

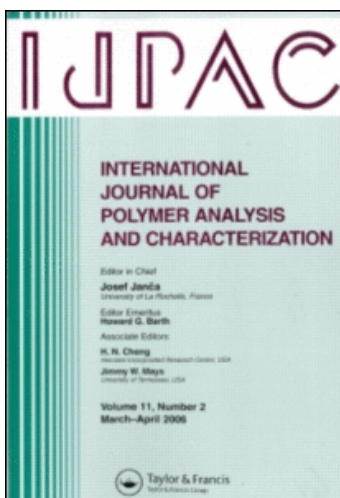
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Graft Copolymerization of Methylmethacrylate onto Acetylated *Saccharum spontaneum* L. Using FAS-KPS as a Redox Initiator and Evaluation of Physical, Chemical, and Thermal Properties

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Abstract: The present work deals with morphological modifications and physicochemical properties of acetylated *Saccharum spontaneum* L. through graft copolymerization with methyl methacrylate (MMA) using ferrous ammonium sulfate-potassium persulfate (FAS-KPS) redox initiator. Different reaction parameters such as reaction temperature, time, initiator molar ratio, monomer concentration, pH, and solvent were optimized to get maximum graft yield (152%). The acetylated *S. spontaneum* L. and its graft copolymer were characterized by FT-IR, SEM, XRD, TGA, DTA, and DTG techniques. Acetylated *S. spontaneum* L. and its graft copolymer have been found to show higher moisture and chemical resistance.

Keywords: Acetylated *Saccharum spontaneum* L.; Chemical resistance; Graft copolymer; Methyl methacrylate; Moisture absorbance

INTRODUCTION

Graft copolymers of natural fibers and their derivatives have advantages over the conventional copolymers due to radiation stability, low

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cost of preparation, low density, and greatest abundance in nature.^[1] However, natural fibers have been found to face problems like moisture sensitivity and low chemical resistance. Cellulose consists of interconnected anhydroglucose units, each of which contains three hydroxyl groups. The properties of cellulose, such as its solubility in different solvents, can be modified through converting the hydroxyl groups to other functionalities. Usually, this can be done either by esterification or by etherification. Graft copolymerization of vinyl monomer onto polymeric materials, including cellulose and cellulosic derivatives, has been studied worldwide.^[2-9] Ali et al.^[10] prepared high α -cellulose from a fast-growing annual plant, *Hibiscus sabdariffa*, and grafting was carried out with acrylonitrile (AN) onto it. Karlsson and Gatenholm^[11] have prepared cellulose fiber-supported hydrogels of hydroxyethyl methacrylate (HEMA) using ozone-induced graft copolymerization. Abdel-Razik^[12] reported the homogeneous grafting of dichloro dimethyl silane onto ethyl cellulose. During the grafting of acrylates and methacrylates onto cellulose and silk in the absence of radical initiator, it was found that polymerization of methacrylates proceeded more easily than that of acrylates and grafting was much higher onto silk than cellulose.^[13] Introduction of acetyl groups by acetylation onto cellulose reduced the bond strength between cellulose molecules and resulted in increased swelling,^[14,15] thereby leading to increased rate of graft copolymerization.

The present work deals with graft copolymerization of MMA onto acetylated *S. spontaneum* fiber using FAS-KPS redox initiator and study of its different physicochemical and thermal properties.

EXPERIMENTAL SECTION

Materials

S. spontaneum L. fiber was purified by refluxing in acetone for 72 h in Soxhlet. Methyl methacrylate (MMA, S.D. Fine-Chem) was purified by washing with 5% NaOH and subsequent drying over anhydrous Na₂SO₄ followed by distillation. Ferrous ammonium sulfate (FAS, S.D. Fine-Chem) was recrystallized from hot water and potassium persulfate (KPS, S.D. Fine-Chem) was used as received. Analytical grade acetic anhydride, acetic acid, and perchloric acid (E-Merck) were used as received.

Methods

Acetylation of *S. spontaneum* L. Fiber

Acetylation of *S. spontaneum* L. fiber was carried out as per the standard method.^[16]

Graft Copolymerization

Acetylated *S. spontaneum* L. fiber (0.5 g) was activated by immersion in 100 mL of distilled water for 24 h prior to carrying out graft copolymerization. A definite ratio of KPS-FAS and a known amount of monomer were added to the reaction flask and the reaction was carried out at a definite temperature for a specific time interval. Homopolymer was extracted with acetone, and the graft copolymer thus obtained was dried at 50°C until a constant weight was attained. Percentage polymer loading (% PL), percentage grafting yield (% GY), percentage graft efficiency (% GE), and percentage homopolymer (% HM) formed (Table I) were calculated as^[17]:

$$\text{Percent polymer loading (\% PL)} = \frac{(W_2 - W_1)}{W_1} \times 100$$

where W_1 and W_2 are the initial and final weight of the sample (before homopolymer extraction).

$$\text{Percent grafting yield (\% GY)} = \frac{W_3 - W_1}{W_1} \times 100$$

The quantity of the grafted polymer is evaluated as the weight increase of the sample (W_3) after extraction of the homopolymer.

$$\text{Percent graft efficiency (\% GE)} = \frac{(W_3 - W_1)}{(W_2 - W_1)} \times 100$$

Percent graft efficiency is the ratio of the quantity of grafted monomer to the total polymerized monomer.

$$\text{Percent homopolymer (\% HM)} = 100 - (\% \text{ GE})$$

Infrared Spectroscopy (IR)

IR spectra were recorded with a Perkin Elmer Fourier transform-infrared (FT-IR) spectrophotometer using KBr pellets.

