *Saccharum ciliare* Fiber

Amar Singh Singha, Anjali Shama, and Vijay Kumar Thakur
Applied Chemistry Research Laboratory, Department of Chemistry, National
Institute of Technology Hamirpur, Himachal Pradesh, India

Abstract: This article deals with the study of graft copolymerization of methylmethacrylate (MMA) onto *Saccharum ciliare* fiber in air in the presence of ferrous ammonium sulfate-potassium persulfate (FAS-KPS) as redox initiator. After optimizing the various reaction parameters such as solvent, time, temperature, concentration of monomer, and initiator to obtain maximum graft yield (58%), the grafted fiber has been characterized by various techniques such as scanning electron microscopy (SEM), Fourier transform-infrared spectrophotometry (FT-IR), X-ray diffraction, and thermogravimetric/differential thermal analysis along with DTG studies. The raw fiber and graft copolymerized fibers were also subjected to evaluation of different physical and chemical properties.

Keywords: Ferrous ammonium sulfate-potassium persulfate; Graft copolymers; Methylmethacrylate; *Saccaharum ciliare*; Swelling behavior

INTRODUCTION

Natural fibers have received much attention during the past few years because of many inherent properties.[1–4] Various techniques are available for modification of natural fibers. Graft copolymerization is known to be

Submitted 7 July 2008; accepted 11 August 2008.

Correspondence: A. S. Singha, Applied Chemistry Research Laboratory, Department of Chemistry, National Institute of Technology Hamirpur–177005, Himachal Pradesh, India. E-mail: assingha@gmail.com

the most suitable method for incorporation of new and desired properties into fibers without affecting the basic properties of the polymeric backbone.[5–8] Acrylate monomers are known to polymerize with great ease in the presence of a wide variety of initiators and copolymerize with almost all types of vinyl monomers.[9–10] These graft copolymerized materials find a number of applications in various fields ranging from paint, adhesives, coating materials, and emulsifiers to molding materials and biomedical instrumentation. But the biggest application has been as compatibilizing agents in the manufacture of polymer blends. Various attempts have been made to incorporate new properties into natural fibers such as jute, wood, bamboo, sisal, cotton, coir, and wheat straw through graft copolymerization.[5–10] The grafting process depends on the reactivity of monomers used, the type of initiation, and cellulose accessibility.[11–15] Attempts have also been made to study the thermal degradation behavior and other properties of graft copolymers.[16–19]

Saccharum ciliare fiber collected from the higher reaches of Himalayan region has been found to contain 58.2% cellulose. A literature survey has revealed that not much study has been done on graft copolymerization of this naturally occurring fibrous material. It has been used by the rural population for making various low-cost articles such as socks, boots, mats, and bags. Since these materials have been found to be moisture sensitive, an attempt has been made to improve their water resistance by graft copolymerization with methyl methacrylate monomer. Subsequently the physicochemical properties of raw and grafted fibers such as swelling behavior, moisture absorbance, wetting power, and chemical resistance have been evaluated. Various techniques like TGA/DTA, DTG, XRD, FT-IR, and SEM have been used to characterize the grafted materials.

Among these techniques, X-ray diffraction (XRD) has been found to be a very important tool for studying the structural changes in graft copolymerized fiber as compared to raw fiber by calculating the degree of crystallinity. This technique gives a clear-cut distinction between amorphous and crystalline regions. Natural cellulosic materials, which show both amorphous and crystalline regions, undergo changes in structure when subjected to graft copolymerization with various vinyl monomers. The amount of crystallinity determines to a large extent the suitability of a polymeric material for a given application. Different polymers crystallize to different extents, and measuring the amount and anisotropy of ordering in polymer samples is a very important application of diffraction and scattering studies.

Cellulose is the most abundant renewable organic material from which various useful products can be derived and is the only natural polymer found under almost every conceivable environmental condition. Since cellulosic materials contain both crystalline and amorphous regions, it is evident that XRD pattern of such materials will show both the region in the form of sharp peaks and diffused patterns.[20] X-ray analysis has shown that cellulose is made up of several linear long chains (each containing about 3000 or more glucose units). These chains lie side by side to form bundles held together by hydrogen bonding between CH_2OH of one chain and C-OH group of the other chain. Cellulose is found in nature in the form of natural fibers such as flax, *Saccaharum ciliare*, *Hibiscus sabdariffa*, and *Grewia optiva*.

