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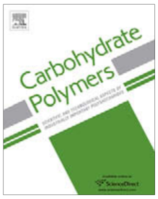

Characterization and evaluation of methyl methacrylate-acetylated *Saccharum spontaneum* L. graft copolymers prepared under microwave

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ABSTRACT

Hybridization of the natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. Synthesis of graft copolymers of methyl methacrylate (MMA) onto acetylated *Saccharum spontaneum* L. fiber using ferrous ammonium sulphate–potassium per sulphate (FAS–KPS) redox initiator under the influence of microwave radiation (MWR) was carried-out. Different reaction parameters such as time, initiator molar ratio, monomer concentration, microwave power, pH and solvent were optimized to get maximum graft yield (72.2%). On grafting, percentage crystallinity decreases rapidly with reduction in its stiffness and hardness. The graft copolymers thus formed were characterized by FTIR, SEM, XRD, TGA, DTA and DTG techniques. Moreover, graft copolymers have been found to be more moisture resistant and also showed higher chemical and thermal resistance.

1. Introduction

Hybridization of the natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. Grafting involves attachment of polymer chains, usually monomer, to the back-bone polymer. It is one of the methods to increase the compatibility between synthetic polymers and cellulose. It has been observed that monomers with polar groups favor the absorption of microwave radiations and modification of fibrous proteins and cellulose through graft copolymerization has been reported (Chauhan, Guleria, Misra, & Kaur, 2000). MWR technique reduces the extent of physico-chemical stresses to which the fibers are exposed during the conventional techniques. It has been reported that properties of fibers treated under MWR are same or even better than those of fibers modified through other conventional techniques (Kaith & Susheel, 2008). Recently grafting of butylacrylate, acrylic acid and acrylonitrile onto starch, acrylamide onto LDPE (low density polyethylene) films (Gupta, Anjum, & Gupta, 2000) and butyl methacrylate onto wool fibers (Gabriel et al., 1998), has been studied using redox initiators under microwave irradiation. Methyl methacrylate has been reported to polymerize under microwave irradiation using very low concentration of initiator (Zhenping, Xiulin, Mingchen, Chen, & Zhang, 2003). Grafting of acrylamide (Singh, Tiwari, Tripathi, & Sanghi, 2004a) and acrylonitrile (Singh, Tiwari, Tripathi, & Sanghi, 2004c) onto chitosan and acrylonitrile onto Guar gum (Singh, Tiwari, Tripathi, & Sanghi, 2004b) under microwave conditions, in very short reaction time and in absence of any redox initiator or catalyst has been reported. Polyacrylamide was graft copolymerized onto chitosan using MWR and maximum grafting 169% was observed in 1.16 min, under optimum reaction conditions (Singh, Tiwari, Tripathi, & Sanghi, 2006).

Grafting under MWR has advantages in terms of time consumption and cost effectiveness. In the present study MMA has been graft copolymerized onto acetylated *S. spontaneum* under the influence of MWR and evaluation of its different physical, chemical and thermal properties have been carried-out.

2. Experimental

2.1. Materials

2.1.1. Purification of materials

Acetylated *S. spontaneum* L. fiber was purified by soxhlet refluxing in acetone for 72 h (Kaith, Singha, & Gupta, 2003). MMA (s. d. fine) was purified by washing with 5% NaOH and subsequent drying over anhydrous Na_2SO_4 followed by distillation. FAS (s. d. fine) was recrystallized from hot water and KPS (s. d. fine) was used as received.

2.2. Microwave equipment

Microwave equipment (LG, Model No. MG-3937C, 1200W) was used for all experiments. The average bulk temperature at the end of the reaction was measured by inserting thermometer in the

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reaction mixture and was found to be less than 100 °C as all the reactions were performed in aqueous medium.

2.3. Methods

2.3.1. Acetylation of *S. spontaneum L.* fiber

Acetylation of *S. spontaneum* L. fiber was carried-out as per the standard method (Furniss, Hannaford, Smith, & Tatchell, 2004).

