Induction of Chemical and Moisture Resistance in *Saccharum spontaneum* L Fiber Through Graft Copolymerization with Methyl Methacrylate and Study of Morphological Changes

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ABSTRACT: In this article, morphological modification of *Saccharum spontaneum* L, a natural fiber through graft copolymerization with methylmethacrylate using ferrous ammonium sulfate—potassium per sulfate redox initiator has been reported. Different reaction parameters such as reaction temperature, time, initiator molar ratio, monomer concentration, pH and solvent were optimized to get maximum graft yield (144%). The graft copolymers thus formed were characterized by Fourier transform infrared, scanning electron microscopy, X-ray diffraction and thermogravimetric, differential thermal analysis, and differential thermogravimetric techniques. Graft copolymer has been found to be more moisture resistant and also showed higher chemical and thermal resistance. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1781–1791, 2009

Key words: *Saccharum spontaneum-graft*-polymethylmethacrylate; chemical resistance; moisture absorbance

INTRODUCTION

During last three to four decades, natural fibers have been studied widely for graft copolymerization with different vinyl monomers in order to get the better end uses. Natural fibers have been found to be moisture sensitive and have least chemical resistance. Graft copolymerization is the simplest tool in the hands of chemists to improve upon the properties of natural fibers. Modification of cellulosic fibers through graft copolymerization provides a significant root to alter the physical and chemical properties of the fibers. As natural fibers are the most abundant organic moieties in nature and are renewable resources, various workers have carried out graft copolymerization onto different cellulosic backbones, using vinyl monomers through various chemical and radiation techniques.[1–10]

Misra and coworkers have extensively studied the modification of natural fibers such as wool[11,12] and gelatin.[13,14] Moreover they also studied the modification of synthetic backbones like poly (vinyl alcohol)[15,16] rayon, and polyamide-6.[17] Different workers have successfully introduced desired physical and chemical properties in the backbones. The field of potential applications could be enlarged by choosing various types of side chains. In recent years, a large number of initiators such as ceric ammonium nitrate,[18] potassium per sulfate (KPS),[19] and ammonium per sulfate (APS)[20] have been developed to initiate the graft copolymerization with increased graft yield under different reaction condition.

Graft copolymerization of methylmethacrylate (MMA) onto different backbones such as poly (butyl acrylate),[21] polymethyl acrylate,[22] acrylic acid, polyvinylidene fluoride,[23] glycol polymers,[24] and cellulose[25] resulted in increased hydrophobicity, chemical resistance, and physical strength of the material.

Saccharum spontaneum L grows as a wasteland weed and lowland ecoregion at the base of the Himalayan range in India, Nepal, China, and Bhutan. It is widely distributed plant and occurs at an altitude ranging from sea level to 1000 m. It belongs to Poaceae family with Magnoliphyta division. Genus *Saccharum* has five extant species of which *S. spontaneum* L is a wild species. *S. spontaneum*, like wheat, rice, corn, and other grains, is of the grass family, characterized by segmented stems, blade-like leaves, and reproduction by seed. It is a perennial grass, growing up to three meters in height. Its ability to quickly colonize in disturbed soil has allowed it to become an invasive species that takes over croplands and pasturelands. It is used as a valuable medicinal herb in traditional systems of medicine in India. It is a first growing biomass with flowers containing fibers. These fibers are distinctly different in

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appearance from other type fibers studied earlier such as cotton, jute, flax, ramie, hemp, etc. These fibers are white/purplish silky and have better strength and fineness.[26,27]

Literature review reveals that graft copolymerization of vinyl monomer onto *S. spontaneum* fiber has not been carried out till date and therefore, it was thought worthwhile to graft copolymerize the methylmethacrylate onto *S. spontaneum*, using ferrous ammonium sulfate—potassium per sulfate (FAS-KPS) as a redox initiator and study its different physical and morphological properties.

EXPERIMENTAL

Materials

Purification of materials

S. spontaneum L fiber was purified through Soxhlet extraction in acetone for 72 h.[28] MMA (S. D. Fine Ltd., Mumbai, India) was purified by washing with 5% NaOH and subsequently drying over anhydrous Na_2SO_4 followed by distillation. FAS (S. D. Fine) were recrystallized from hot water, and KPS (S. D. Fine) was used as received.

Methods

IR spectra of the *S. spontaneum* L and Ss-*g*-poly (MMA) were recorded with a Perkin-Elmer Fourier Transform Infrared spectrometer, using KBr pellets (Sigma Aldrich). Scanning Electron Micrographs (SEM) of *S. spontaneum* L and its graft copolymers were obtained by using JEOL (JSM-6100) Scanning Electron Microscope. X-ray diffraction studies were performed on X-ray diffractometer (X'-Pert-Pra-PAN-Analyzer) under ambient conditions, using Cu Kα (1.5418 Å) radiation, N-filter and scintillation counter as 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 antiscattering slit. The particle size of each sample of Ss-*g*-poly (MMA) and *S. spontaneum* fiber was reduced and put into the sample holder, which was made of polymethylmethacrylate with a round central cavity. Crystallinity index (CI) 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 material and the peak intensity at 18° corresponds to the amorphous material in cellulose.[29] Percentage crystallinity (% Cr) and crystallinity index (CI) were calculated as follows[30]:

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

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

where I_{22} and I_{18} are the crystalline, and amorphous intensities at 2θ-scale close to 22° and 18°, respectively. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and Differential Thermogravimetric analysis (DTG) of the *S. spontaneum* fiber and Ss-*g*-poly(MMA) were carried out in air on a thermal analyzer Perkin-Elmer (Pyris Diamond).

