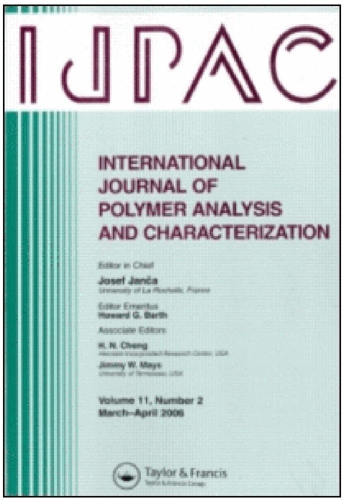

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Balbir Singh Kaith[a]; Rajeev Jindal[a]; Asim Kumar Jana[b]; Mithu Maiti[a]
[a] Department of Chemistry, Dr BRA National Institute of Technology, Jalandhar, Punjab, India [b] Department of Bio-Technology, Dr BRA National Institute of Technology, Jalandhar, Punjab, India

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Rapid Synthesis of Graft Copolymer of MMA Onto *Saccharum spontaneum* L. Under Microwave Irradiation for Enhanced Thermal Modifications

Balbir Singh Kaith,[1] Rajeev Jindal,[1]
Asim Kumar Jana,[2] and Mithu Maiti[1]
[1]Department of Bio-Technology, Dr BRA National Institute
of Technology, Jalandhar, Punjab, India
[2]Department of Chemistry, Dr BRA National Institute
of Technology, Jalandhar, Punjab, India

Abstract: In this article, synthesis of graft copolymers of methyl methacrylate (MMA) onto *Saccharum spontaneum* L. fiber under the influence of microwave radiation (MWR) was carried out. Different reaction parameters such as time, initiator molar ratio, monomer concentrations, microwave power, pH, and solvent were optimized for maximum graft yield (62.3%). The graft copolymers thus formed were characterized by FT-IR, SEM, XRD, and TGA, DTA, and DTG techniques. Moreover, graft copolymers have been found to be more moisture resistant and also showed higher chemical and thermal resistance.

Keywords: Chemical resistance; Graft copolymer; Microwave radiation (MWR); Moisture absorbance; *Saccharum spontaneum* L.

INTRODUCTION

Hybridization of natural polymers with synthetic polymers is of great interest because of their applications to the biomedical and biodegradable materials. The chemical combination of natural and

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Correspondence: Balbir Singh Kaith, Department of Bio-Technology, Dr BRA National Institute of Technology, Jalandhar 144011, Punjab, India. E-mail: bskaith@yahoo.co.in

synthetic polymers yields new materials, which could have desirable properties, including biodegradability.[1] Natural fiber is a biopolymer and the most easily available organic material in nature.[2] Natural polymer backbones have been widely studied over the past decade because of their biodegradability and the fact they represent renewable resources. Modification of natural fibers by graft copolymerization provides a significant route to alter their physical and chemical properties.[3] Graft copolymerization of different vinyl monomers has been successfully attempted onto natural fiber by different workers.[4] Mishra and coworkers have studied the modification of natural polymer such as wool[5] and gelatin.[6] Concurrent homopolymer formation is the main constrain in graft copolymerization, leading to low graft yield and resulting in little commercialization of the grafting procedures. The main advantage lying with microwave radiation (MWR) is instantaneous "in core" heating of materials in a homogeneous and selective manner.[7] Microwave heating can result in rapid transfer of energy into the bulk of the reaction mixture; the depth of the materials is of the same order of magnitude of the wavelength, and, therefore, vinyl monomer can interact with substances of appreciable thickness.[8] Microwave heating is rapid, efficient, clean, cheap, convenient and a "green" method of polymer synthesis.[9] It is used for enhancement of polymerizations including addition polymerization,[10,11] condensation polymerization,[12] and graft copolymerization.[13] Monomers containing polar groups favor the absorption of microwave radiation.

Recently, grafting of butylacrylate,[14] acrylic acid,[7] and acrylonitrile[15] onto starch, acrylamide onto LDPE (low-density polyethylene) films,[16] and butyl methacrylate onto wool fibers[17] has been studied using redox initiators under microwave irradiation. Methyl methacrylate has been reported to polymerize under microwave irradiation using very low concentration of initiators.[16] Grafting of acrylamide[18] and acrylonitrile[19] onto guar gum and acrylonitrile onto chitosan[20] under microwave conditions in very short reaction time and in the absence of any redox initiator or catalyst has been reported.

Polyacrylamide was graft copolymerized onto chitosan and guar gum using microwave radiation method and maximum grafting of 169% and 66.66% was observed in 1.16 and 0.22 min respectively.[1]

Saccharum spontaneum L. grows as a wasteland weed in the lowland eco-region at the base of the Himalayan range in India, Nepal, China, and Bhutan. It is a widely distributed plant that occurs at an altitude ranging from sea level to 1000 m. It belongs to the Poaceae family within the Magnoliphyta division. The genus *Saccharum* has five extant species of which *Saccharum spontaneum* L. is a wild species. *Saccharum 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 valuable medicinal herb in traditional systems of medicine in India. It is a fast growing biomass with flowers containing fibers that are distinctly different in appearance from other types of fibers studied earlier such as cotton, jute, flax, ramie, and hemp. These fibers are white/purplish in color, silky in texture, and have better strength and fineness.

A literature review reveals that graft copolymerization of vinyl monomer onto *S. spontaneum* fiber has not been carried out to date. Therefore, in this article, the attempts to carry out graft copolymerization of methyl methacrylate (MMA) onto *S. spontaneum* fiber under the influence of microwave radiation and to study its different physicochemical properties are reported.