Thermal analysis of natural polymers gives us good account of thermal stability of the materials. In the case of cellulosic materials, there is a drastic change in their thermal behavior upon graft copolymerization. The thermal analysis comprises various methods such as thermogravimetric analysis (TGA)/differential thermal analysis (DTA), and derivative thermogravimetry (DTG). TGA is used to characterize the decomposition and thermal stability of materials under a variety of conditions and to examine the kinetics of the physicochemical processes occurring in the sample. Basically, in this method, a change in thermal stability is examined in terms of percentage weight loss as a function of temperature. The mass change characteristics of a material are strongly dependent on the experimental conditions such as sample mass, volume and physical form, the shape and nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber, and the scanning rate; all have important influences on the characteristics of the recorded TG curve. At the same time, DTA involves comparing the precise temperature difference between a sample and an inert reference material while heating both.

DTG is a type of thermal analysis in which the rate of material weight change upon heating versus temperature is plotted and is used to simplify reading of weight-versus-temperature thermogram peaks that occur close together. DTG peaks are characterized by the peak maximum (T_{max}) and the peak onset temperature (T_e). The area under the DTG curve is proportional to the mass change, and the height of the peak at any temperature gives the rate of the mass change at that temperature. DTG curves are frequently preferred when comparing results with DTA curves because of the visual similarity.

EXPERIMENTAL SECTION

Materials

Natural fiber *Saccharum ciliare*, prior to its use, was freed from lignin by chemical treatment.[5] Purification of methyl methacrylate (MMA) and ferrous ammonium sulfate (FAS) was done by the method reported earlier.[6] The potassium persulfate (KPS) was used as received.

Methods

Graft Copolymerization

The natural fiber *Saccaharum ciliare* fiber (0.5 g) was thoroughly washed and then immersed in a definite amount of distilled water for 24 h. A known amount of initiator (FAS-KPS) and monomer (MMA) was then added to the flask containing the fiber. The reaction mixture was then stirred at a fixed temperature for 120 min. Optimum conditions of solvent, time, temperature, initiator (FAS-KPS ratio), and monomer concentration were evaluated for maximum graft yield (Table I). The homopolymer formed during graft copolymerization was removed by extraction with acetone in a Soxhlet extraction apparatus for 48 h. The graft copolymer free from homopolymer was then dried in a hot air oven to a constant weight. The percentage grafting (P_g) and percent efficiency (P_e) were calculated as per the procedure reported earlier.[5–7]

Swelling, Moisture Absorbance, Chemical Resistance, and Water Uptake Studies

Swelling of grafted and ungrafted fibers was carried out in different solvents such as dimethyl formamide, water, methanol, and isobutyl alcohol as per the method reported earlier.[5–6] Moisture absorbance study at various humidity levels was carried out as per the method reported earlier.[5–6]

Water uptake capacity of grafted and ungrafted fibers was also studied by the method reported earlier.[6] Percent water uptake (P_w) was calculated as follows:

$$P_w = \frac{T_f - D}{T_f} \times 100$$

where T_f is total fiber length and D is the distance traveled by water in the fiber wicks.

The chemical resistance of grafted as well as ungrafted fibers towards acid and base in terms of percentage weight loss was studied as per the method reported earlier.[5–6]

The infrared spectra of raw fiber and grafted fiber were recorded on a PerkinElmer spectrometer.

Scanning Electron Micrographs (SEM)

SEMs of raw fiber and its graft copolymer were studied on a Leo 435 VP. On comparing the scanning electron micrographs of raw fiber and its

Table I. Evaluation of various reaction parameters for maximum graft copolymerization of MMA onto *S. ciliare* fiber