Table I. Evaluation of optimum reaction parameter for grafting of MMA onto acetylated *S. spontaneum*

No.	Reaction time (min)	Reaction temp. (°C)	pH	Solvent (mL)	Molar ratio (FAS:KPS)	[MMA] $\times 10^{-3}$ mol/L	% PL	% GY	% GE	% HM
1	60	45	7.0	100	1:1	2.45	180.4	80.2	44.4	55.6
2	90	45	7.0	100	1:1	2.45	206.4	99.6	48.2	51.8
3	120	45	7.0	100	1:1	2.45	208.2	65	31.2	68.8
4	150	45	7.0	100	1:1	2.45	198.4	55.6	28	72
5	180	45	7.0	100	1:1	2.45	192.4	42.1	21.8	78.2
6	90	30	7.0	100	1:1	2.45	190.4	59.2	31	69
7	90	35	7.0	100	1:1	2.45	202.0	82.1	40.6	59.4
8	90	40	7.0	100	1:1	2.45	228.4	100.2	43.8	56.2
9	90	45	7.0	100	1:1	2.45	200.6	87.6	43.6	56.4
10	90	50	7.0	100	1:1	2.45	198.4	62.6	31.5	68.5
11	90	55	7.0	100	1:1	2.45	196.2	51	25.9	74.1
12	90	40	2.0	100	1:1	2.45	182.4	47	25.7	74.3
13	90	40	4.0	100	1:1	2.45	160.4	65	40.5	59.5
14	90	40	7.0	100	1:1	2.45	216.4	102.4	47.3	52.7
15	90	40	8.0	100	1:1	2.45	198.6	68	34.2	65.8
16	90	40	9.0	100	1:1	2.45	190.4	47.2	24.7	75.3

(Continued)

Table I. Continued

No.	Reaction time (min)	Reaction temp. (°C)	pH	Solvent (mL)	Molar ratio (FAS:KPS)	[MMA] $\times 10^{-3}$ mol/L	% PL	% GY	% GE	% HM
17	90	40	7.0	50	1:1	2.45	182.4	75	41.1	58.9
18	90	40	7.0	75	1:1	2.45	204.2	86	42.1	57.9
19	90	40	7.0	100	1:1	2.45	220.2	101.1	45.9	54.1
20	90	40	7.0	125	1:1	2.45	236.2	135.6	57.4	42.6
21	90	40	7.0	150	1:1	2.45	199.2	89.2	44.7	55.3
22	90	40	7.0	175	1:1	2.45	195	75	38.4	61.6
23	90	40	7.0	125	1:0.5	2.45	168.4	30	17.8	82.2
24	90	40	7.0	125	1:0.75	2.45	242	139	57.4	42.6
25	90	40	7.0	125	1:1	2.45	224.2	96.1	42.8	57.2
26	90	40	7.0	125	1:1.25	2.45	186.4	67.4	36.1	63.9
27	90	40	7.0	125	1:1.50	2.45	184.2	52.1	28.2	71.8
28	90	40	7.0	125	1:0.75	1.47	146.2	39.7	26.9	73.1
29	90	40	7.0	125	1:0.75	1.96	168.2	59.5	35.5	64.7
30	90	40	7.0	125	1:0.75	2.45	184.6	102.4	55.4	44.6
31	90	40	7.0	125	1:0.75	2.94	222.4	152.6	68.6	31.4
32	90	40	7.0	125	1:0.75	3.43	204.2	78.7	38.5	61.5

% PL = percentage polymer loading, % GY = percentage grafting, % GE = percentage graft efficiency, % HM = percentage homopolymer.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) results were obtained using a JEOL JSM-6100 scanning electron microscope.

X-Ray Diffraction (XRD) Studies

X-ray diffraction studies were performed on an X-ray diffractometer (X'pert Pro-PAN-Analyzer) under ambient conditions using Cu K α (1.5418 Å) radiation, *N*-filter, and scintillation counter detector at 45 KV and 35 mA on rotation between 5 and 40° (2θ scale) at 1 s step size and increment of 0.01° with 0.5 or 1.0 mm of divergent and anti-scattering slit.

Thermogravimetric Analysis/Differential Thermal Analysis/Differential Thermogravimetric Analysis (TGA/DTA/DTG)

Thermogravimetric analysis, differential thermal analysis, and differential thermogravimetric analysis were carried out in air on a thermal analyzer (Perkin Elmer, Pyris Diamond).

Moisture Absorbance Study

Moisture absorbance studies at various relative humidities were carried out as per the standard method.^[18] Percent moisture absorbance was found by placing a known weight (W_i) of dry grafted and ungrafted acetylated samples in a humidity chamber for about two hours, and the final weight (W_f) of the samples exposed to a specific RH was taken and calculated as:

$$\% \text{ moisture absorbance (\% Mabs)} = [(W_f - W_i)/W_i] \times 100$$

Acid and Base Resistance

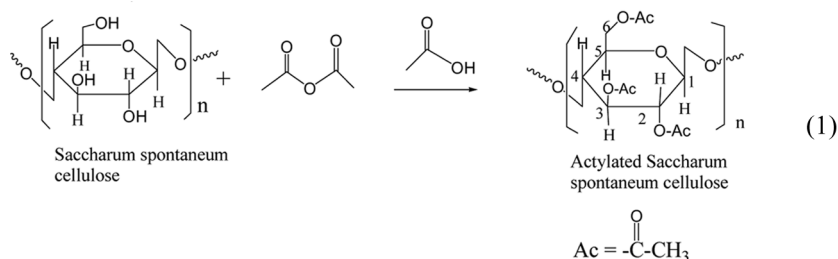
Acid and base resistance studies were carried out as per the method reported earlier.^[18] Acid and base resistance was found by placing a known weight (W_i) in a fixed volume of 5N HCl and 5N NaOH and the weight of the sample was noted at 12 h intervals until a constant final weight (W_f) was reached and was calculated as:

$$\% \text{ weight loss} = [(W_i - W_f)/W_i] \times 100$$

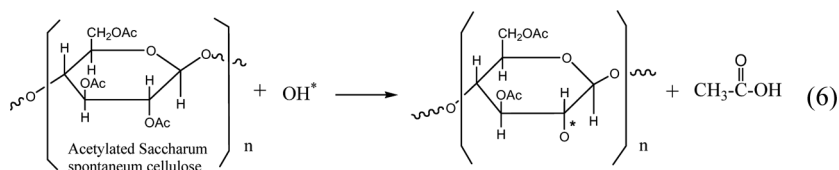
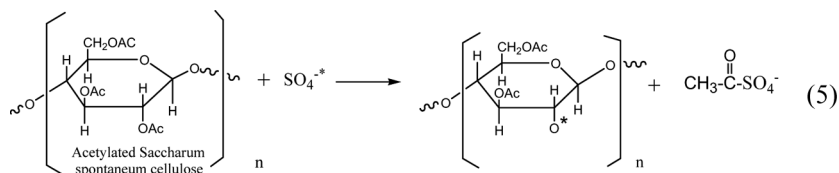
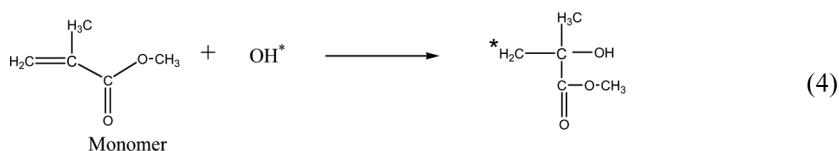
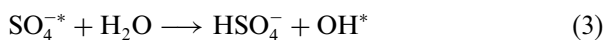
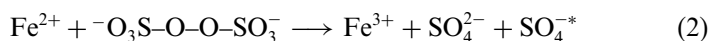
RESULTS AND DISCUSSION

Mechanism

C_2 , C_3 , and C_6 hydroxyls of *S. spontaneum* L. (Equation (1)) were acetylated using the standard method.^[16]



C_2 , C_3 , and C_6 esters and C-H groups are the active sites for the incorporation of polymeric chains through grafting onto acetylated *S. spontaneum*. Reaction of Fe^{2+} with KPS (Equation (2)) generated $\text{SO}_4^{\cdot -}$ ions. Interaction of $\text{SO}_4^{\cdot -}$ with H_2O generated OH^{\cdot} (Equation (3)), which are responsible for further chain propagation (Equations (4)–(9)), thereby resulting in the formation of graft copolymer (Equation (10)) along with homopolymer (Equation (12)) and can be explained through the following mechanism:



On the basis of this mechanism it can be concluded that both $\text{SO}_4^{\cdot-}$ and OH^{\cdot} are involved in graft copolymerization. However, in the case of grafting carried out in the absence of swelling agent, the initiation of the reaction by $\text{SO}_4^{\cdot-}$ (Equation (5)) is unlikely to occur as the concentration of persulfate used is very small, whereas in the presence of swelling agent, $\text{SO}_4^{\cdot-}$ reacts with H_2O to generate OH^{\cdot} (Equation (3)) and initiates the grafting through abstraction of acetyl group from the backbone polymer, resulting in the formation of a macro-radical on acetylated *S. spontaneum* backbone (Equation (6)). Similarly, OH^{\cdot} radicals react with monomer molecules, resulting in monomer free radicals sites (Equation (4)) and give rise to an active homopolymer (Equation (7)). Moreover, the reaction between active backbone and active homopolymer resulted in graft copolymer (Equation (10)). The termination of grafting may occur by either process (Equation (10)) or (Equation (11)) or both. The presence of Fe^{3+} has great impact on graft yield as it is involved in the termination of growing chains. Because Fe^{3+} was produced by the reaction between FAS with KPS (Equation (2)), the relative amounts of KPS and FAS in the initiating system played an important role in graft yield. An increase in Fe^{3+} ion concentration attacked the growing graft copolymer chains, thereby resulting in termination of the reaction with reduction of Fe^{3+} to Fe^{2+} (Equation (11)). The reactions between growing MMA chains also resulted in the termination of reaction and formation of the homopolymer (Equation (12)). Hence, the concentrations of initiator and monomer, variations of time, temperature, pH, and volume of the solvent affect the graft yield, as these factors determine the relative population of various radical species generated in different steps during the course of the reaction.

Optimization of Different Reaction Parameters

Effect of Reaction Temperature

Reaction temperature has been found to play an important role in getting maximum graft yield (Table I). The effect of temperature was studied in the temperature range from 25° to 55°C. It was found that an increase in temperature beyond 40°C resulted in decreased graft yield. It could be due to the fact that the reaction at temperatures beyond 40°C occurred with poor selectivity. Under such conditions, various hydrogen abstraction and other chain transfer reactions might be accelerated and thus lead to a decrease in % GY. The decrease in % GY at higher temperatures may also be due to loss of water-soluble constituents of acetylated backbone and also due to excessive homopolymerization.

Effect of Reaction Time

% GY has been found to increase gradually with increase in reaction time and was found to be maximum at 90 min (Table I). This could be explained by the fact that with increased reaction time, the interaction of OH^* and SO_4^{*-} with acetylated *S. spontaneum* backbone and MMA resulted in more extensive generation of free radical sites, thereby leading to more % GY. However, a decrease in % GY beyond optimum reaction time could be due to predominance of homopolymerization over graft copolymerization and disintegration of grafted poly(MMA) chains from grafted backbone.

Effect of pH of Reaction Medium

The pH of the the reaction medium plays an important role during the grafting process. Maximum graft yield has been found at pH 7.0 (Table I). Further decrease or increase in pH resulted in a decreased graft yield. This could be due to premature termination of the polymerization with increase in pH.