EXPERIMENTAL SECTION

Materials

Purification of Materials

S. spontaneum L fiber was purified in a Soxhlet apparatus by refluxing in acetone for 72 h.[21] MMA (S. D. Fine-Chem Ltd.) was purified by washing with 5% NaOH and subsequently drying over anhydrous Na_2SO_4 followed by distillation. Ferrous ammonium sulfate (FAS; S. D. Fine-Chem Ltd.) was recrystallized from hot water, and potassium persulfate (KPS; S. D. Fine-Chem Ltd.) was used as received.

Microwave Equipment

A microwave oven (LG, model no. MG-3937C, 1200 W) was used for all the experiments. The average bulk temperature at the end of the reaction was measured by inserting a thermometer in the reaction mixture and was less than 100°C, as the all the reactions were performed in aqueous medium.

Methods

Graft Copolymerization

Activation of *S. spontaneum* L. fiber (0.5 g) was done at room temperature by immersing it in 25 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 of the reaction mixture. The reaction was carried out under the influence of MWR at definite reaction temperature and time. Homopolymer was removed on refluxing with acetone and 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 the following methods (Table I):[22]

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

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

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

The quantity of the grafted polymer is evaluated as the weight increase of the sample (W_3) after the extraction of the homopolymer. Percent graft efficiency, which is the ratio between the quantity of grafted monomer and the total polymerized monomer, was calculated as:

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

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

Infrared Spectroscopy (IR)

IR spectra of the *S. spontaneum* L. and Ss-g-poly(MMA) were recorded with a Perkin Elmer Fourier transform-infrared (FT-IR) spectrophotometer using KBr pellets.

Scanning Electron Microscopy (SEM)

Scanning electron micrographs (SEM) of *S. spontaneum* L. and its graft copolymers were obtained by using a scanning electron microscope (JEOL, JSM-6100).

X-Ray Diffraction (XRD) Studies

X-ray diffraction studies were performed on an X-ray diffractometer (X'-Pert-Pra-PAN-Analyzer) under ambient conditions using CuKα (1.5418 Å) radiation, N-filter, and scintillation counter as detector at

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

Sample no.	Reaction time (s)	pH	Solvent (mL)	Molar ratio (FAS:KPS)	$[\mathrm{MMA}] \times 10^{-3}$ mol/L	%MW	%PL	%GY	%GE	%HM
1	60	7.0	20	1:0.500	2.45	80	49.3	15.00	30.42	69.58
2	90	7.0	20	1:0.500	2.45	80	77.9	23.00	29.52	70.48
3	120	7.0	20	1:0.500	2.45	80	97.8	40.00	40.89	59.11
4	150	7.0	20	1:0.500	2.45	80	82.9	37.00	44.63	55.37
5	180	7.0	20	1:0.500	2.45	80	79.5	30.28	38.08	61.92
6	120	2.0	20	1:0.500	2.45	80	43.8	15.00	34.24	65.76
7	120	4.0	20	1:0.500	2.45	80	76.4	21.35	27.94	72.06
8	120	6.0	20	1:0.500	2.45	80	56.5	33.00	58.40	41.60
9	120	7.0	20	1:0.500	2.45	80	92.9	42.00	45.35	54.65
10	120	8.0	20	1:0.500	2.45	80	86.2	36.00	41.76	58.24
11	120	9.0	20	1:0.500	2.45	80	76.2	18.00	23.62	76.38
12	120	7.0	15	1:0.500	2.45	80	55.9	17.00	30.41	69.59
13	120	7.0	20	1:0.500	2.45	80	69.1	34.00	49.20	50.80
14	120	7.0	25	1:0.500	2.45	80	86.2	44.00	51.04	48.96
15	120	7.0	30	1:0.500	2.45	80	79.4	37.25	46.91	53.09
16	120	7.0	35	1:0.500	2.45	80	66.2	29.00	43.80	56.20
17	120	7.0	40	1:0.500	2.45	80	46.3	20.00	43.19	56.81
18	120	7.0	25	1:0.125	2.45	80	42.9	15.00	34.96	65.04

(continued)

Table I. Continued

Sample no.	Reaction time (s)	pH	Solvent (mL)	Molar ratio (FAS:KPS)	$[\mathrm{MMA}] \times 10^{-3}$ mol/L	%MW	%PL	%GY	%GE	%HM
19	120	7.0	25	1:0.250	2.45	80	98.2	46.00	46.84	53.16
20	120	7.0	25	1:0.375	2.45	80	70.6	40.00	56.65	43.35
21	120	7.0	25	1:0.500	2.45	80	65.8	33.00	50.15	49.85
22	120	7.0	25	1:0.625	2.45	80	32.4	19.00	58.84	41.16
23	120	7.0	25	1:0.250	1.47	80	38.1	14.00	36.74	63.26
24	120	7.0	25	1:0.250	1.96	80	53.0	30.00	56.60	43.40
25	120	7.0	25	1:0.250	2.45	80	82.6	50.00	60.53	39.47
26	120	7.0	25	1:0.250	2.94	80	74.4	41.00	55.10	44.90
27	120	7.0	25	1:0.250	3.43	80	70.6	33.00	46.74	53.26
28	120	7.0	25	1:0.250	2.45	60	103.8	48.00	46.24	53.76
29	120	7.0	25	1:0.250	2.45	70	109.8	62.30	56.73	43.27
30	120	7.0	25	1:0.250	2.45	80	90.1	50.00	55.49	44.51
31	120	7.0	25	1:0.250	2.45	90	74.7	45.00	60.24	39.76
32	120	7.0	25	1:0.250	2.45	100	66.7	40.00	59.97	40.03

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

45 KV and 35 mA with 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. The small particle size of each sample of Ss-g-poly(MMA) and *S. spontaneum* fiber was made and was put into a sample holder, made of PMMA, with a round central cavity.