Exp. no.	Solvent (mL)	Monomer mol/L × 10^{-3}	FAS-KPS ratio	Time (min)	Temp.°C	P_g	P_e
1	50	4.9	1:1	120	35	13.6	2.08
2	75	4.9	1:1	120	35	25.0	3.82
3	100	4.9	1:1	120	35	28.7	4.39
4	125	4.9	1:1	120	35	38.4	5.87
5	150	4.9	1:1	120	35	31.7	4.85
6	125	4.9	1:1	30	35	21.4	3.28
7	125	4.9	1:1	60	35	41.0	6.27
8	125	4.9	1:1	90	35	47.0	7.19
9				120	35	38.4	5.88
10	125	4.9	1:1	150	35	37.5	5.74
11	125	4.9	1:1	180	35	35.0	5.36
12	125	4.9	1:1	90	15	13.3	0.20
13	125	4.9	1:1	90	25	23.1	3.54
14	125	4.9	1:1	90	35	47.0	7.19
15	125	4.9	1:1	90	45	03.0	.46
16	125	4.9	1:1	90	55	01.6	.24
17	125	4.9	0.125:1	90	35	13.3	2.04
18	125	4.9	0.250:1	90	35	19.0	2.91
19	125	4.9	0.5:1	90	35	41.6	6.37
20	125	4.9	1:1	90	35	47.0	7.19
21	125	4.9	1.250:1	90	35	30.3	4.64
22	125	4.9	1.50:1	90	35	29.6	4.53
23	125	4.9	1:1	90	35	15.3	2.34
24	125	4.9	1:1	90	35	47.0	7.19
25	125	4.9	1:1	90	35	44.0	6.73
26	125	4.9	1:1	90	35	10.5	1.61
27	125	4.9	1:1	90	35	13.0	.20
28	125	4.9	1:1	90	35	00.0	Nil
29	125	2.45	1:1	90	35	15.0	2.30
30	125	3.68	1:1	90	35	19.0	2.91
31		4.9	1:1	90	35	47.0	7.19
32	125	6.11	1:1	90	35	41.0	7.68
33	125	7.35	1:1	90	35	58.0	8.88
34	125	8.56	1:1	90	35	30.5	4.67

graft copolymers (Figures 1–3), it has been found that upon graft copolymerization, a considerable amount of monomer gets deposited onto the fiber backbone, which changes the morphology of the fiber.

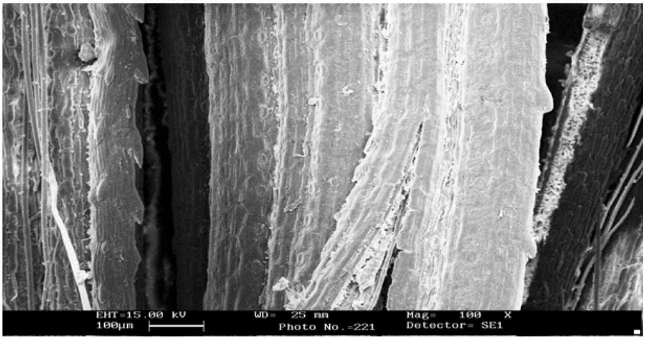

Figure 1. SEM of raw fiber.

Thermal Behavior

Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetry (DTG) studies were carried out in air on a thermal analyzer (PerkinElmer).

X-ray Diffraction Studies

X-ray diffraction analyses of samples were carried out on a Philips PW 1710 diffractometer using Cu as anode tube, radiation wavelength $\alpha 1$ 1.54060 Å and $\alpha 2$ 1.54439, Ni filter and scintillation counter as detector at 40 kV and 30 mA on rotation between 140 and 340 at 2θ scale in 1 s, and receiving slit 0.1 with diverging slit 10.

Graft copolymers of MMA and raw fiber of *S. ciliare* were converted into fine powder by grinding in a mortar. The sample was mixed properly before the X-ray diffraction studies. After passing the X-rays, the scattering angle of the diffracted X-rays with respect to the angle of the incident

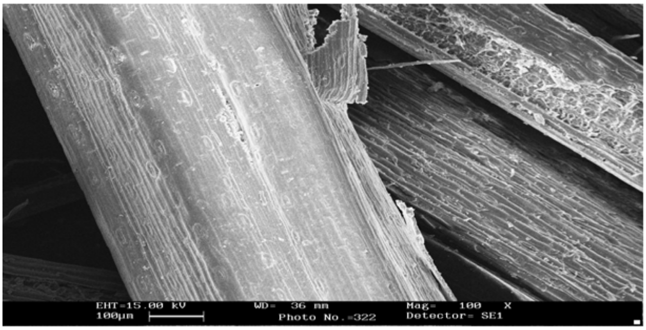

Figure 2. SEM of lignin-free fiber.