Effect of Solvent

It is evident from Table I that graft yield increased with increase in volume of the solvent and maximum % GY was found at 125 mL. However, further increase in solvent volume resulted in decrease of percentage grafting. This generally occurs on the setting up of various hydrogen abstraction reactions. This could also be due to a decreased SO_4^{*-} and OH^* free radical concentration.

Effect of Molar Ratio of Initiator

Graft yield was found to be affected by FAS-KPS molar ratio (Table I). Initially % GY was found to increase with increase in molar ratio, but after reaching critical ratio further increase in molar ratio resulted in decreased graft yield. This could be due to the fact that at the beginning, the Fe^{2+} ions get oxidized to Fe^{3+} , resulting in generation of more and more SO_4^{*-} ions (Equation (3)). However, further increase in Fe^{2+} ion concentration resulted in more generation of Fe^{3+} ions, which terminate the grafting process with reduction to Fe^{2+} , and a decreased graft yield was observed.

Effect of Monomer Concentration

Table I shows that with an increase in concentration of MMA, % GY increased continuously and reached maximum value (152%) at 2.94×10^{-3} mol/L. However, further increase in monomer concentration resulted in decreased % GY. This behavior could be explained by the fact that an increase in monomer concentration leads to the accumulation of monomer free radicals in a close proximity to the backbone and gives rise to graft copolymerization. This leads to depletion in the available MMA concentration as well as reduction in the active sites on the backbone as graft copolymerization proceeds. However, at higher monomer concentration, the primary radicals attack the monomer instead of reacting with the backbone, thereby, initiating homopolymerization reaction and resulting in low graft yield.

Characterization of Graft Copolymers

FT-IR Spectroscopy

S. spontaneum L. fiber showed broad peaks at 3390.6cm^{-1} due to hydrogen bonded ($-\text{OH}$), a peak at 2921.7cm^{-1} due to C-H stretching and at 1436cm^{-1} and 1052.7cm^{-1} arising from C-C and C-O stretching respectively (Figure 1). The introduction of acetyl moiety in the acetylated *S. spontaneum* L. fiber was confirmed by this spectral analysis.

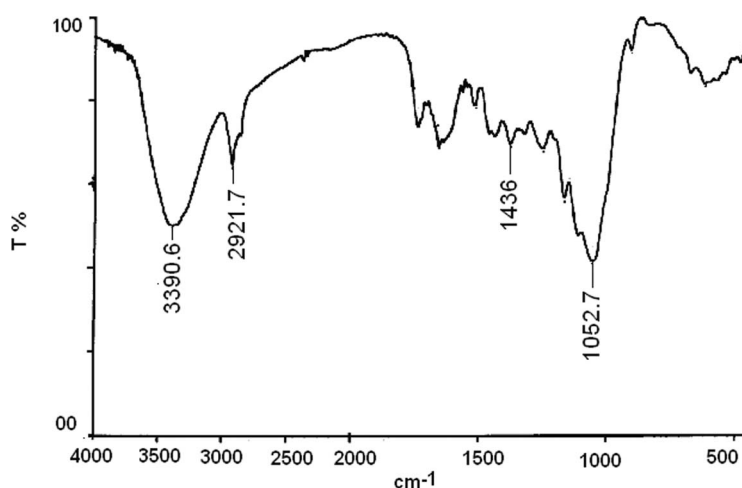


Figure 1. IR spectra of *S. spontaneum* fiber.

A comparison of the spectrum of *S. spontaneum* L. fiber and acetylated *S. spontaneum* L. fiber clearly indicated the introduction of acetyl moiety through a peak at 1751.6cm^{-1} due to C=O and the intensity of the broad peak due to hydrogen bonded -OH was found to decrease (Figure 2). On grafting, the IR bands due to characteristic functional groups incorporated into acetylated *S. Spontaneum* L. were seen apart from the previously listed bands of MMA: 1738.8cm^{-1} due to C=O of MMA (Figure 3).

Scanning Electron Microscopy (SEM)

It is quite evident from Figures 4–6 that a clear morphological distinction exists between the SEMs of grafted, acetylated, and raw *S. spontaneum* samples.

XRD Studies

Crystallinity index (C.I.), which measures the orientation of the cellulose crystals with respect to fiber axis, was determined by using the wide-angle X-ray diffraction counts at 2θ scale close to 22° and 18° . The counter reading at the peak intensity at 22° represents the crystalline part and the peak intensity at 18° corresponds to the amorphous region in cellulose material.^[19] Percentage crystallinity (% Cr) and C.I. were calculated as follows^[20–22]:

$$\% \text{ Cr} = [I_{22}/(I_{22} + I_{18})] \times 100$$

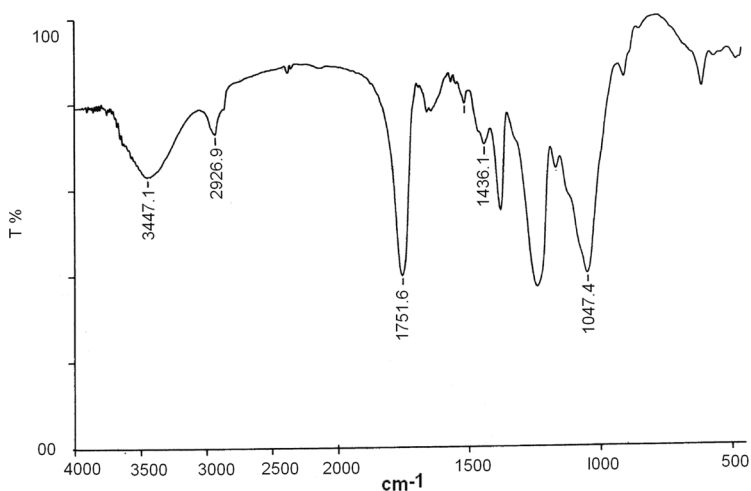


Figure 2. IR spectra of acetylated *S. spontaneum* fiber.