Crystallinity index (C.I.), which measures the orientation of the cellulose crystals in a fiber to the 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.[23] Percentage crystallinity (%Cr) and crystallinity index (C.I.) were calculated as follows:[24–26]

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

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

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

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

Thermogravimetric analysis, differential thermal analysis, and differential thermogravimetric analysis of the *S. spontaneum* fiber and Ss-g-poly(MMA) were carried out in air on a thermal analyzer (Perkin Elmer, Pyris Diamond).

Moisture Absorption Study of *S. spontaneum* L. fiber and Ss-g-poly(MMA)

Moisture absorbance percentage was found by placing a known weight (W_i) of dry grafted and ungrafted samples in a humidity chamber for about two hours, then taking the final weights (W_f) of the samples exposed to different relative humidities ranging from 20–100%. The percentage moisture absorbance was calculated from increase in initial weight in the following manner:[23]

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

Acid and Base Resistance

Acid and base resistance was studied by placing a known weight (W_i) of dry grafted and ungrafted samples in a fixed volume of 5 N HCl and 5 N

NaOH and noting the final weight (W_f) of the samples after every 12 h interval until constant weight was reached:[23]

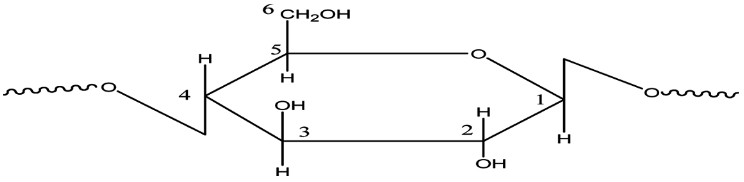
$$\% \text{ of weight loss} = [(W_i - W_f)/W_i] \times 100$$

RESULTS AND DISCUSSION

Mechanism

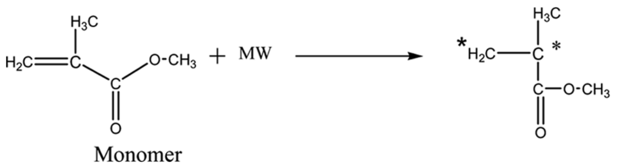
C_2, C_3, and C_6 hydroxyls and C–H groups are active sites for the incorporation of polymer chains through grafting onto cellulosic fibers. KPS is known to take part in a redox reaction with Fe^{2+} through mechanism (1).

$$Fe^{2+} + {}^{-}O_3S\text{–}O\text{–}O\text{–}SO_3^{-} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-*} \tag{1}$$



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. On the other hand, microwave irradiation also produces free radicals on polymeric backbone and monomer, which can be explained through mechanisms (2)–(14).

$$SO_4^{-*} + H_2O \longrightarrow HSO_4^{-} + OH^* \tag{2}$$



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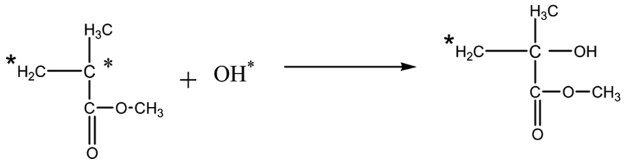
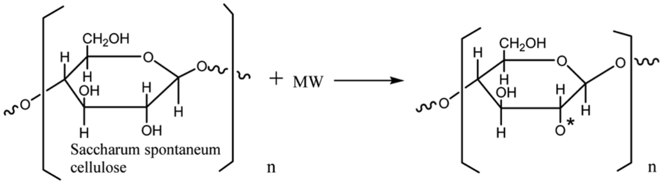
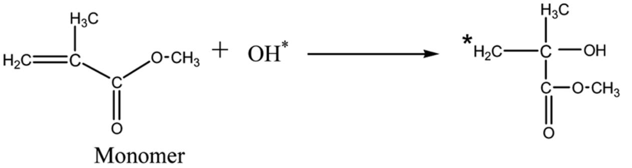


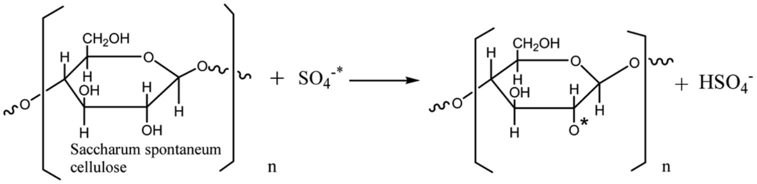
(4)


Saccharum spontaneum cellulose
+ MW
n

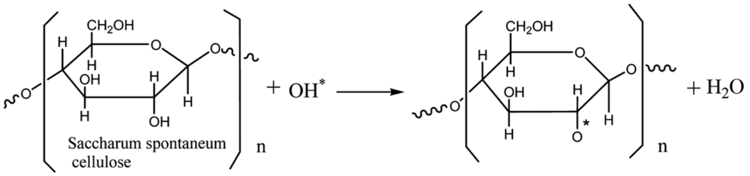
(5)


Monomer
+ OH*

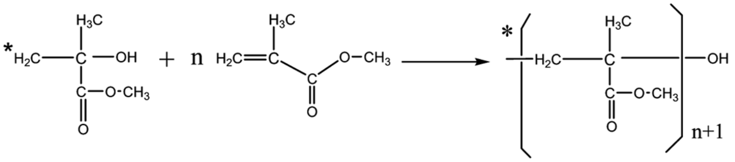
(6)