Graft copolymerization

Activation of *S. spontaneum* L fiber (0.5 g) was done at room temperature by immersing in 100 mL of distilled water for 24 h prior to carrying out graft copolymerization. A definite molar ratio of FAS-KPS was added to the reaction flask followed by drop by drop addition of monomer with continuous stirring to the reaction mixture. Reaction was carried out at definite reaction temperature and time. Homopolymer was removed on refluxing with acetone and the graft copolymer obtained was dried at 50°C until a constant weight was attained. Percentage polymer loading (%PL), percentage grafting yield (%GY), percentage grafting efficiency (%GE), and percentage homopolymer (%HM) formed, were calculated as per following methods (Table I)[31]:

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

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

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

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

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

Percent graft efficiency which is the ratio between the quantity of grafted monomer and the total polymerized monomer was calculated.

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

Moisture absorption study

Moisture absorbance studies at various relative humidity levels were carried out as per the method

TABLE I
Evaluation of Optimum Reaction Parameter for Grafting of MMA onto *S. spontaneum*

S. 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	90	40	7.0	100	1 : 1.00	2.45	49.3	29.0	40.5	59.5
2	120	40	7.0	100	1 : 1.00	2.45	177.9	47.0	26.4	66.40
3	150	40	7.0	100	1 : 1.00	2.45	367.8	65.0	12.7	87.3
4	180	40	7.0	100	1 : 1.00	2.45	312.9	89.0	28.4	71.6
5	210	40	7.0	100	1 : 1.00	2.45	179.5	38.0	21.1	78.9
6	180	25	7.0	100	1 : 1.00	2.45	43.8	20.0	34.2	65.8
7	180	30	7.0	100	1 : 1.00	2.45	186.4	52.0	39.6	60.4
8	180	35	7.0	100	1 : 1.00	2.45	246.5	71.0	28.8	71.2
9	180	40	7.0	100	1 : 1.00	2.45	312.9	89.0	28.4	71.6
10	180	45	7.0	100	1 : 1.00	2.45	386.2	84.28	20.7	79.3
11	180	50	7.0	100	1 : 1.00	2.45	376.2	46.0	12.2	87.8
12	180	55	7.0	100	1 : 1.00	2.45	325.9	39.0	11.96	88.04
13	180	40	2.0	100	1 : 1.00	2.45	309.1	47.0	15.2	84.8
14	180	40	4.0	100	1 : 1.00	2.45	366.2	73.0	19.9	80.1
15	180	40	6.0	100	1 : 1.00	2.45	369.4	106.4	21.0	79.0
16	180	40	8.0	100	1 : 1.00	2.45	386.2	89.0	21.6	78.4
17	180	40	9.0	100	1 : 1.00	2.45	326.3	68.0	20.8	79.2
18	180	40	6.0	50.0	1 : 1.00	2.45	342.9	95.0	21.2	78.8
19	180	40	6.0	75.0	1 : 1.00	2.45	368.2	97.48	25.9	74.1
20	180	40	6.0	125	1 : 1.00	2.45	370.6	129.0	34.8	65.2
21	180	40	6.0	150	1 : 1.00	2.45	355.8	94.0	34.8	65.2
22	180	40	6.0	175	1 : 1.00	2.45	312.4	75.0	35.5	64.5
23	180	40	6.0	125	1 : 0.50	2.45	362.1	20.0	64.9	35.1
24	180	40	6.0	125	1 : 0.75	2.45	293.0	132.0	36.4	63.6
25	180	40	6.0	125	1 : 1.00	2.45	302.6	94.0	32.0	68.0
26	180	40	6.0	125	1 : 1.25	2.45	304.4	69.0	22.7	77.3
27	180	40	6.0	125	1 : 1.50	2.45	310.6	48.0	12.3	87.7
28	180	40	6.0	125	1 : 0.75	1.49	153.8	34.0	14.4	85.6
29	180	40	6.0	125	1 : 0.75	1.96	242.8	59.7	23.0	77.0
30	180	40	6.0	125	1 : 0.75	2.45	290.1	109.0	37.5	62.5
31	180	40	6.0	125	1 : 0.75	2.94	324.7	144.0	44.3	55.7
32	180	40	6.0	125	1 : 0.75	3.43	344.7	74.0	21.4	78.6
33	180	40	6.0	125	1 : 0.75	3.92	346.8	51.0	14.7	85.3

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

reported earlier.[32] Moisture absorbance percentage was found out by placing a known weight (W_i) of dry grafted and ungrafted samples in a humidity chamber for about two hours and then the final weight (W_f) of the samples exposed to different relative humidities ranging from 20 to 100% were taken. The percentage of moisture absorbance was calculated from the increase in initial weight in the following manner:

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

Acid and base resistance

Acid and base resistance studies were carried out as per the method reported earlier.[33] Acid and base resistance was studied by placing a known weight (W_i) of dry grafted and ungrafted samples in fixed volume of 5*N* HCl and 5*N* NaOH, and the final weight (W_f) of the samples were noted down after every 12-h interval until the constant weight was reached.

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

RESULTS AND DISCUSSION

Characterization of the grafted *S. spontaneum* fibers

FTIR

S. spontaneum L fiber showed a broad peak at 3390.6 cm^{-1} (due to —OH), 2921.7 cm^{-1} (C—H stretching), and 1436.0 cm^{-1} and 1052.7 cm^{-1} (arising from C—C, and C—O stretchings, respectively) (Fig. 1). On grafting, IR bands due to characteristic functional groups incorporated into *S. spontaneum* L have been witnessed apart from the previously listed bands: MMA; 1732.7 cm^{-1} (C=O) and 1058.4 cm^{-1} (C—O) (Fig. 2).