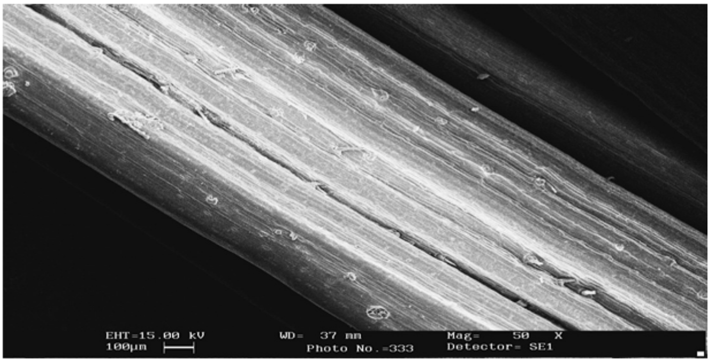

Figure 3. SEM of grafted fiber.

beam was measured and continuous scans with different d-spacing (Å) and relative intensity (I) of each sample were obtained. Percent degree of crystallinity was calculated by Segal's formula:[20]

$$D_\sigma = \frac{I_{22}}{I_{22} + I_{14}} \times 100$$

where I = relative intensity and D_{cr} = degree of crystallinity.

On comparing the X-ray diffraction studies of raw fiber and its graft copolymer, it has been found that upon graft copolymerization, degree of crystallinity decreases (Table II).

Evidence of Grafting

The IR spectra of raw *Saccharum ciliare* fiber showed a broad peak at $3370\,cm^{-1}$, which is due to bonded OH groups and at 2922.4, 1438, and $1043\,cm^{-1}$, which are due to $-CH_2$, C–C, and C–O stretching respectively. In the case of grafted fiber, an additional peak at $1735.6\,cm^{-1}$ was seen due to the presence of carbonyl group of vinyl monomer (MMA).

RESULTS AND DISCUSSION

It has been observed that polymeric materials containing cellulose, C_2, C_3, and C_6–OH groups, and C-H sites are the active centers for grafting of polymeric chains onto polymeric backbone.[5–7] Potassium persulfate takes part in the redox reaction with Fe^{2+}, as given below:

$$Fe^{2+} + {}^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \longrightarrow Fe_{3+} + SO_4^{2-} + SO_4^{-*}$$

Table II. X-ray diffraction studies on raw fiber and its graft copolymers

	2θ	14.860		23.195		
Exp. no.	Sample code (P_g)	d $\acute{\alpha}_1$ [A]°	I [%]	d $\acute{\alpha}_1$ [A]°	I [%]	D_{cr}
1	F_{raw}	5.9575	15.6	3.8374	98.5	67.5
2	F_{lig}	5.9868	16.2	3.8770	100.0	64.8
3	Cotton	5.9568	37.6	3.8317	100.0	67.6
4	Sc-3 (23.1%)	5.8859	34.5	3.8778	100.0	61.26
5	Sc-1 (38.4%)	5.3854	19.8	3.8612	100.0	58.74
6	Sc-4 (41.6%)	5.3747	20.2	3.8862	100.0	58.69
7	Sc-5 (44%)	6.0335	20	3.8820	100.0	57.53
8	Sc-2 (47%)	6.0030	28.6	3.8621	100.0	56.45
9	Sc-6 (58%)	6.0315	44.9	3.9005	100.0	54.17

d = d spacing, I = relative intensity, D_{cr} = degree of crystallinity, F_{raw} = raw fiber, and F_{lig} = lignin-free fiber.

Interaction of SO_4^{-*} with H_2O generates OH free radicals and these free radicals are responsible for carrying out graft copolymerization onto *S. ciliare* fiber.

Optimization of Different Reaction Parameters for Grafting of MMA onto *S. ciliare* Fiber

The optimization of various reaction parameters like amount of the solvent, reaction time, temperature, ratio of the initiator (FAS-KPS ratio), and concentration of the monomer was carried out for graft copolymerization of MMA onto *S. ciliare* fiber. The optimum conditions for maximum graft yield (58.0%) as given in Table I were: solvent, 125 mL; time, 90 min; temperature, 35°C; FAS: KPS, 1:1; and monomer, (7.35×10^{-3} mol/L).

Effect of Monomer, Solvent, Time, and Temperature on Grafting

As is evident from Figure 4, P_g increases with increase in monomer concentration, and after reaching the maximum P_g of 58%, further increase in MMA concentration results in decrease of graft yield. This may be due to the formation of more homopolymer as compared to graft copolymer at higher monomer concentration.

With further increase in amount of solvent (Figure 5), reaction time (Figure 6), and temperature (Figure 7), P_g was found to increase. The maximum grafting took place when 125 mL solvent was used. The

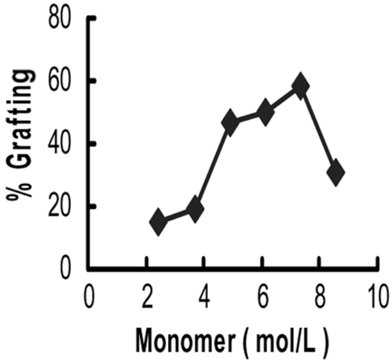

Figure 4. Variation of grafting with monomer concentration.

increase in solvent resulted in decreased graft yield, probably due to the dilution of reaction medium, which lowers the concentration of monomer radical per unit volume, and hence less grafting takes place.