Saccharum spontaneum cellulose
+ SO4-*
+ HSO4-
n

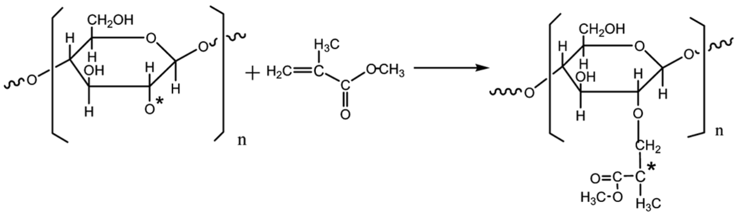
(7)


Saccharum spontaneum cellulose
+ OH*
+ H2O
n

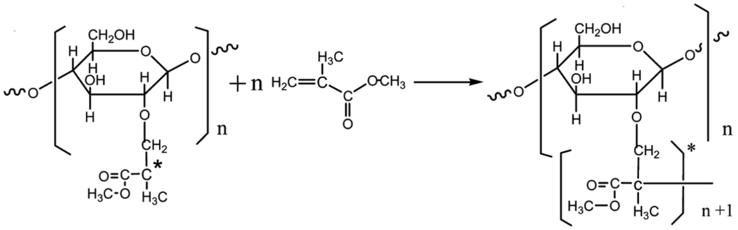
(8)


+ n
n+1

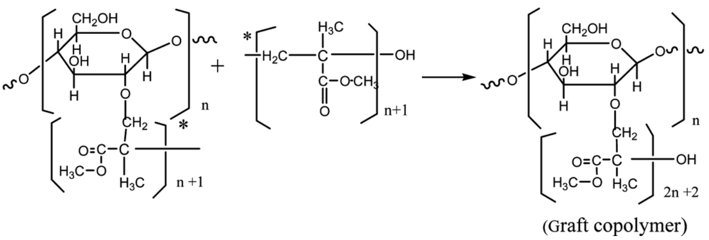
(9)


n

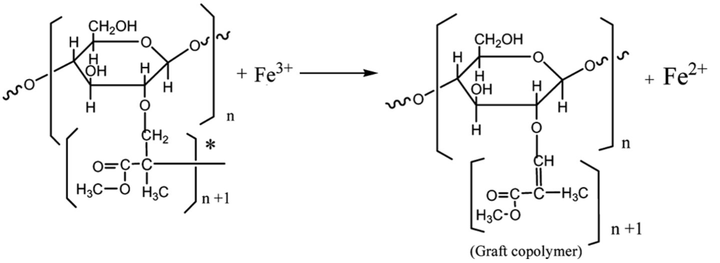
(10)


+ n
n
n +1

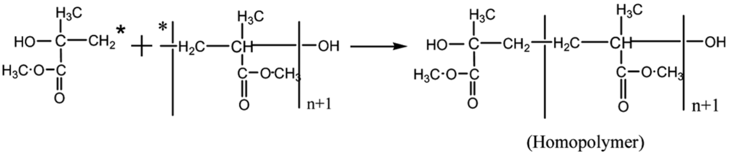
(11)



(12)



(13)



(14)

On the basis of this mechanism it can be concluded that microwaves (MW), SO_4^{-*}, and OH^* 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 SO_4^{-*} (Equation (7)) 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 macro-radical of *S. spontaneum* fiber (Equation (8)). Similarly, OH^* radicals react with active monomer molecules (Equation (4)), which further react with monomer moieties, thereby resulting in active homopolymer (Equation (9)). MWR also initiates the grafting reaction by generating macro-radical onto *S. spontaneum* fiber and monomer chains (Equations (3) and (5)). Moreover, the reaction between active backbone and monomer gives active graft copolymer, which further reacts with monomers and the grafting propagates (Equations (10) and (11)). Termination of grafting may occur by either process (Equation (12) or Equation (13)) or both. Presence of Fe^{3+} has a great impact on graft yield as it is involved in the termination of growing chains. Since the Fe^{3+} is produced by the reaction between FAS with KPS (Equation (1)), the relative amounts of KPS and FAS in the initiating system play an important role in graft yield. Initially, the Fe^{2+}

ions are oxidized to Fe^{3+} with the generation of SO_4^{-*} ions, which further propagate the polymerization reaction. However, an increase in Fe^{3+} ion concentration attacks the growing graft copolymer chains, thereby resulting in termination of the reaction with the reduction of Fe^{3+} to Fe^{2+} (Equation (13)). The reactions between growing MMA chains also result in termination of the reaction and formation of homopolymer (Equation (14)). Hence, the concentrations of initiator and monomer, variations of time, microwave power, 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 Time

Figure 1 shows the effect of reaction time on the %GY, and it is clear that as reaction time increases, %GY increased gradually, reached maximum value in 2 min, and then decreased. The increase in grafting yield with time could be explained on the basis of interactions between MW and *S. spontaneum* backbone as well as SO_4^{-*} and *S. spontaneum* backbone that are increased with increase in time interval, resulting in more generation of free radical sites on the backbone as well as MMA chains, thereby giving rise to more %GY. However, a decrease in %GY beyond the 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 the optimum reaction time, thereby resulting in decreased %GY.

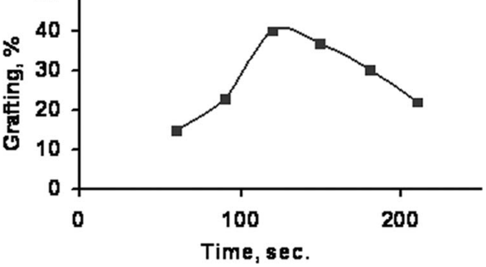


Figure 1. Effect of reaction time on grafting. *S. spontaenum* fiber, 0.5 g; [MMA], 2.45×10^{-3} molL^{-1}; FAS:KPS, 1:0.5; pH, 7; solvent, 30 mL; MW %, 80.