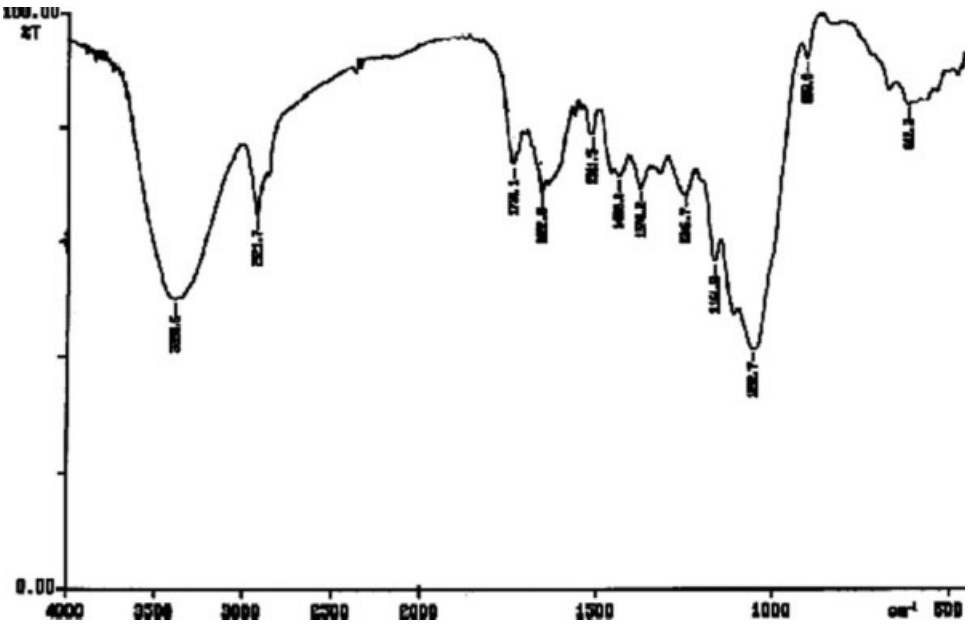


Figure 1 IR spectra of *S. spontaneum* fiber.

Scanning electron microscopy

The changes in the topography and morphology of fiber surfaces were studied by SEM. It can be observed that the surface of the grafted fibers is highly rough in comparison with the ungrafted fiber (Figs. 3 and 4), which is attributed to the high graft density. Some researches[34,35] have proved that the adhesion of the grafted fiber to other materials improved with an increase in the roughness of its surface due to an increase in surface area for bonding and mechanical interlocking. So the rougher surface on the grafted *S. spontaneum* L is expected to be of benefit to improve the adhesion of grafted *S. spontaneum* L fiber to other polymers and, hence, improve the mechanical performance of composites.

X-ray diffraction studies

As is evident from Figure 5, percentage crystallinity and crystallinity index was found to decrease with increase in percentage grafting of MMA onto *S. spontaneum* fiber. Since incorporation of monomer moiety in the backbone impairs the natural crystallinity of the fiber, the graft copolymerization of MMA onto

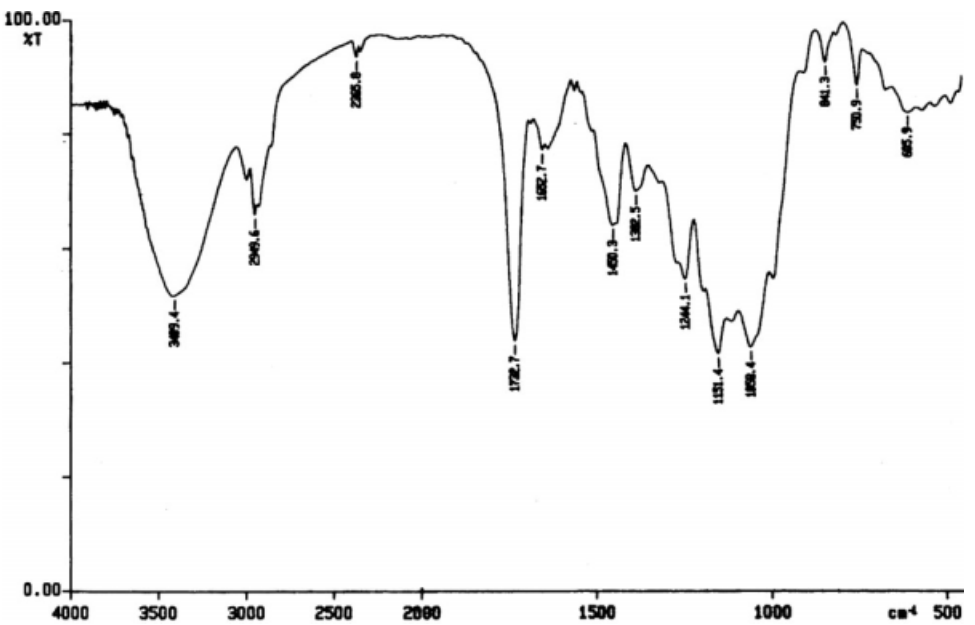


Figure 2 IR spectra of Ss-*g*-poly(MMA).

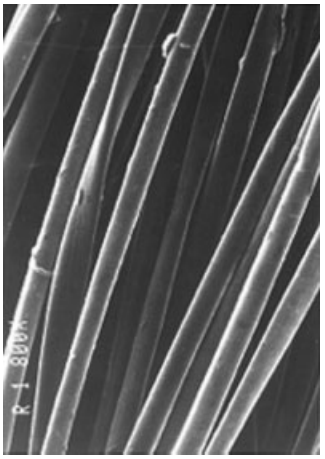


Figure 3 Scanning electron microscograph of *S. spontaneum* fiber.

S. spontaneum fiber resulted in impaired crystallinity, and increased amorphous region of the fiber (Table II). Thus with increase in percentage grafting, the percentage crystallinity and crystallinity index decreased along with reduction in stiffness and hardness. Since crystallinity index (CI) is the quantitative measure of the orientation of the crystal lattice to the fiber axis, the lower crystallinity index in case of graft copolymers stands for poor order of crystal lattice in the fiber. Thus the misorientation of the crystal lattice to the fiber axis during grafting resulted in graft copolymer with low crystallinity and crystallinity index. This clearly indicates that the cellulose crystals are better oriented in *S. spontaneum* fiber followed by *Ss-g*-poly(MMA).