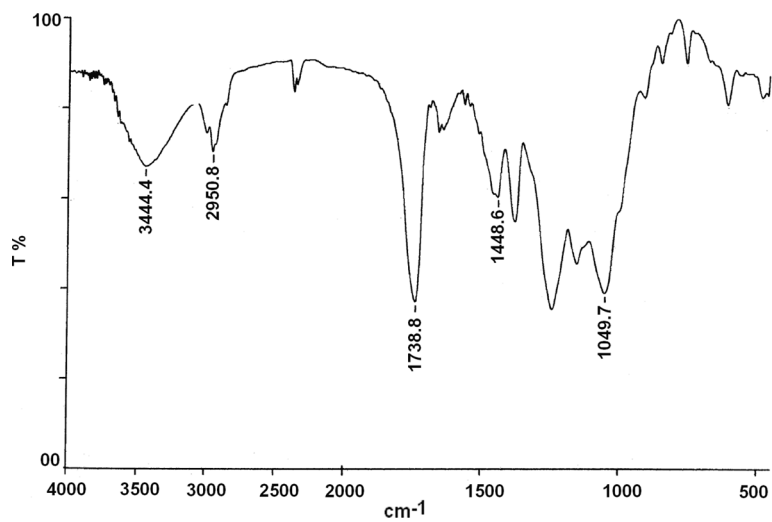


Figure 3. IR spectra of Ss-g-poly(MMA).

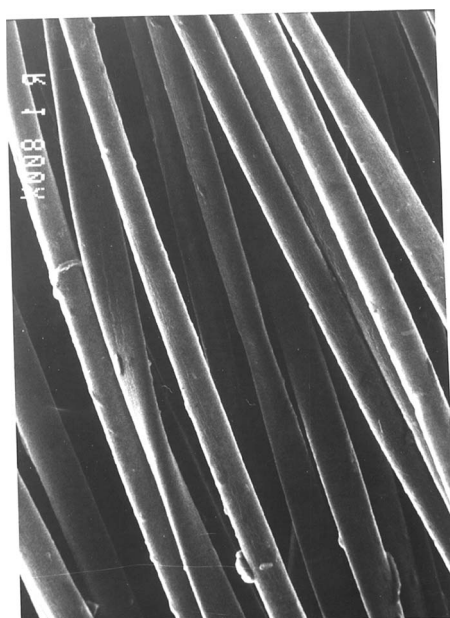


Figure 4. Scanning electron micrograph of *S. spontaneum* fiber.

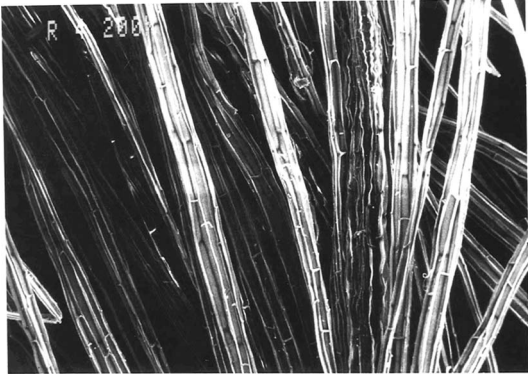


Figure 5. Scanning electron micrograph of acetylated *S. spontaneum* fiber.

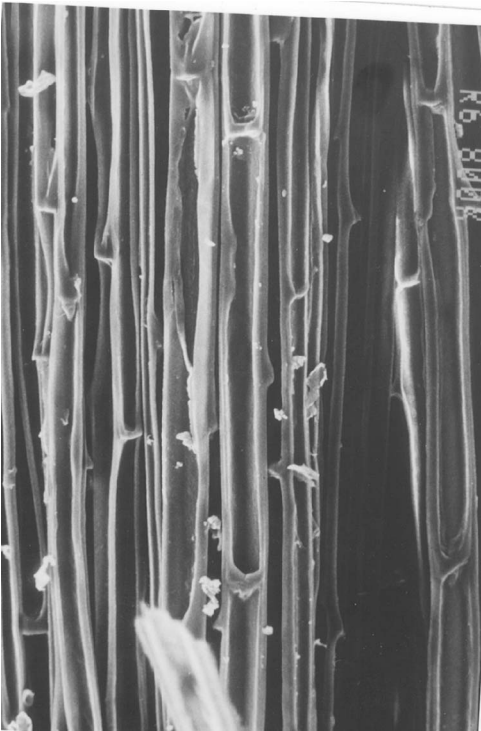


Figure 6. Scanning electron micrograph of Ss-g-poly(MMA).

Table II. Percentage crystallinity (% Cr) and crystallinity index (C.I.) of *S. spontaneum* and graft copolymers

Sample	% GY	2 θ scale		% Cr	C.I.
		I_{22}	I_{18}		
Ss-1	—	436	75	85.32	0.82
Ss-2	—	400	75	84.21	0.81
Ss-3	52.1	298	80	78.83	0.73
Ss-4	82.1	274	80	77.40	0.70
Ss-5	135.6	165	78	67.90	0.52
Ss-6	152.6	141	79	64.09	0.43

Ss-1, raw fiber; Ss-2, acetylated fiber; Ss-3, Ss-4, Ss-5, Ss-6, grafted fibers.

$$\text{C.I.} = [(I_{22} - I_{18})/I_{22}]$$

where I_{22} and I_{18} are the crystalline and amorphous intensities at 2θ scale close to 22° and 18° , respectively.

As is evident from Table II, the percentage crystallinity and crystallinity index were found lower in acetylated *S. spontaneum* fiber than in the raw fiber. Moreover, an increase in percentage grafting resulted in further decrease in % Cr and C.I. Since the incorporation of acetyl group and monomer moiety in the backbone impairs the natural crystallinity of the fiber, graft copolymerization of MMA onto acetylated *S. spontaneum* fiber resulted in impaired crystallinity and increased amorphous region of the fiber (Figure 7). Thus with increase in percentage grafting, the percentage crystallinity and crystallinity index decreased along with the reduction in stiffness and hardness.