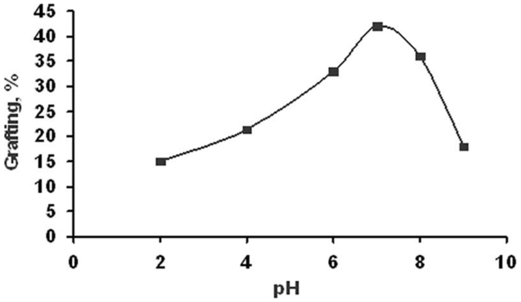


Figure 2. Effect of pH on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} molL^{-1}; time, 120 s; FAS:KPS, 1:0.5; solvent, 30 mL; MW %, 80.

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 7.0 (Figure 2). Further decrease or increase in pH resulted in decreased grafting yield. This could be due to premature termination of the polymerization with increase in pH.

Effect of Solvent

It is evident from Figure 3, 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.

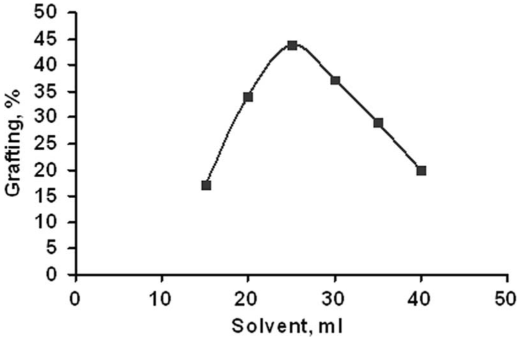


Figure 3. Effect of solvent on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} molL^{-1}; time, 120 s; FAS:KPS, 1:0.5; pH, 7; MW %, 80.

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

Effect of Molar Ratio of Initiator

It has been observed that under the influence of microwave radiation, a small amount of initiator (FAS:KPS = 1:0.250) was needed for achieving the maximum %GY as compared to the conventional methods. This can be due to the fact that MWR was also involved in the initiation of grafting reaction (Equations (3) and (5)). The graft copolymerization was conducted at different molar ratios of FAS-KPS and it was found that %GY was greatly influenced by FAS-KPS molar ratio (Figure 4). Initially, the percentage graft yield was found to increase with increase in molar ratio, but after reaching the 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+} is oxidized to Fe^{3+} on reaction with KPS, resulting in generation of more and more SO_4^{-*}, which initiated the grafting reaction by the 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 a decreased graft yield. It was also observed that formation of homopolymer was quite low at lower initiator concentration, while

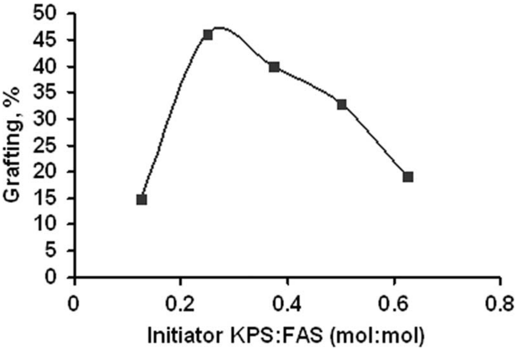


Figure 4. Effect of concentration of initiator (FAS:KPS molar ratio) on grafting. *S. spontaneum* fiber, 0.5 g; [MMA], 2.45×10^{-3} molL^{-1}; time, 120 s; pH, 7; solvent, 25 mL; MW %, 80.

there was 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 (Equations (1) and (13)).

Effect of Monomer Concentration

It was observed that with increase in concentration of MMA, %GY increased continuously and reached a maximum value (50%) at 2.94×10^{-3} mol/L (Figure 5). 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 gives 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. sponteneum* 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; thus, low graft yield was observed beyond optimum monomer concentration.

Effect of MW Power

Grafting was found to increase with increase in MW power up to 70%, and further increase in MW power resulted in decreased %GY (Figure 6). This behavior could be explained by an increase in the graft yields as power is increased, thus generating more macro-radicals. At

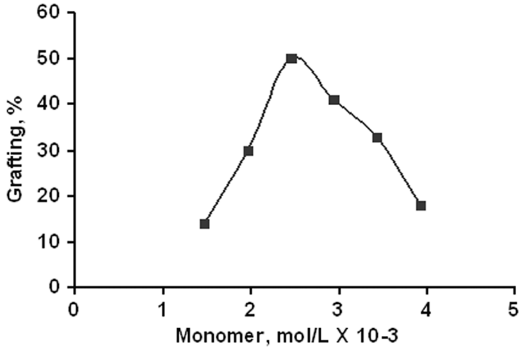


Figure 5. Effect of monomer concentration on grafting. *S. spontaneum* fiber, 0.5 g; time, 120 s; FAS: KPS, 1:0.25; pH, 7; solvent, 25 mL; MW %, 80.

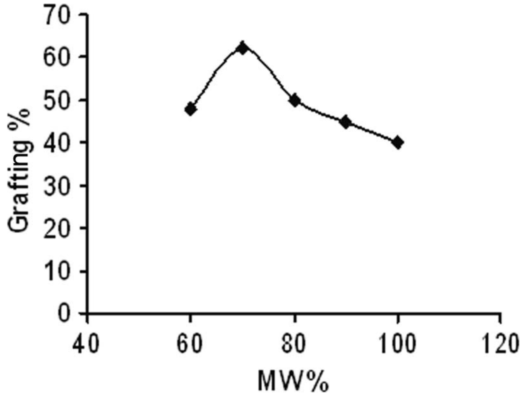


Figure 6. Effect of microwave power on grafting. *S. spontaneum* fiber, 0.5 g; time, 120 s; [MMA], 2.45×10^{-3} molL^{-1}; FAS: KPS, 1:0.25; pH, 7; solvent, 25 mL.