TGA, DTA, and DTG

TGA of ungrafted and grafted *S. spontaneum have* been studied as a function of wt % loss versus temperature. Cellulosic *S. spontaneum* degrades by dehydration, glycogen formation, and depolymerization. In case of *S. spontaneum*, two-stage decomposition has been found in the temperature range from 225 to 320°C with 60% weight loss and 320–416°C with 25.33% weight loss. The former stage is attributed to loss by dehydration and volatilization processes, whereas the later stage is attributed to loss by depolymerization process. Ss-*g*-poly(MMA) showed single stage decomposition. After the initial loss of moisture, decomposition continues beyond 250°C with 75.17% weight loss and 10.49% weight loss in temperature range from 384 to 500°C. Thus it is evident from the TGA data that grafted fiber is thermally more stable than the raw fibers. This may be due to the incorporation of poly(MMA) chains on backbone polymer through covalent bonding.

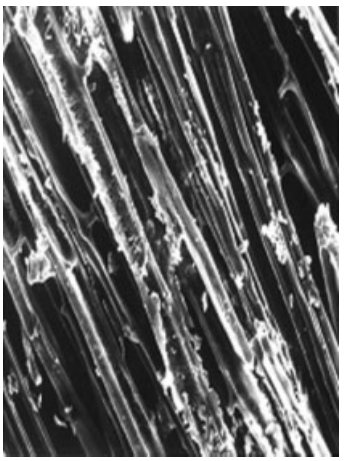
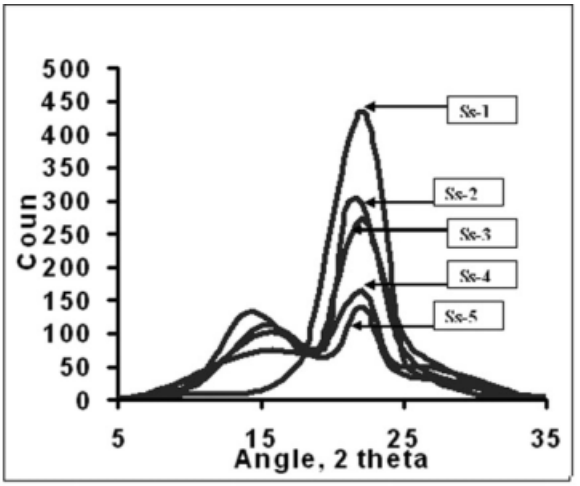


Figure 4 Scanning electron microscograph of Ss-*g*-poly(MMA).



whereas Ss-1 = S. spontaneum fiber; Ss-2 = Ss-g-poly(MMA),[GY = 29.00%]; Ss-3 = Ss-g-poly(MMA),[GY = 84.28%]; Ss-4 = Ss-g-poly(MMA),[GY = 106.42%]; Ss-5 = Ss-g-poly(MMA),[GY = 144.00%];

Figure 5 X-ray diffraction studies.

In case of DTA studies, *S. spontaneum* has been found to exhibit two exothermic peaks at 313°C (63 μV) and 422°C (137 μV). Exothermic peak at 313°C corresponds to decomposition stage between 225 and 320°C, whereas the exothermic peak at 422°C corresponds to second decomposition stage (320–416°C) in TGA (Fig. 6). However, Ss-*g*-poly(MMA) exhibited

TABLE II
Percentage Crystallinity (%Cr) and Cryatallinity Index (C.I.) of *S. spontaneum* and Graft Copolymers

S. no.	Sample	%GY	At 2θ-scale I_{22}	At 2θ-scale I_{18}	% Cr	C.I.
1	Ss-1	–	436	75	85.32	0.82
2	Ss-2	29.00	298	80	78.83	0.73
3	Ss-3	84.28	274	80	77.40	0.70
4	Ss-4	106.42	165	72	69.62	0.56
5	Ss-5	144.00	140	70	66.66	0.50

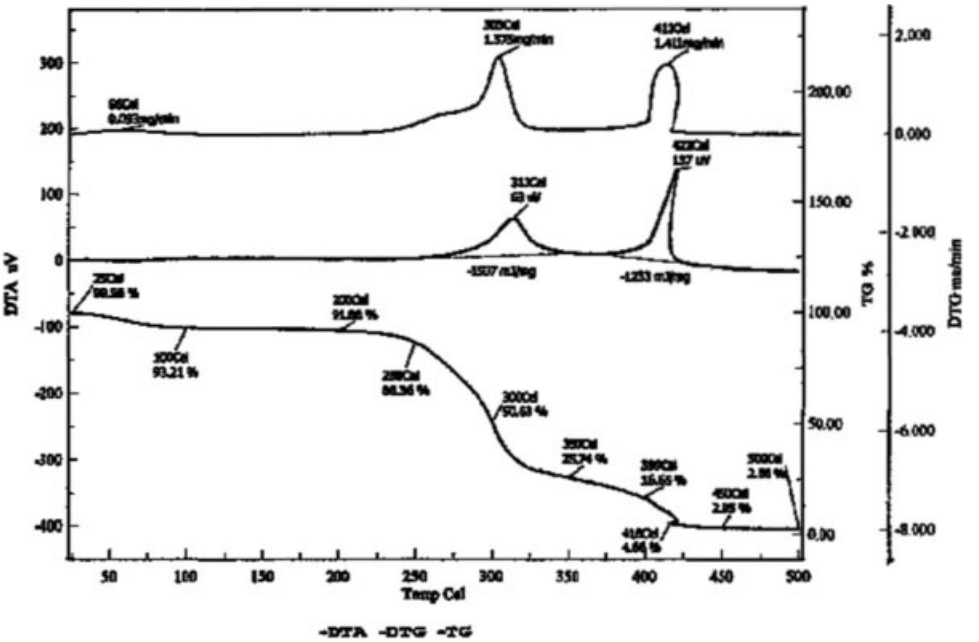


Figure 6 TGA, DTA, and DTG curves of *S. spontaneum* fiber.

exothermic decomposition at 312°C (12 μV) and 375°C (46 μV). Exothermic peak arising at 312°C corresponds to onset of degradation reactions of Ss-*g*-poly(MMA) chains, whereas peak at 375°C corresponds to the thermal decomposition taking place in the temperature range between 250 and 384°C in TGA (Fig. 7).