The optimum reaction temperature and time has been found to be 35°C and 90 min respectively. With further increase in temperature and time, a decline in P_g has been observed due to the possible occurrence of various hydrogen abstraction reactions, along with some other side chain reactions as well as excessive homopolymerization.

Effect of Initiator

The optimum molar ratio for the maximum graft yield was found to be 1:1 (Figure 8). It has been observed that with further increase in molar ratio, $P_g$was found to decrease. This is probably due to formation of more Fe^{3+} ions at higher molar ratio, which results in the termination of growing chains.

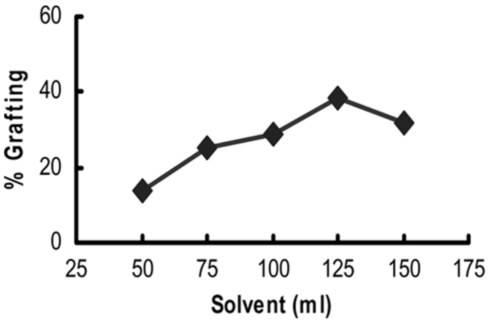

Figure 5. Variation of grafting with solvent.

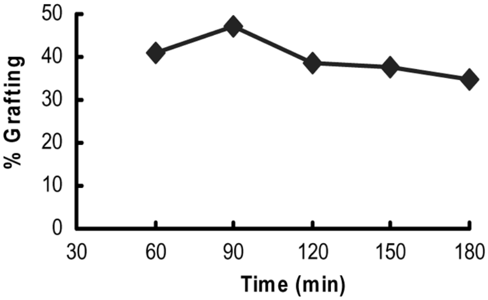

Figure 6. Variation of grafting with time.

Swelling, Moisture Absorbance, and Water Uptake Studies

Grafted and ungrafted fibers show different swelling behavior in different solvents (Table III). The swelling behavior of ungrafted fiber in different solvents follows the trend of $H_2O > CH_3OH >$ iso-BuOH $>$ dimethylformamide (DMF) due to greater affinity of water for OH groups present in the raw *S. ciliare* fiber, whereas in grafted fiber, it varies as a function of P_g and follows the trend DMF $> CH_3OH > H_2O >$ iso-BuOH. This reversal in swelling behavior may be due to blockage of active sites on the polymeric substrate by polymethylmethacrylate (PMMA) chains, which causes the change in the sorption of different solvents. Since PMMA chains on grafted fiber are more solvolyzed by dipolar aprotic solvents (DMF) than water or alcohol, more swelling took place in DMF than in other solvents.

Moisture absorbance behavior at different humidity levels as a function of P_g has been depicted in Table IV. It has been found that moisture absorbance (M_{abs}) decreases with the increase in P_g. The raw fiber shows more M_{abs} than grafted fibers. This behavior of grafted fibers

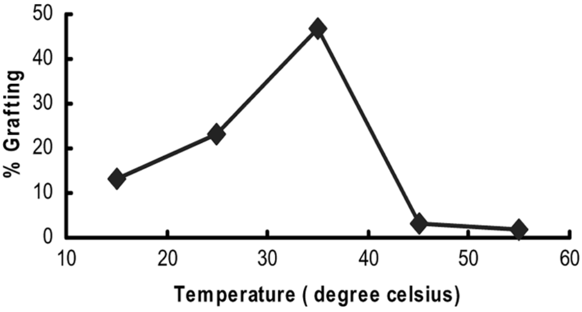

Figure 7. Variation of grafting with temperature.

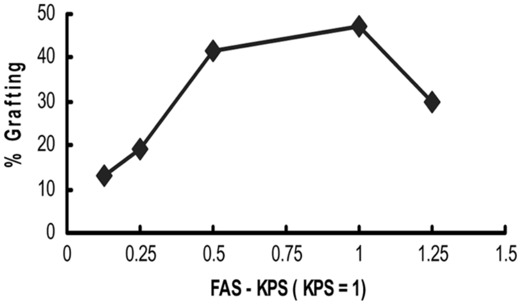

Figure 8. Variation of grafting with initiator ratio.

may be due to the attachment of PMMA chains grafted onto the fiber, which shows less affinity toward water.