MW power more than 70%, yield starts decreasing, which may be due either to more homopolymerization at high powers or to the decomposition of graft copolymers, which may take place at MW power greater than 70%.

Characterization of Graft Copolymers

Fourier Transform-Infrared (FT-IR) Spectroscopy

S. spontaneum L fiber showed peaks at 3390 cm^{-1} (–OH), 2921 cm^{-1} (C–H stretching), and 1436 cm^{-1} and 1052 cm^{-1} arising from C–C, C–O stretchings, respectively. On grafting, IR bands due to characteristic functional groups (–COOCH$_3$) incorporated into *S. spontaneum* L have been observed at 1732.9 cm^{-1} (C=O) and 1058.6 cm^{-1} (C–O) apart from the usual bands observed in the case of ungrafted fiber (Figures 7 and 8).

Scanning Electron Microscopy (SEM) Analysis

The changes in the topography and morphology of fiber surfaces were studied by SEM (Figures 9 and 10). It can be observed that the surface of the grafted fibers is extremely rough in comparison with the ungrafted fiber (Figures 9 and 10), which is attributed to the high graft density. Research has 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

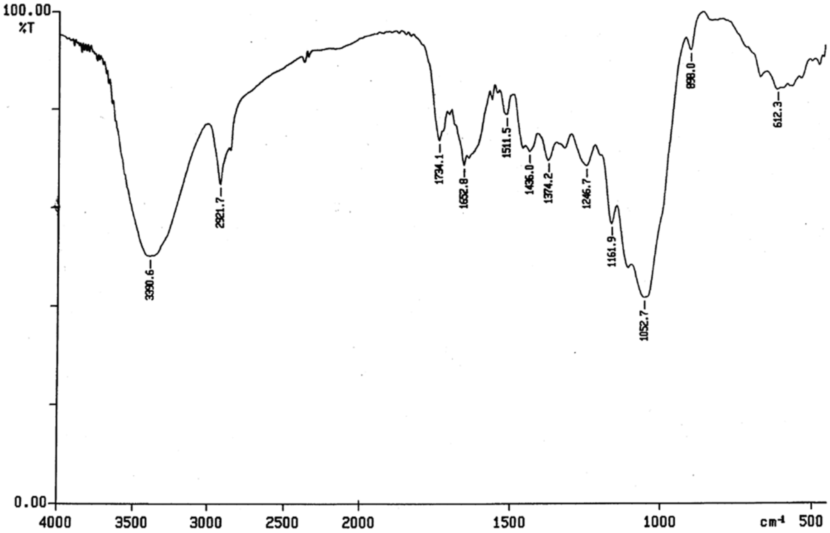


Figure 7. IR spectra of *S. spontaneum* fiber.

in surface area for bonding and mechanical interlocking.[27] Therefore, the rough surfaces are expected to be beneficial for improvement of adhesion in the case of graft copolymer and hence for improvement of the mechanical performance of the composites.

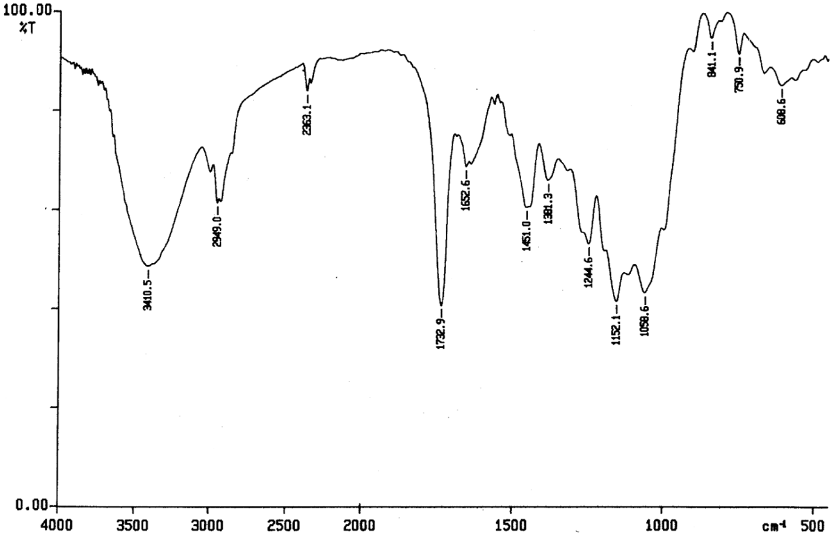


Figure 8. IR spectra of Ss-g-poly(MMA).

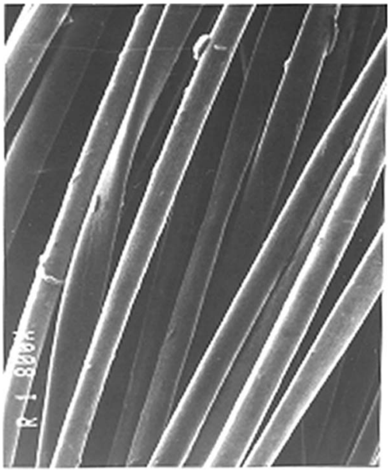


Figure 9. Scanning electron micrograph of *S. spontaneum* fiber.

X-RD Studies

As is evident from Figure 11, percentage crystallinity and crystallinity index were found to decrease with increase in percentage grafting of MMA onto *S. spontaneum* fiber. Since the incorporation of monomer moiety in the backbone impairs the natural crystallinity of the fiber, graft copolymerization of MMA onto *S. spontaneum* fiber resulted in

Figure 10. Scanning electron micrograph of Ss-g-poly(MMA).