DTG analysis of grafted and ungrafted *S. spontaneum* has been studied as a function of rate of weight loss (mg/min) versus temperature. In case of *S. spontaneum* decomposition at 303 and 413°C has been found with 1.575 and 1.411 mg/min weight loss, respectively. However, in case of Ss-*g*-poly (MMA), decomposition was observed at 276 and 361°C with 0.472 and 0.961 mg/min weight loss, respectively. Thus it could be concluded from the DTG studies that the rate of thermal decomposition was higher in case of *S. spontaneum* fiber (1.575 mg/min at 303°C, 1.411 mg/min at 413°C), whereas in case of Ss-*g*-poly(MMA), the rate of thermal decomposition is lower (0.472 mg/min at 276°C and 0.961 mg/min at 361°C). The better thermal resistance of graft copolymer was due to incorporation of more covalent bonding through inclusion of poly(MMA) chains onto the polymer backbone (Figs. 6 and 7).

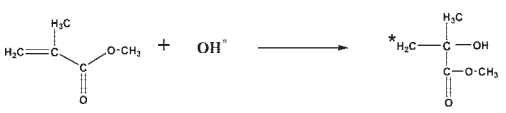
Mechanism

C_2, C_3, and C_6 hydroxyls and C—H groups are the active sites for the incorporation of polymeric chains through grafting onto cellulosic fibers like *S. spontaneum*. KPS is known to take part in a redox reaction with Fe^{2+} through the following reaction:

$$Fe^{2+} + {}^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^- \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-*} \quad (1)$$

Interaction of SO_4^{-*} with H_2O generates OH* and these free radicals are responsible for free radical generation on polymer backbone and monomer as well as further chain propagation, thereby resulting in the formation of graft copolymer along with homopolymer. It can be explained through the following mechanism:

$$SO_4^{-*} + H_2O \longrightarrow HSO_4^- + OH^* \quad (2)$$



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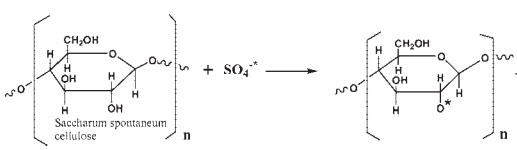

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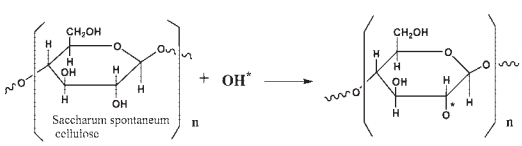

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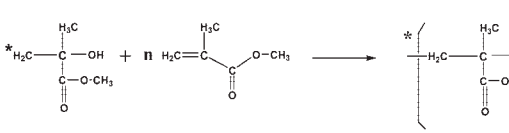

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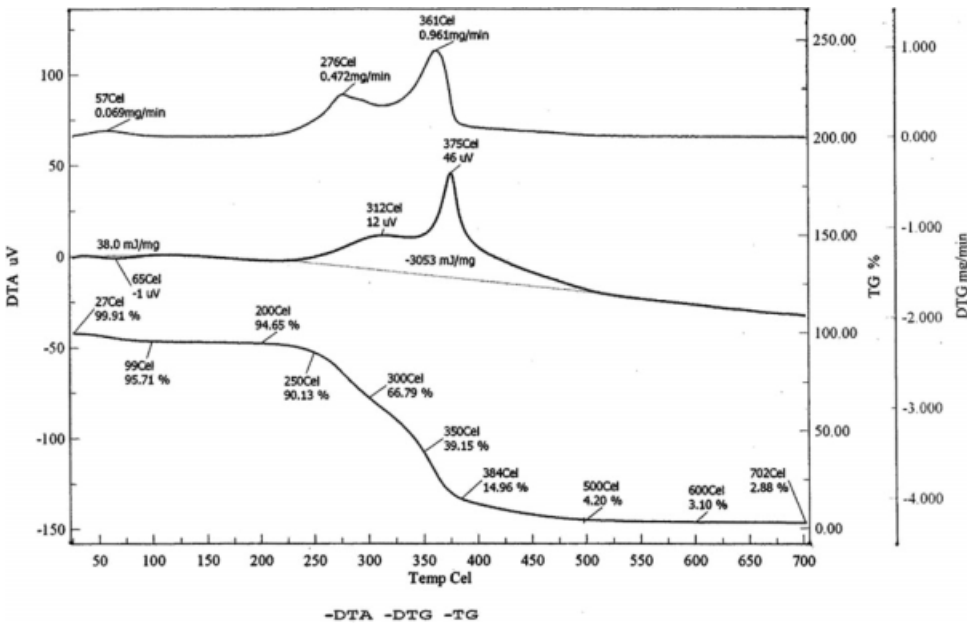
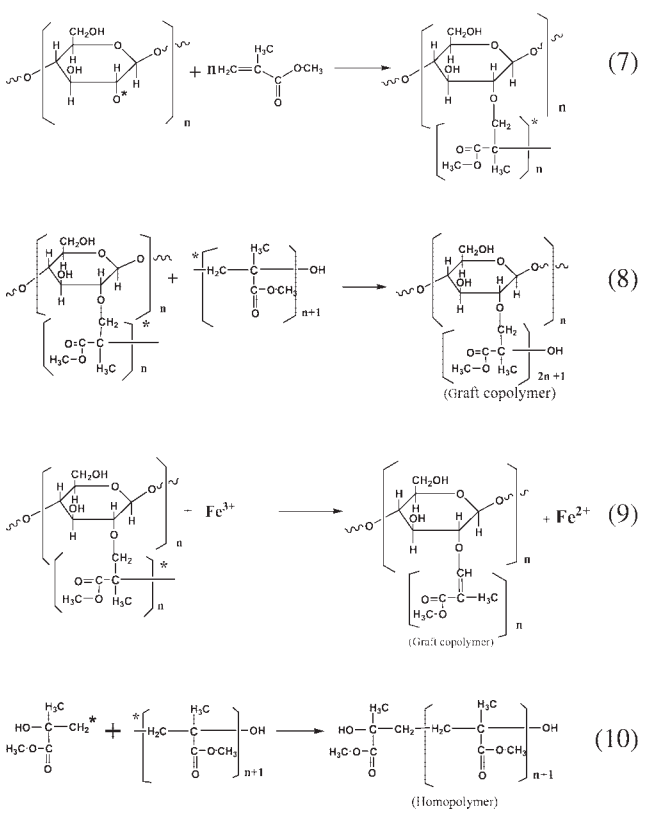