2.3.2. Graft copolymerization

Activation of acetylated *S. spontaneum* L. fiber (0.5 g) was done at room temperature by immersing 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. A known amount of monomer was added drop by drop with continuous stirring to the reaction mixture and the reaction was carried-out under the influence of MWR for a definite time interval. Homopolymer was extracted with acetone and the graft copolymer thus obtained was dried at 50 °C till a constant weight was attained. Percentage polymer loading (%PL), percentage graft yield (%GY), percentage graft efficiency (%GE) and percentage homopolymer (%HM) formed (Table 1) were calculated as (Princi et al., 2005):

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

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

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

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

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

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

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

2.4. Infrared spectroscopy (IR)

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

2.5. Scanning electron microscopy (SEM)

Scanning electron micrograph (SEM) was obtained using JEOL – JSM – 6100 – scanning electron microscope.

2.6. X-ray diffraction (XRD) studies

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 degree with 0.5 or 1.0 mm of divergent and anti-scattering slit. Crystallinity index (CI) which measured the orientation of the cellulose crystals with respect to fiber axis was determined by using the wide angle X-ray diffraction

Table 1
Evaluation of optimum reaction parameter for grafting of MMA onto acetylated *S. spontaneum*.

Sr. No.	Reaction time (s)	pH	Solvent (ml)	Molar ratio (FAS:KPS)	[MMA] × 10^{-3} (mol/L)	%MW	%PL[a]	%GY[b]	%GE[c]	%HM[d]
1	60	7.0	20	1: 0.500	2.45	80	44.4	21.2	47.7	52.3
2	90	7.0	20	1: 0.500	2.45	80	46.3	26.8	57.8	42.2
3	120	7.0	20	1: 0.500	2.45	80	64.2	43.7	68.0	32.0
4	150	7.0	20	1: 0.500	2.45	80	52.3	36.9	70.5	29.5
5	180	7.0	20	1: 0.500	2.45	80	51.2	26.2	51.1	48.9
6	90	2.0	20	1: 0.500	2.45	80	45.2	18.6	41.1	58.9
7	90	4.0	20	1: 0.500	2.45	80	47.9	27.3	56.9	43.1
8	90	6.0	20	1: 0.500	2.45	80	52.3	35.7	68.8	31.2
9	90	7.0	20	1: 0.500	2.45	80	67.7	46.9	69.2	30.8
10	90	8.0	20	1: 0.500	2.45	80	62.4	34.8	55.7	44.3
11	90	9.0	20	1: 0.500	2.45	80	58.9	21.9	37.1	62.9
12	90	7.0	15	1: 0.500	2.45	80	49.1	19.9	40.5	59.5
13	90	7.0	20	1: 0.500	2.45	80	53.4	38.1	71.3	28.7
14	90	7.0	25	1: 0.500	2.45	80	72.1	49.8	69.0	31.0
15	90	7.0	30	1: 0.500	2.45	80	65.3	38.3	58.3	41.7
16	90	7.0	35	1: 0.500	2.45	80	55.2	27.4	49.6	50.4
17	90	7.0	40	1: 0.500	2.45	80	51.6	22.2	43.3	56.7
18	90	7.0	25	1: 0.125	2.45	80	55.1	19.4	35.2	64.8
19	90	7.0	25	1: 0.250	2.45	80	75.2	52.4	69.6	30.4
20	90	7.0	25	1: 0.375	2.45	80	71.9	45.5	63.2	36.8
21	90	7.0	25	1: 0.500	2.45	80	70.8	34.1	48.1	51.9
22	90	7.0	25	1: 0.625	2.45	80	61.6	26.8	43.5	56.5
23	90	7.0	25	1: 0.250	1.47	80	54.4	15.2	27.9	72.1
24	90	7.0	25	1: 0.250	1.96	80	58.7	34.6	58.9	41.1
25	90	7.0	25	1: 0.250	2.45	80	77.3	62.4	80.7	19.3
26	90	7.0	25	1: 0.250	2.94	80	72.9	49.9	68.4	31.6
27	90	7.0	25	1: 0.250	3.43	80	66.3	35.7	53.8	46.2
28	90	7.0	25	1: 0.250	2.45	60	61.4	45.6	74.3	25.8
29	90	7.0	25	1: 0.250	2.45	70	75.3	64.3	85.3	14.7
30	90	7.0	25	1: 0.250	2.45	80	81.3	72.2	88.2	11.8
31	90	7.0	25	1: 0.250	2.45	90	71.2	47.2	66.2	33.8
32	90	7.0	25	1: 0.250	2.45	100	69.8	42.1	60.3	39.7