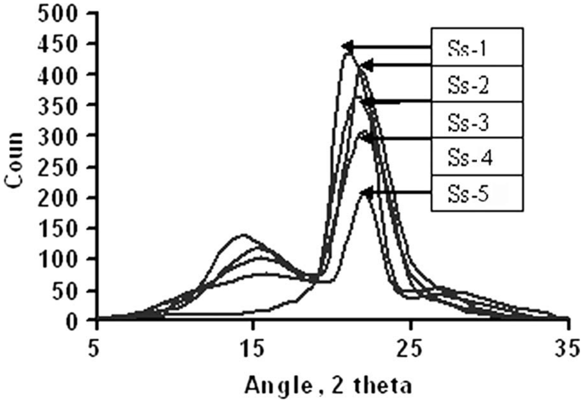


Figure 11. X-ray diffraction study; Ss-1 = *S. spontaneum* fiber; Ss-2 = Ss-g-poly(MMA), [GY = 15.00%]; Ss-3 = Ss-g.poly(MMA), [GY = 29.00%]; Ss-4 = Ss-g-poly(MMA), [GY = 44.00%]; Ss-5 = Ss-po1y(MMA), [GY = 62.3%].

impaired crystallinity and increased the amorphous region of the fiber (Table II). Thus, with increase in percentage grafting, the percentage crystallinity and crystallinity index decreased along with the reduction in stiffness and hardness. Crystallinity index (C.I.) is the quantitative measure of the orientation of the crystal lattice to the fiber axis. Lower crystallinity index in the 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-copolymers.

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

			At 2θ scale			
Sample no.	Sample	%GY	I_{22}	I_{18}	%Cr	C.I.
1	*S. spontaneum* L. fiber	–	436	75	85.32	0.82
2	Ss-g-poly MMA-1	15	400	76	84.03	0.81
3	Ss-g-poly MMA-2	29.00	365	80	82.02	0.78
4	Ss-g-poly MMA-3	44.00	310	80	79.48	0.74
5	Ss-g-poly MMA-4	62.30	206	70	74.63	0.66

TGA, DTA, and DTG

TGA of ungrafted and grafted *S. spontaneum* was studied as a function of wt.% loss versus temperature. Cellulosic *S. spontaneum* degrades by dehydration, glycogen formation, and depolymerization. In the case of *S. spontaneum*, two-stage decomposition was found in the temperature range from 225° to 320°C with 60% weight loss and in the range 320°–416°C with 25.33% weight loss. The former stage is attributed to the loss by dehydration and volatilization processes, whereas the latter stage is attributed to the loss by depolymerization process. Ss-g-poly(MMA) showed single-stage decomposition. After the initial loss of moisture, the decomposition continues beyond 250°C with 77.67% weight loss and 05.80% weight loss in the temperature range from 385° to 451°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.

In the case of DTA studies, *S. spontaneum* was found to exhibit two exothermic peaks at 313°C (63 μV) and 422°C (137 μV). The exothermic peak at 313°C corresponds to decomposition stage between 225° and 320°C while the exothermic peak at 422°C corresponds to second decomposition stage (320°–416°C) in TGA (Figure 12). However, Ss-g-poly(MMA) exhibited exothermic decomposition at 382°C (31 μV).

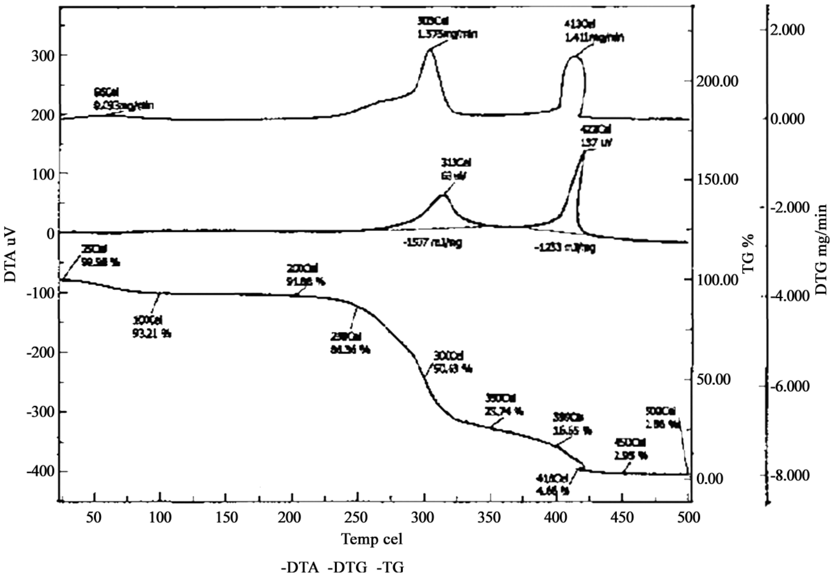


Figure 12. TGA, DTA, and DTG curves of *S. spontaneum* fiber.

An exothermic peak arising at 382°C corresponds to the thermal decomposition taking place in the temperature range between 250° and 385°C in TGA (Figure 13).

DTG analysis of grafted and ungrafted *S. spontaneum* was studied as a function of rate of weight loss (mg/min) versus temperature. In the case of *S. spontaneum* decomposition at 303°C and 413°C was found with 1.575 mg/min and 1.411 mg/min weight loss, respectively. However, in the case of Ss-g-poly(MMA), the decomposition was observed at 365°C and 378°C with 0.826 mg/min and 1.399 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, whereas in the case of Ss-g-poly(MMA), the rate of thermal decomposition is lower. The better thermal resistance of graft copolymer was due to the incorporation of more covalent bonding through inclusion of poly(MMA) chains onto the polymer backbone (Figures 12 and 13).