Figure 7 TGA, DTA, and DTG curves of Ss-*g*-poly (MMA).



On the basis of this mechanism it can be concluded that both SO_4^{-}* and OH* are involved in graft copolymerization. However, in case of grafting carried out in the absence of swelling agent, the initiation of reaction by SO_4^{-}* [eq. (4)] is unlikely to occur as the concentration of persulfate used is very small, whereas in presence of swelling agent, SO_4^{-}* reacts with H_2O to generate OH*, which can also initiate the grafting reaction. The resulting OH*abstracts hydrogen atom from the backbone polymer and generates the macroradical of *S. spontaneum* fiber [eq. (5)]. Similarly, OH* radicals react with monomer molecules resulting in free radical sites on the monomer [eq. (3)] which further react with monomer moieties thereby resulting in active homopolymer [eq. (6)]. Moreover, reaction between active backbone and monomers gives active graft copolymer and the grafting propagates [eq. (7)]. Termination of grafting may occur by either process [eq. (8)] or [eq. (9)] or both. Presence of Fe^{3+} has great impact on graft yield as it is involved in the termination of growing chains. Because Fe^{3+} is produced by the reaction between FAS with KPS [eq. (1)], so the relative amounts of KPS and FAS in the initiating system plays an important role in graft yield. Initially Fe^{2+} ions get oxidized to Fe^{3+} with the generation of SO_4^{-}* ions which further propagates the polymerization reaction. However, increase in Fe^{3+} ions concentration, attacks the growing graft copolymer chains, thereby resulting in termination of reaction with reduction of Fe^{3+} to Fe^{2+} [eq. (9)]. Reactions between growing MMA chains also result in the termination of reaction and formation of homopolymer [eq. (10)]. Hence, concentrations of initiator and monomer, variations of time, temperature, pH, and volume of the solvent affect the graft yield as these factors determine

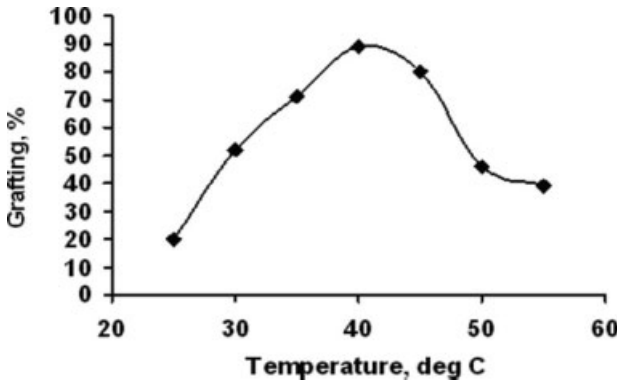


Figure 8 Effect of reaction temperature on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} mol/L; time, 180 min; FAS-KPS, 1 : 1; pH, 7; solvent, 100 mL.

the relative population of various radical species generated in different steps during the course of 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 (Fig. 8). The effect of temperature was studied by changing the reaction temperature from 25 to 55°C and keeping the other reaction conditions constant. It has been found that increase in temperature beyond optimum (40°C) resulted in decreased graft yield. At low temperature, the reaction between SO_4^-* and OH group of *S. spontaneum* was slow, the amount of macro radicals generated was small, and thus %GY was low. However increase in temperature, beyond optimum reaction temperature, the graft copolymerization occurs with poor selectivity. Under such reaction conditions various hydrogen abstraction and other chain transfer reactions might be accelerated and thus lead to decrease in %GY. The decrease in %GY at higher temperature may also be due to loss of water soluble constituents of backbone and also due to excessive of homopolymerization.

Effect of reaction time

Figure 9 shows the effect of reaction time on the %GY. It is clear from Figure 5 that as reaction time, increases, %GY increased gradually and reached maximum value (89%) in 180 min and then decreased. The increase in graft yield with time could be explained on the basis that with increase in time, interaction between SO_4^-* and *S. spontaneum* the backbone increased. As a result there was more generation of free radical sites on the backbone as well as MMA chains, which resulted in more %GY. However decrease in %GY beyond optimum reaction time could be due to predominance of homopolymerization over graft copolymerization. This could also be due to disintegration of poly(MMA) chains grafted on backbone polymers beyond optimum reaction time, thereby resulting in decreased %GY.