Water uptake capacity of graft copolymers was found to decrease with increase in grafting (Table V). The explanation was already given above.

Chemical Resistance Studies

It has been observed that resistance towards chemicals increases with the increase in percent grafting (Tables VI and VII). This may be due to blockage of active sites vulnerable to the chemical attack by PMMA on the polymeric backbone resulting in more resistance towards the chemicals.

X-ray Diffraction Studies

From XRD studies, it has been observed that cotton on a 2θ scale showed peaks at 14.860, 16.865, 23.195, and 34.965 with relative intensity 37.6, 34.7, 100.0, and 10.4 respectively, and raw *S. ciliare* fiber showed peaks at 14.236 and 22.510 with relative intensity 15.6 and 98.5 respectively.

Table III. Effect of grafting on % swelling behavior of *S. ciliare* fiber in different solvents

	% Grafting						
Solvent	0	23.1	38.4	41.6	44	47	58
DMF	48	88	98	102	106	111	122
Water	160	71	60	55	50	44.5	34.2
Methanol	104	51.4	42.5	40	36.7	30	23
Isobutyl alcohol	86	44.6	32	30	26.3	21	15

Table IV. Effect of grafting on % moisture absorbance of *S. ciliare* fiber at different humidity levels

	% Grafting						
Humidity (%)	0	23.1	38.4	41.6	44	47	58
20	2.1	0.84	0.62	0.6	0.58	0.54	0.4
40	2.67	1.22	0.96	0.86	0.82	0.76	0.64
60	3.1	1.52	1.2	1.12	1.06	1	0.86
80	3.76	1.8	1.66	1.58	1.52	1.42	1.14
100	4.2	1.86	1.68	1.6	1.54	1.46	1.18

In lignin-free *S. ciliare* fiber, the peaks were observed at 14.785, 22.920, and 22.330 with relative intensity 16.2, 100, and 92.8. The graft copolymers of MMA showed peaks at 14.670, 22.890 (Sc-1), 14.745, 23.010 (Sc-2), 15.040, 22.915 (Sc-3), 14.303, 23.015 (Sc-4), 16.480, 22.865 (Sc-5), 14.675, and 22.780 (Sc-6) with relative intensity 19.8 and 100.0, 28.6 and 100.0, 34.5 and 100.0, 20.2 and 100.0, 20.0 and 100.0, 44.9 and 100.0 respectively. From the (Table II), it has been observed that grafted fiber and ungrafted fiber show different diffraction patterns and also with the increase in percent grafting degree of crystallinity has been found to decrease.

Since cellulosic materials contain both crystalline and amorphous regions, it is evident that XRD pattern of such materials will show both the region in the form of sharp peaks and diffused patterns. Percent degree of crystallinity was calculated by Segal's formula.[20] Further through graft copolymerization of cellulosic material with a vinyl monomer like MMA, decrease in crystallinity has been observed. This is evident from the results given in Table II, where ungrafted and grafted fibers show different diffraction patterns. It has been observed that degree of crystallinity of ungrafted fiber is reduced after graft copolymerization. The change is found to increase with increase in percent grafting.

Table V. Effect of grafting on % water uptake behavior of *S. ciliare* fiber

	% Grafting						
Time (h)	0	23.1	38.4	41.6	44	47	58
24	9.4	4.3	2.6	2.2	1.8	1.4	0.7
48	14	7.2	4.7	4	3.6	2.8	1
72	17.8	10	7.6	7	6.2	5.4	2.3
96	21	12.8	10.2	9.5	8.8	8	4.8
120	23	14.3	12.8	11.4	10.3	10.1	5.2

Table VI. Effect of grafting on chemical resistance (in terms of % wt. loss) of *S. ciliare* fiber against 1 N HCl

	% Grafting						
Time (h)	0	23.1	38.4	41.6	44	47	58
24	34	19.5	16.3	15	12.9	10.8	7.5
48	40.4	23.2	20	19	16.2	14.6	11
72	48	27	24	22.8	20	18	15
96	55.4	32	28.8	27.9	25	23	20
120	62	35.2	31.8	31	28.7	27.3	23.4

This change in diffraction pattern occurs due to the creation of disorder in the crystalline pattern of the main polymeric backbone by the grafted units of the PMMA chains.[7]