[a] Percentage polymer loading.
[b] Percentage graft yield.
[c] Percent graft efficiency.
[d] Percentage homopolymer.

counts at 2θ-scale close to 22° and 18°. The counter reading at the peak intensity at 22° represent the crystalline part and the peak intensity at 18° corresponds to the amorphous region in cellulose material (Mwaikambo & Ansell, 2002). Percentage Crystallinity (% Cr) and Crystallinity index (CI) were calculated as follows (Agrawal, Manek, Kolling, & Neau, 2003; Reddy & Yang, 2005).

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

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

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

2.7. Thermogravimetric analysis/differential thermal analysis/ differential thermogravimetric analysis (TGA/DTA/DTG)

TGA, *DTA* and *DTG* were carried-out in air on a thermal analyzer (Perkin-Elmer, Pyris Diamond).

2.8. Moisture absorbance study

Moisture absorbance studies at various relative humidities were carried-out as per the standard method (Kaith et al., 2003). Moisture absorbance (%) was found out by placing a known weight (W_i) of dry grafted and ungrafted acetylated samples in a humidity chamber for 2 h and the final weight (W_f) of the samples exposed to a specific RH was taken and calculated as:

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

2.9. Acid and base resistance

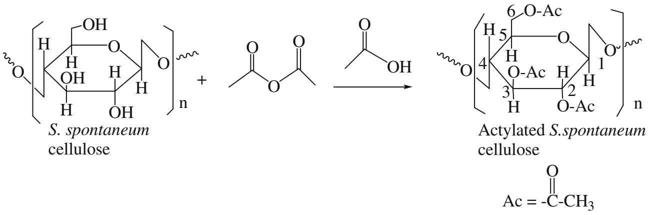
Acid and base resistance studies were carried-out as per the method reported earlier (Kaith et al., 2003). Acid and base resistance was found out by placing a known weight (W_i) in fixed volume of 5 N HCl and 5 N NaOH and the weight of the sample was noted down at 12 h intervals until a constant final weight (W_f) was reached and was calculated as:

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

3. Results and discussion

3.1. Mechanism

C_2, C_3 and C_6 hydroxyls of *S. spontaneum* L. were acetylated using the standard method (Furniss et al., 2004) (Eq. (1)).



(1)

Interaction of $SO_4{}^{-*}$ with H_2O generated OH^* and these free radicals were responsible for free radical generation on back-bone and monomer as well as further chain propagation, thereby, resulted in the formation of graft copolymer along with homopolymer. On the other hand micro wave irradiation also produced free radicals on polymeric back-bone and monomer which could be explained through the following mechanism:

$$Fe^{2+} + {}^{-}O_3S\text{—}O\text{—}O\text{—}SO_3 \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-*} \tag{2a}$$