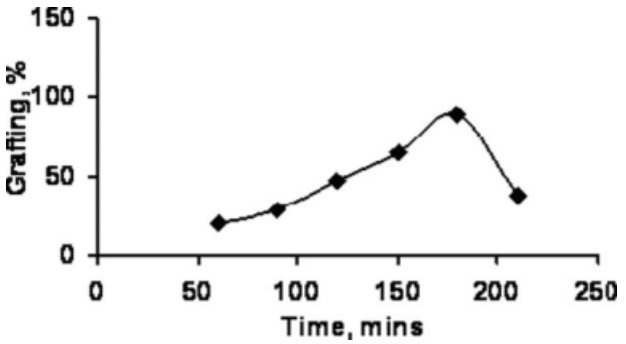


Figure 9 Effect of reaction time on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} mol/L; temperature, 40°C; FAS-KPS, 1 : 1; pH, 7; solvent, 100 mL.

Effect of pH of reaction medium

The pH of the reaction medium plays an important role during the grafting process. Maximum grafting yield has been found at pH 6.0 (Fig. 10). Further decrease or increase in pH resulted in decreased graft yield. This could be due to premature termination of polymerization with increase in pH

Effect of solvent

As it is evident from Figure 11, that graft yield increases with increase in the volume of the solvent. After reaching the optimum value, further increase of volume of solvent resulted in declined percentage grafting. This generally occurs on the setting up of various hydrogen abstraction reactions as well as with increase of viscosity of the reaction medium.

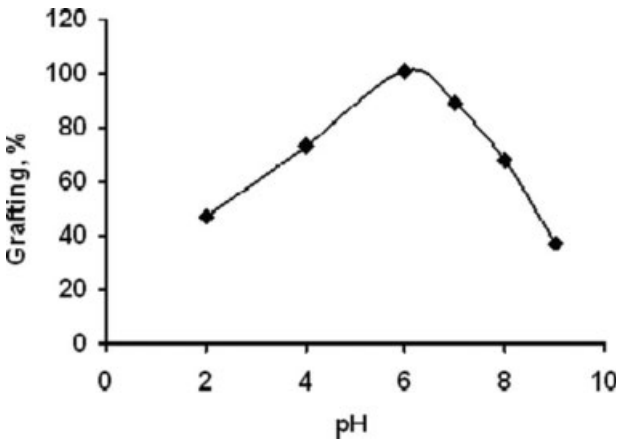


Figure 10 Effect of pH on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} mol/L; time, 180 min; temperature, 40°C; FAS-KPS, 1 : 1; solvent, 100 mL.

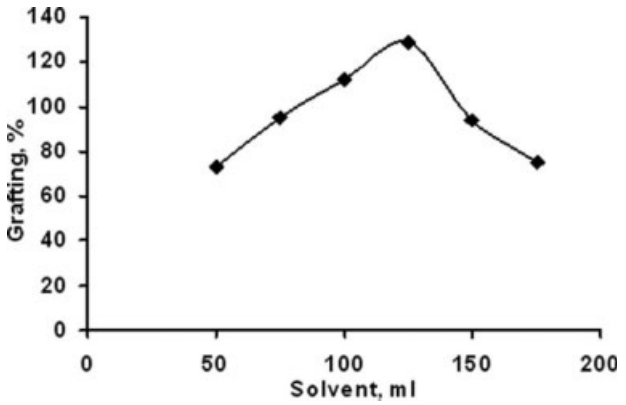


Figure 11 Effect of solvent on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} mol/L; time, 180 min; temperature, 40°C; FAS-KPS, 1 : 1; pH, 6.

Initially viscosity of the reaction mixture increases rapidly with the formation of homopolymer. Increased viscosity of the medium creates hindrance for the free radical ions in reaching the active sites. However, increased solvent volume beyond optimum, resulted in decreased graft yield. This could be due to decreased SO_4^-* and OH* free radical concentration. Hence lesser generation of free radical sites on backbone polymer as well as on monomer moieties and low graft yield.

Effect of molar ratio of initiator

The graft copolymerization was conducted at different molar ratio *of* FAS-KPS. Graft yield was greatly affected by FAS-KPS molar ratio (Fig. 12). Initially percentage graft yield 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 in the beginning Fe^{2+} gets oxidized to Fe^{3+} on reaction with KPS resulting in generation of more

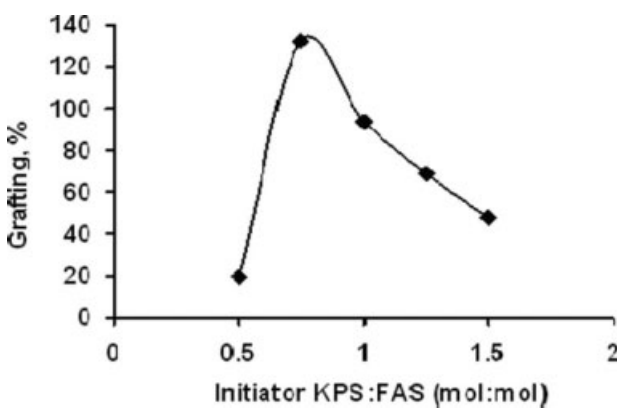


Figure 12 Effect of concentration of initiator (FAS : KPS molar ratio) on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} mol/L; time, 180 min; temperature, 40°C; pH, 6; solvent, 125 mL.