Thermal Studies

Thermogravimetric analysis (TGA) of raw fiber and grafted fibers revealed the percent weight loss with increase in temperature. In the case of raw fiber, in the beginning, the depolymerization, dehydration, and glucosan formation took place between the temperatures of 26.0° and 201.0°C followed by the cleavage of C-H, C-C, and C-O bonds. For raw fiber, the initial decomposition temperature (IDT) is 262°C and final decomposition temperature (FDT) has been found to be 461.0°C. On the other hand, in the case of grafted fiber, the process is a single-stage decomposition; the IDT is 270.0°C, and the final decomposition of the grafted fiber took place at 392.0°C with the total loss of crystalline structure. IDT, FDT, and decomposition temperature (DT) for every 10% weight loss are presented in Table VIII. The percent residue of grafted fiber left is 2.06%, while for *S. ciliare* fiber it is 5.52%.

Table VII. Effect of grafting on chemical resistance (in terms of % wt. loss) of *S. ciliare* fiber against 1 N NaOH

	% Grafting						
Time (h)	0	23.1	38.4	41.6	44	47	58
24	42.8	32.8	26.5	25.2	23.6	22.2	17
48	53.6	42.5	36.4	35	33	31.8	26.9
72	61	49	44.2	43.3	39.4	37.4	32.6
96	72	58.5	53.5	49.7	48	46	39.2
120	78	62.7	57.4	52.5	52.7	51	43.1

Table VIIIa. Thermogravimetric analysis of *Saccharum ciliare* raw fiber and its grafted fiber

Sample	Primary reactions (°C)	% Wt loss	IDT (°C)	% Wt loss	FDT (°C)	% Wt loss	Final residue (%)
Poly-g-MMA	26.0 – 200.0	95.12	270.0	88.0	392.0	3.0	2.06
Raw fiber	26.0 – 201.0	90.69	262.0	86.0	461.0	6.0	5.52

Table VIIIb. Data on decomposition temperature after every 10% weight loss of *Saccharum ciliare* fiber and poly-g-MMA

Sample	IDT (°C)	FDT (°C)	DT (°C	DT (°C	DT (°C)	DT (°C)	DT (°C)	DT (°C)	DT (°C)	DT (°C)	DT (°C)	DT (°C)
			10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
Raw fiber	262.0	461.0	10	222	275	292	305	319	337	375	420	439
Poly-g-MMA	270.0	392.0	40	242	284	302	320	344	350	362	380	396

As shown in Table IX, DTA of raw fiber shows exothermic peaks at 328.0°C (81.0 μV) and 433.0°C (203 μV), and there was continuous exothermic combustion of the sample at the furnace temperature in the presence of atmospheric oxygen, which indicates the complete breakdown of C–C and C–O bonds of the crystalline region with total evolution of −6882 mJ/mg of energy (ΔH = −ve).

In the case of graft copolymer, a continuous exothermic rise in temperature was observed. An exothermic peak is observed at 381.0°C (271 μV), which shows the loss of amorphous and crystalline structure of grafted fiber in the presence of atmospheric air, with total evolution of −4369 mJ/mg of energy (ΔH = −ve).

Further DTG studies also show that the grafted sample exhibits double decomposition behavior. The first peak is observed at 351°C with maximum decomposition of 3.102 mg/min. Similarly, second peak is

Table IX. Differential thermal analysis of raw *S. ciliare* fiber and its graft copolymer

Exp. no.	Sample	Exothermic peak at temperature (μV)
1	Raw fiber	328.0 (81); 433.0 (203)
2	Poly-g-MMA	381.0 (271)

Table X. DTG data on raw *S. ciliare* fiber and its graft copolymer

Exp. no.	Sample	Exothermic peak at temperature (mg/min)
1	Raw fiber	313.0 (.732); 429.0 (1.159)
2	Poly-g-MMA	351 (3.102); 381 (0.83)

observed at 381°C with maximum decomposition of 0.83 mg/min; in the case of raw fiber, the first peak is observed at 313°C with maximum decomposition of 0.732 mg/min and the second peak is observed at 429.0°C with maximum decomposition of 1.159 mg/min (Table X).

CONCLUSIONS

It has been observed that upon grafting, the properties of raw fiber like swelling behavior, water resistance, chemical resistance and water uptake, etc. have been found to improve to a greater extent. X-Ray diffraction and thermal studies have revealed that the crystallinity as well as thermal stability of the fiber decreases with the increase in grafting.