Moisture Absorbance Study of *S. spontaneum* and Ss-g-poly(MMA)

It was observed that the graft copolymerization of MMA onto *S. spontaneum* has a great impact on the moisture absorbance behavior

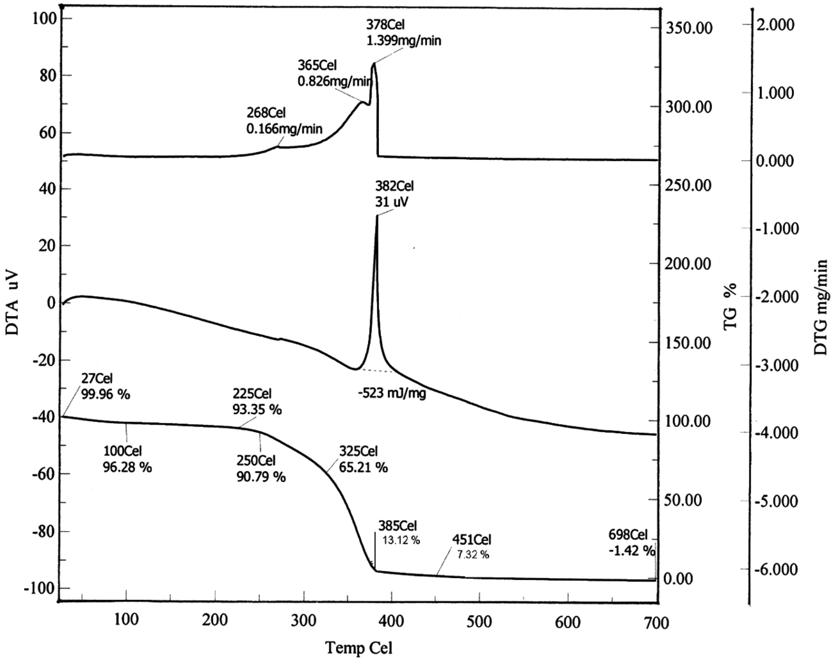


Figure 13. TGA, DTA, and DTG curves of Ss-g-poly(MMA).

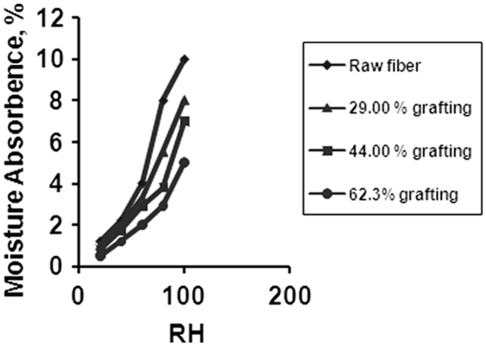


Figure 14. Effect of grafting on moisture absorbance at different humidity levels.

(Figure 14). There was a decrease in percent moisture absorbance with increase in graft yield. This could be due to the fact that with increase in graft yield, the sites vulnerable for moisture get blocked with poly(MMA) chains.

Acid and Base Resistance Study of *S. spontaneum* and Ss-g-poly(MMA)

It was observed that acid and base resistance of the fiber increases with increase in percent grafting (Figures 15 and 16). This is due to the fact that poly(MMA) chains grafted onto *S. spontaneum* fiber have less affinity for acid and base than hydroxyl groups and other functional groups present in ungrafted fiber. Therefore, the resistance of fiber towards acid increases with increase in grafting.

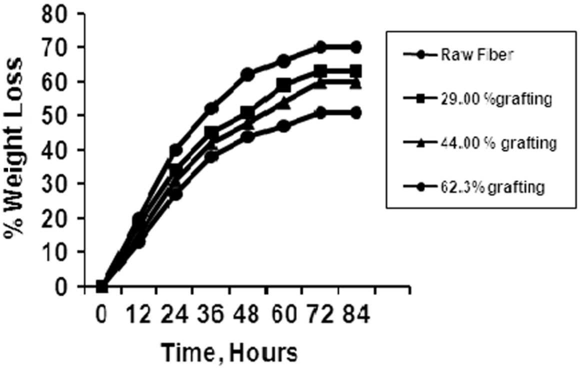


Figure 15. Effect of grafting on acid resistance.

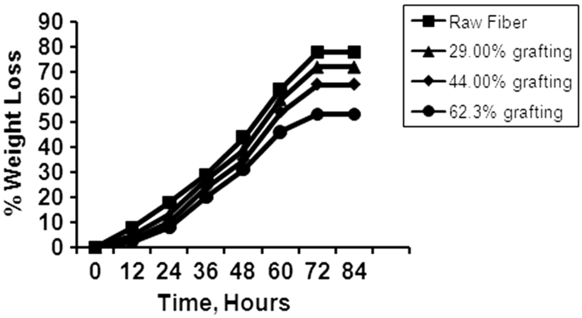


Figure 16. Effect of grafting on base resistance.

CONCLUSIONS

Microwave irradiation-induced grafting is an effective method for modifying the properties of natural fibers in terms of graft yield, time consumption, and cost effectiveness. Thus with increase in grafting, percent crystallinity and crystallinity index decreased, but the incorporation of poly(MMA) chains on backbone polymer could result in higher acid, base, and thermal resistance as well as in decrease in moisture absorbance as compared to the raw fiber. Moreover, on grafting, the morphological changes with respect to surface topography take place and graft copolymer was found to exhibit different physical and chemical properties than raw fiber.

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