TGA, DTA, and DTG Analysis of Ungrafted, Acetylated, and Grafted *S. spontaneum*

TGA of ungrafted, acetylated, and grafted *S. spontaneum* was studied as a function of percentage of weight loss versus temperature. Cellulosic *S. spontaneum* degrades by dehydration, glycogen formation, and depolymerization. In the case of *S. spontaneum*, two-stage decompositions were found in the temperature range from $225^\circ\text{--}320^\circ\text{C}$ with 60% weight loss and $320^\circ\text{--}416^\circ\text{C}$ with 25.33% weight loss. The former stage was attributed to loss by dehydration and volatilization processes, whereas the later stage was attributed to loss by depolymerization process. In the case of acetylated *S. spontaneum*, two-stage decompositions were also found in the temperature range from $250^\circ\text{--}325^\circ\text{C}$ with 48.90% weight loss and from 325° to 500°C with 36.61% weight loss.

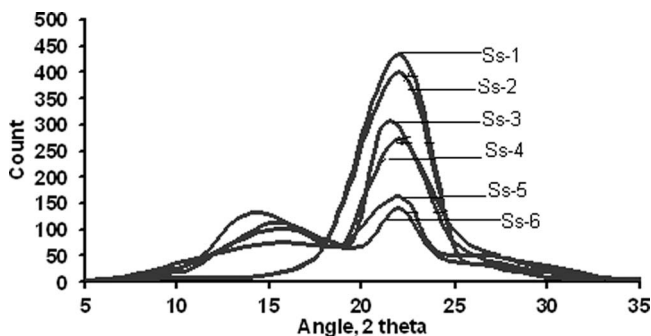


Figure 7. X-ray diffraction studies.

Ss-g-poly(MMA) showed single-stage decomposition. After the initial loss of moisture, the decomposition continued beyond 250°–499°C with 88.95% weight loss. Thus it was evident from the TGA data that grafted and acetylated fibers were thermally more stable than raw fibers. This might be due to the incorporation of poly(MMA) chains and acetyl group on backbone polymer through covalent bonding.

In the case of DTA studies, *S. spontaneum* was found to exhibit two exothermic peaks at 313°C (−1507 mJ/mg) and 422°C (−1233 mJ/mg). The exothermic peak at 313°C corresponds to decomposition stage between 225° and 320°C, while the exothermic peak at 422°C corresponds to the second decomposition stage (320°–416°C) in TGA (Figure 8). However, the acetylated fiber showed broad exothermic decomposition at 337°–452°C (−2706 mJ/mg) (Figure 9), and Ss-g-poly(MMA) exhibited the exothermic decomposition at 359°C (−723 mJ/mg). In the case of Ss-g-poly(MMA), the exothermic peak arising at 359°C corresponds to the thermal decomposition taking place in the temperature range from 250° to 499°C in TGA (Figure 10).

DTG analysis of grafted, acetylated, and ungrafted *S. spontaneum* was made as a function of rate of weight loss (mg/min) versus temperature. In the case of *S. spontaneum*, the decompositions at 303°C and 413°C were found with 1.575 mg/min and 1.411 mg/min weight loss, respectively. However, in the case of acetylated fiber, the decomposition at 307°C and 450°C occurred with 1.056 mg/min and 0.224 mg/min weight loss, and in Ss-g-poly(MMA), the decomposition was observed at 353°C with 1.023 mg/min weight loss, respectively. Thus it could be concluded from the DTG studies that the rate of thermal decomposition was higher in the case of *S. spontaneum* fiber than for acetylated and grafted fibers. Better thermal resistance of the acetylated and graft

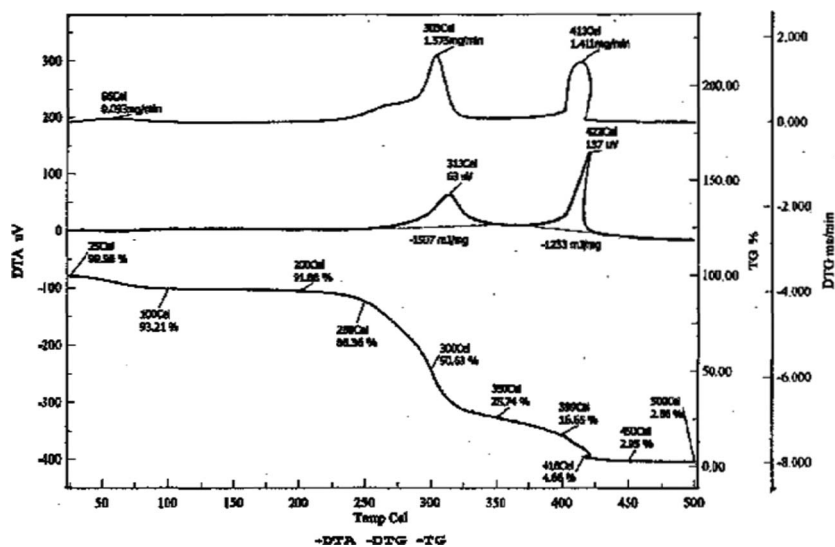


Figure 8. TGA, DTA, and DTG curves of *S. spontaneum* fiber.