REFERENCES

[1] Singha, A. S., and V. K. Thakur. (2008). Mechanical properties of natural fiber reinforced polymer composites. *Bull. Mater. Sci.* **31**(5), 791–99.

[2] Singha, A. S., and V. K. Thakur. (2008). *Saccaharum cilliare* fiber reinforced polymer composites. *E-Journal Chem.* **5**(4), 782–791. Available at http://www.e-journals.in/open/vol5/No4/0860-782-791.pdf

[3] Singha, A. S., and V. K. Thakur. (2008). Synthesis and characterization of Grewia Optiva fiber reinforced PF matrix based polymer composites. *Int. J. Polym. Mater.* **57**(12), 1059–74.

[4] Singha, A. S., and V. K. Thakur. (2008). Fabrication of *Hibiscus Sabdariffa* fibre reinforced polymer composites. **17**(7), 541–553. Available at http://journal.ippi.ac.ir/manuscripts/IPJ-2008-07-3225.pdf

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

[6] Singha, A. S., A. Shama, and B. N. Misra. (2008). Pressure induced graft co- polymerization of binary vinyl monomer mixtures onto Saccharum Cilliare fiber and evaluation of some physical, chemical and thermal properties. *J. Polym. Mater*. **25**(1), 91–99.

[7] Chauhan, G. S., I. Kaur, B. N. Misra, A. S. Singha, and B. S. Kaith. (2000). Evaluation of optimum grafting parameters and the effect of ceric ion

initiated grafting of methyl methacrylate onto jute fiber on the kinetics of thermal degradation and swelling behaviour. *Polym. Degradation Stab.* **69**, 261–265.

[8] Kaith, B. S., A. S. Singha, S. Kumar, and S. Kalia. (2008). Mercerization of flax fiber improves the mechanical properties of fiber reinforced composites. *Int. J. Polym. Mater.* **57**(1), 54–72.

[9] Imoto, M., K. Takemoto, H. Azuma, N. Kita, and M. Kondo. (1967). Vinyl polymerization. 170: Grafting of some acrylate and methacrylate onto cellulose and silk in absence of radical initiators. *Makromol. Chem.* **107**, 188–195.

[10] Okieimen, F. E., and D. Ogbeifun. (1996). Graft copolymerization of modified cellulose: Grafting of methyl acrylate, ethyl acrylate and ethyl methacrylate on carboxy methyl cellulose. *Eur. Polym. J.* **32**, 311–315.

[11] Singha, A. S., S. Kumar, and B. S. Kaith. (2005). Preparation of flax-graft co-polymer reinforced phenol formaldehyde composites and evaluation of their physical and mechanical properties. *Int. J. Plast. Technol.* **9**, 427–435.

[12] Kaith, B. S., A. S. Singha, S. Kumar, and B. N. Misra. (2005). FAS-H_2O_2 initiated graft co-polymerization of methyl methacrylate onto flax and evaluation of some physical and chemical properties. *J. Polym. Mater.* **22**, 425–432.

[13] Singha, A. S., and A. Shama. (2007). Pressure induced graft-co-polymerization of methyl methacrylate onto Saccharum Cilliare fiber and evaluation of physico-chemical and thermal. *Int. J. Chem. Sci.* **5**(3), 1404–1416.

[14] Singha, A. S., B. S. Kaith, and B. D. Sarwade. (2002). Modification of flax fiber through graft co-polymerization with methyl methacrylate and evaluation of swelling, moisture absorbance and thermal behavior. *Hung. J. Ind. Chem.* **30**, 289–293.

[15] Ali, F., C. N. Saikia, and S. R. Sen. (1997). Grafting of acrylonitrile onto high a-cellulose extracted from Hibiscus Sabdariffa. *Ind. Crops Prod.* **6**, 121–129.

[16] Abdel-Razik, E. A. (1994). Homogeneous grafting of dichlorodimethylsilane onto ethyl cellulose. *Eur. Polym. J.* **30**, 313–317.

[17] Kaith, B. S., and S. Kalia. 2007. Synthesis and characterization of graft co-polymers of flax fiber with binary vinyl monomers. Int. *J. Polym. Anal. Charact.* **12**, 401–412.

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

[19] Bhattacharya, A., and B. N. Misra. (2004). Grafting: A versatile means to modify polymers: Techniques, factors and applications. *Prog. Polym. Sci.* **29**, 767–814.

[20] Segal, L. C., A. E. Martin, and C. M. Conrad. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Tex. Res. J.* **29**, 786–794.