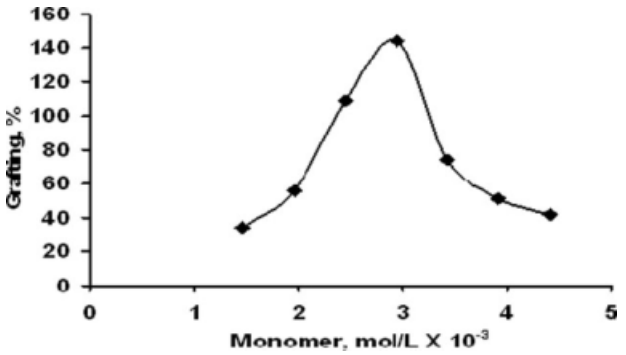


Figure 13 Effect of monomer concentration on grafting. *S. spontaneum* fiber, 0.5 g; time, 180 min; temperature, 40°C; pH, 6; solvent, 125 mL; FAS : KPS, 1 : 0.75.

and more SO_4^-*, which initiated the grafting reaction by generation of free radical sites on *S. spontaneum*. However, further increase in Fe^{2+}concentration results in generation of more Fe^{3+} ions which terminate the grafting reaction with reduction to Fe^{2+} and have a decreased graft yield. It was also observed that formation of homopolymer was considerably less at low initiator concentration while there was a significant homopolymer formation beyond the critical ratio. This is due to the fact that the excess concentration of Fe^{2+} ions beyond optimum concentration resulted in generation of poly(MMA) chains alone with excess Fe^{3+} ions which ultimately resulted in termination of growing chains [eqs. (1) and (9)].

Effect of monomer concentration

Figure 13 showed the effect of concentration of MMA on graft copolymerization. With increase in concentration of MMA, %GY increased continuously and reached maximum value (144.4%) at 2.94×10^{-3} mol/L. However, further increase in monomer concentration resulted in decreased graft yield. This behavior could be explained by the fact that an increase of monomer concentration leads to the accumulation of monomer free radicals in close proximity to the backbone and give rise to graft copolymerization. This leads to depletion in the available MMA concentration as well as a reduction in the active sites on the *S. spontaneum* backbone as graft copolymerization proceeds. However, at higher monomer concentration, the primary radicals attack the monomer instead of reacting with the backbone polymer, thereby initiating homopolymerization reaction and thus the low graft yield was observed beyond optimum monomer concentration.

Moisture absorbance study

It was found that graft copolymerization of MMA onto *S. spontaneum* has a great impact on the

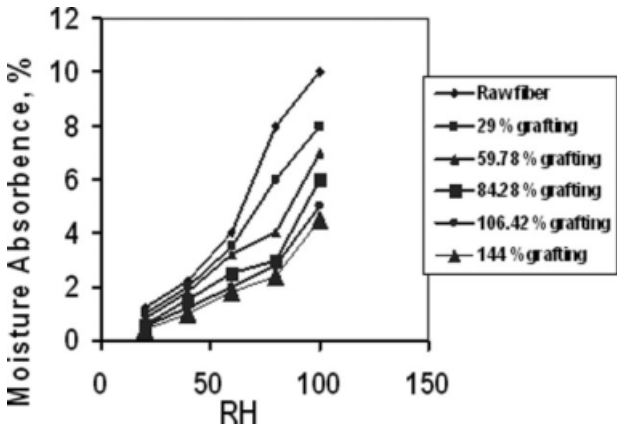


Figure 14 Effect of grafting on moisture absorbance at different humidity levels.

moisture absorbance behavior (Fig. 14). It has been observed that with increase in graft yield, there has been a decrease in percent moisture absorbance. This could be due to the fact that with increase in graft yield, the sites vulnerable for moisture absorbance get blocked with hydrophobic poly(MMA) chains, thereby, converting the fiber less sensitive towards moisture.

Acid resistance study

It has been observed that acid resistance of the fiber increases with increase in percent grafting (Fig. 15). This is due to the fact that poly (MMA) chains grafted onto *S. spontaneum* fiber have less affinity for acid as compared to hydroxyl and other functional groups present in ungrafted fiber. Therefore, the resistance of fiber towards acid increases with the incorporation of poly (MMA) chains onto fiber.

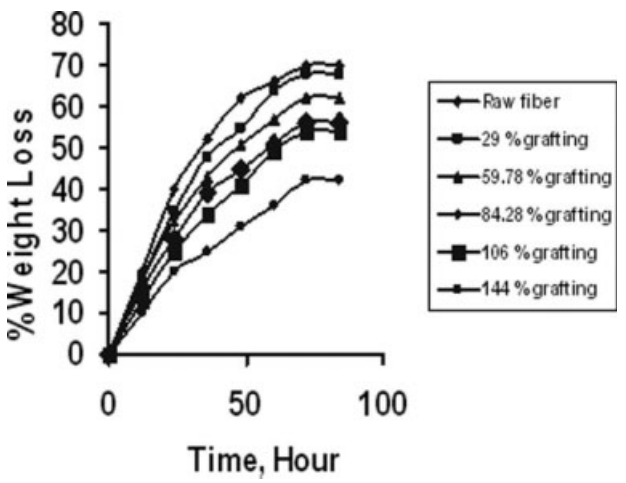


Figure 15 Effect of grafting on acid resistance.

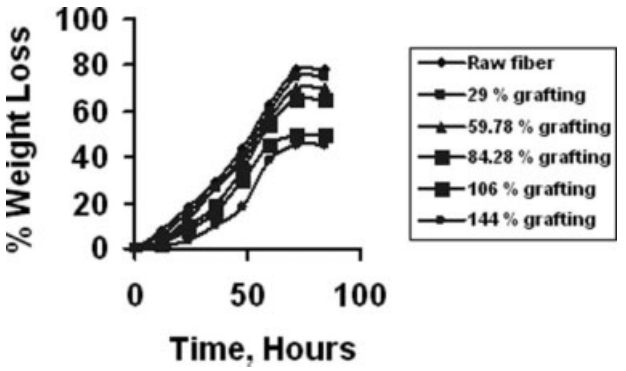


Figure 16 Effect of grafting on base resistance.

Base resistance study

It is evident from the Figure 16 that base resistance of the fiber increases with increase in percent grafting which could be due to the fact that poly(MMA) chains grafted onto *S. spontaneum* fiber have less affinity for base as compared to hydroxyls and other functional groups present in ungrafted fiber. Thus, base resistance of the fiber increased with increase in %GY.

CONCLUSIONS

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

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