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

On the basis of this mechanism it could be concluded that MW, $SO_4{}^{-*}$ and OH^* were involved in graft copolymerization. However, in case of grafting carried-out in the absence of swelling agent, initiation of reaction by $SO_4{}^{-*}$ (Eq. (7)) was unlikely to occur as the concentration of persulphate used was very small, whereas in presence of swelling agent, $SO_4{}^{-*}$ reacted with H_2O to generate OH^*, which could also initiate the grafting reaction. The resulted OH^* abstracted acetyl group from the back-bone polymer and generated the macro radical of acetylated *S. spontaneum* fiber (Eq. (6)). Similarly, OH^* radicals reacted with monomer molecules resulting in free radical sites on the monomer (Eq. (8)) which further reacted with monomer moieties, thereby, resulting in active homopolymer (Eq. (9)). MW radiation also initiated the grafting process by generating macro radical onto *S. spontaneum* fiber and monomer chains (Eqs. (5) and (3)). Moreover, reaction between active back-bone and monomer gave active graft copolymer which further reacted with monomers and the grafting propagates (Eqs. (10) and (11)). Termination of grafting may occur by either process (Eq. (12)) or (Eq. (13)) or both. Presence of Fe^{3+} had great impact on graft yield as it was involved in the termination of growing chains. Because Fe^{3+} was produced by the reaction between FAS with KPS (Eq. (2a)), so the relative amounts of KPS and FAS in the initiating system played an important role in graft yield. Initially Fe^{2+} ions get oxidized to Fe^{3+} with the generation of $SO_4{}^{-*}$ ions which further propagate the polymerization reaction. However, increase in Fe^{3+} ions concentration, attacked the growing graft copolymer chains, thereby, resulting in termination of reaction with the reduction of Fe^{3+} to Fe^{2+} (Eq. (13)). Reactions between growing MMA chains also resulted in the termination of reaction with the formation of homopolymer (Eq. (14)). Hence, 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 reaction.

3.2. Optimization of different reaction parameters

3.2.1. Effect of reaction time

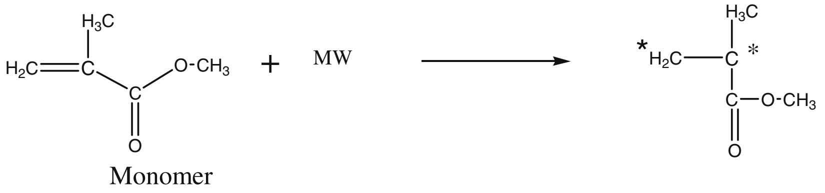
It was found that with increase in reaction time %GY increased gradually and reached maximum value (43.7%) in 90 s (Table 1). Increase in graft yield with time could be explained on the basis of increased interactions between MW, $SO_4{}^{-*}$, monomer and acetylated *S. spontaneum* back-bone resulted in more generation of free radical sites on the back-bone as well as MMA chains. However, decrease in %GY beyond optimum reaction time could be due to predominance of homopolymerization over graft copolymerization and also due to disintegration of poly(MMA) chains grafted on back-bone.

3.2.2. Effect of pH of reaction medium

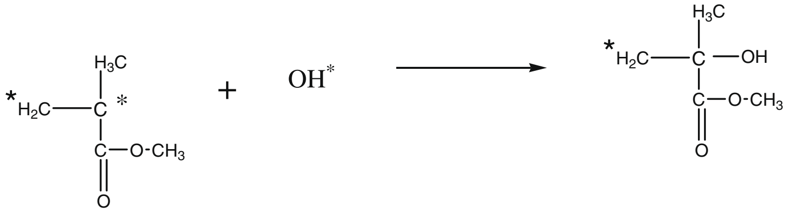
pH of the reaction medium played an important role during the grafting process. Maximum graft yield had been found at pH 7.0 (Table 1). Further decrease or increase in pH resulted in decreased graft yield. This could be due to pre-mature termination of polymerization reaction.