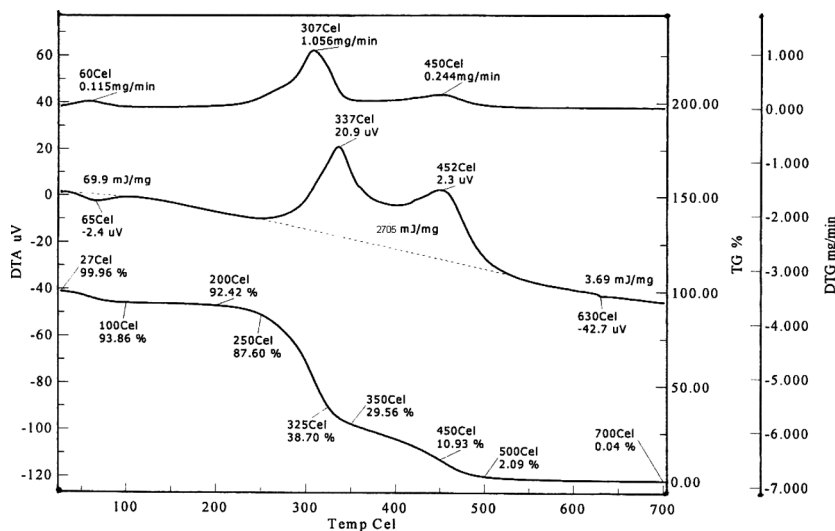


Figure 9. TGA, DTA, and DTG curves of acetylated *S. spontaneum* fiber.

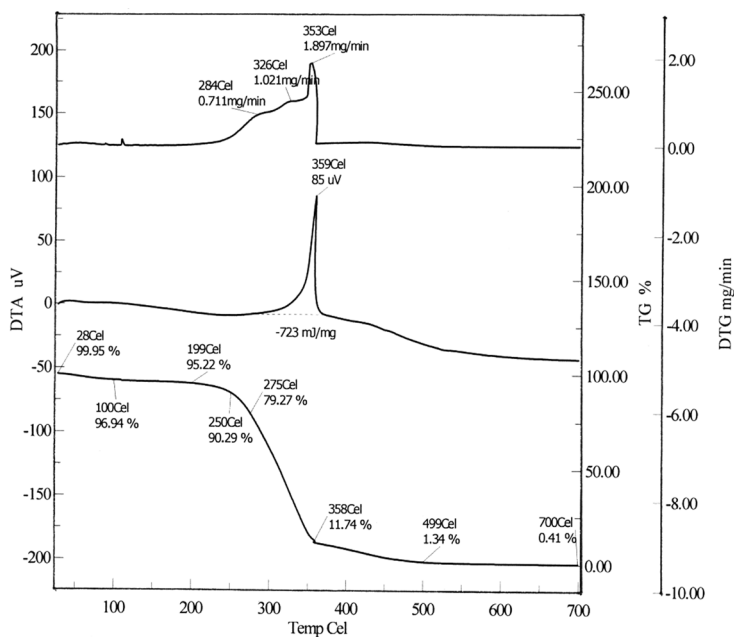


Figure 10. TGA, DTA, and DTG curves of Ss-g-poly (MMA).

copolymers was due to the incorporation of more covalent bonding through inclusion of acetyl and poly(MMA) chains onto the polymer backbone (Figures 8–10).

Moisture Absorbance Study

It was found that graft copolymerization of MMA onto *S. spontaneum* has a great impact on the moisture absorbance behavior (Figure 11). With increase in graft yield, moisture absorbance has been found to decrease. This could be due to the fact that the sites vulnerable for moisture absorbance get blocked with hydrophobic poly(MMA) chains on grafting, thereby changing the fiber to be less sensitive towards moisture.

Acid and Base Resistance Study

It was observed that acid and base resistance of the fiber increased with increase in percent grafting (Figures 12 and 13). This is due to the fact that poly(MMA) chains grafted onto *S. spontaneum* fiber have less affinity for acid and base than for hydroxyl and other functional groups present in ungrafted fiber. Therefore, the resistance of fiber towards acid

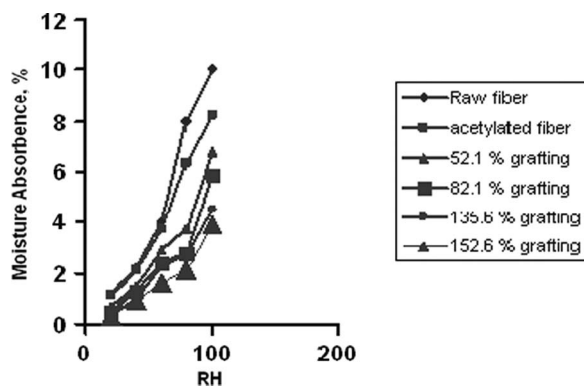


Figure 11. Effect of grafting on moisture absorbance at different humidity levels.

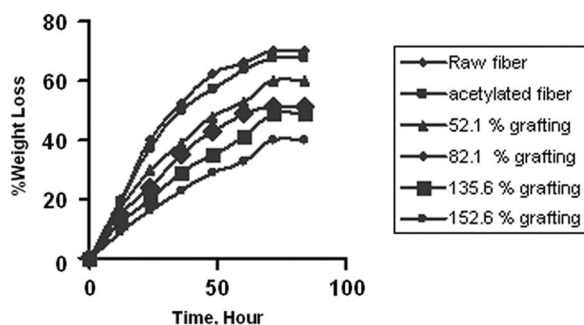


Figure 12. Effect of grafting on acid resistance.

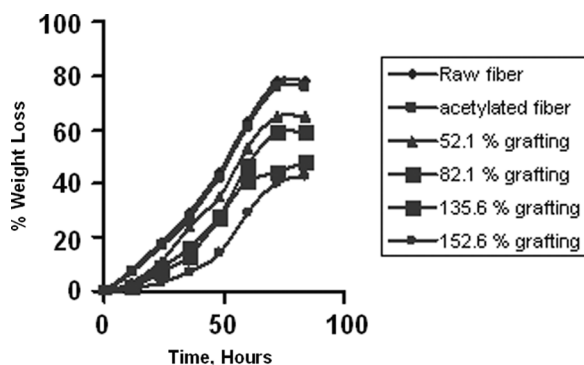


Figure 13. Effect of grafting on base resistance.

and base increased with increase in incorporation of poly(MMA) chains onto the backbone.

CONCLUSION

Grafting of MMA onto *S. spontaneum* L. fiber in the presence of FAS-KPS as redox initiator has been found to have physicochemical as well as morphological impact. Different reaction parameters like reaction time, temperature, pH, volume of solvent, initiator, and monomer concentration had great influence on graft copolymerization. With increase in grafting, percentage crystallinity and crystallinity index decreased, but the incorporation of poly(MMA) chains onto the backbone polymer could result in higher moisture, acid, base, and thermal resistance. Moreover, on grafting, the morphological changes with respect to surface topography have taken place and graft copolymer has been found to exhibit different physical and chemical properties than raw fiber.

REFERENCES

- [1] Joshi, J. M., and V. K. Sinha. (2006). Graft copolymerization of 2-hydroxyethylmethacrylate onto carboxymethyl chitosan using CAN as an initiator. *Polymer* **47**, 2198–2204.
- [2] Li, Z., P. Li, and J. Huang. (2006). Synthesis and characterization of amphiphilic graft copolymer poly(ethylene oxide)-graft-poly(methyl acrylate). *Polymer* **47**, 5791–5798.
- [3] Peng, D., X. Zhang, C. Feng, G. Lu, S. Zhang, and X. Huang. (2007). Synthesis and characterization of amphiphilic graft copolymers with hydrophilic poly(acrylic acid) backbone and hydrophobic poly(methyl methacrylate) side chains. *Polymer* **48**, 5250–5258.
- [4] Leena, N., S. Holappa, H. Mikkonen, and S. Jukka. (2004). Controlled grafting of acetylated starch by atom transfer radical polymerization of MMA. *Eur. Polym. J.* **43**, 372–1382.
- [5] Dai, I., W. DaZhen, Z. Zhang, and Y. Qiang. (2003). Preparation of monodisperse poly(methyl methacrylate) particles by radiation-induced dispersion polymerization using vinyl terminus polysiloxane macromonomer as a polymerizable stabilizer. *Polymer* **44**, 73–77.
- [6] Chen, H. J., X. H. Shi, Y. F. Zhu, Y. Zhang, and J. R. Xu. (2003). Polypropylene surface modification by entrapment of polypropylene-graft-poly(butyl methacrylate). *Appl. Surf. Sci.* **254**, 2521–2527.
- [7] Elizalde-Peña, E. A., N. Flores-Ramirez, G. Luna-Barcenas, S. R. Vásquez-Garcia, G. Arámbula-Villa, B. Garcia-Gaitaán, J. G. Rutiaga-Quiñones, and J. González-Hernández. (2007). Synthesis and characterization of chitosan-g-glycidyl methacrylate with methyl methacrylate. *Eur. Polym. J.* **43**(9), 3963–3972.

- [8] Margutti, S., S. Vicini, N. Proietti, D. Capitani, G. Conio, E. Pedemonte, and A. L. Segre. (2002). Physical–chemical characterisation of acrylic polymers grafted on cellulose. *Polymer* **43**(23), 6183–6194.
- [9] Shen, D., and Y. Huang. (2004). The synthesis of CDA-g-PMMA copolymers through atom transfer radical polymerization. *Polymer* **45**, 7091–7097.
- [10] Ali, F., C. N. Saikia, and S. R. Sen. (1997). Grafting of acrylonitrile onto high α -cellulose extracted from *Hibiscus sabdariffa*. *Ind. Crops Prod.* **6**(2), 121–129.
- [11] Karlsson, J. O., and P. Gatenholm. (1997). Preparation and characterization of cellulose-supported HEMA hydrogels. *Polymer* **38**, 4727–4731.
- [12] Abdel-Razik, E. A. (1994). Homogeneous grafting of dichlorodimethylsilane onto ethyl cellulose. *Eur. Polym. J.* **30**, 313–317.
- [13] Imoto, M., K. Takemoto, H. Azuma, N. Kita, and M. Kondo. (1967). Vinyl polymerization. 170: Grafting of some acrylates and methacrylates onto cellulose and silk in absence of radical initiators. *Makromol. Chem.* **107**, 188–195.
- [14] Nurmi, N., S. Holappa, H. Mikkonen, and J. Seppala. (2007). Controlled grafting of acetylated starch by atom transfer radical polymerization of MMA. *Eur. Polym. J.* **43**, 1372–1382.
- [15] Sodhi, N. S., and N. Singh. (2004). Characteristics of acetylated starches prepared using starches separated from different rice cultivars. *J. Food Eng.* **70**, 117–127.
- [16] Furniss, B. S., A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell. (2004). *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., 465. Singapore: Pearson Education Pte. Ltd.
- [17] Princi, E., S. Vicini, E. Pedemonte, A. Mulas, E. Franceschi, G. Luciano, and V. Trefiletti. (2005). Thermal analysis and characterisation of cellulose grafted with acrylic monomers. *Thermochim. Acta* **425**, 173–179.
- [18] Kaith, B. S., A. S. Singha, and S. K. Gupta (2003). Graft copolymerization of flax fibres with binary vinyl monomer mixtures and evaluation of swelling, moisture absorbance and thermal behaviour of the grafted fibres. *J. Polym. Mater.* **20**(2), 195–199.
- [19] 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.
- [20] Agrawal, A. M., R. V. Manek, W. M. Kolling, and S. H. Neau. (2003). Studies on the interaction of water with ethylcellulose: Effect of polymer particle size. *AAPS PharmSciTech* **4**, article 60.
- [21] Reddy, N., and Y. Yang. (2005). Structure and properties of high quality natural cellulose fibers from cornstalks. *Polymer* **46**, 5494–5500.
- [22] 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.