3.2.3. Effect of solvent

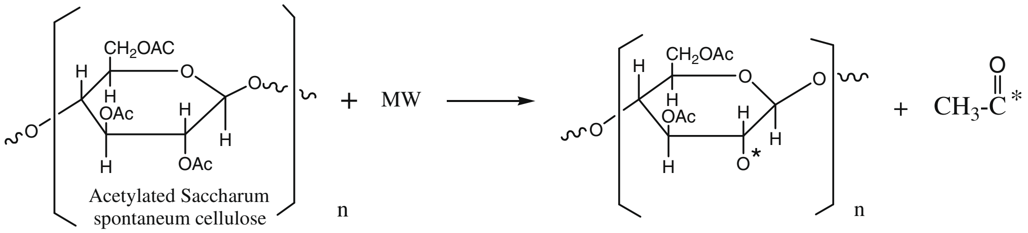
As is evident from (Table 1) that graft yield increased with increase in volume of the solvent and maximum %GY was found at


Monomer
MW

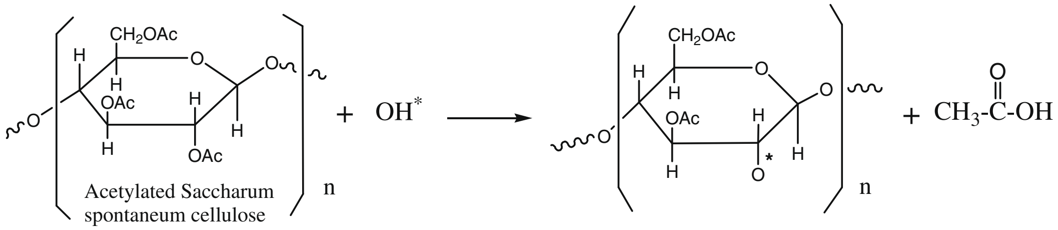
(3)


OH*

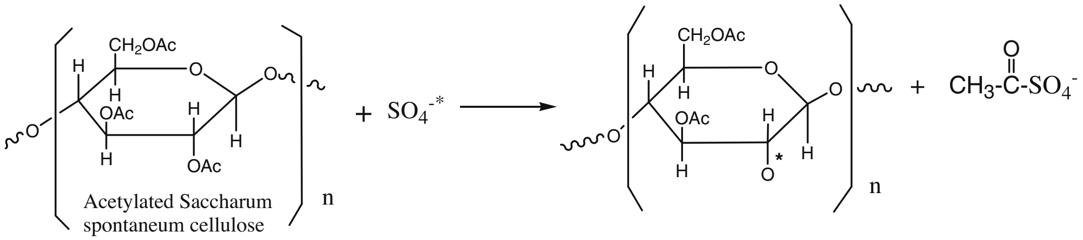
(4)


Acetylated Saccharum spontaneum cellulose
MW
n
n

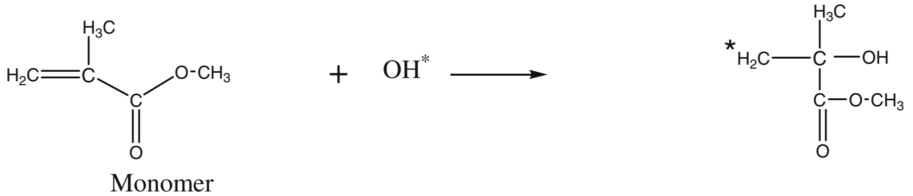
(5)


Acetylated Saccharum spontaneum cellulose
OH*
n
n

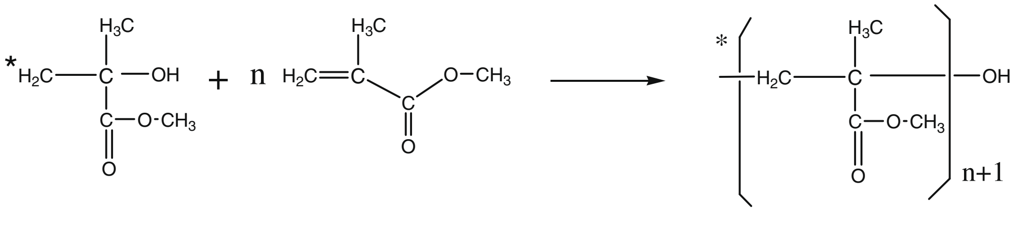
(6)


Acetylated Saccharum spontaneum cellulose
SO4-*
n
n

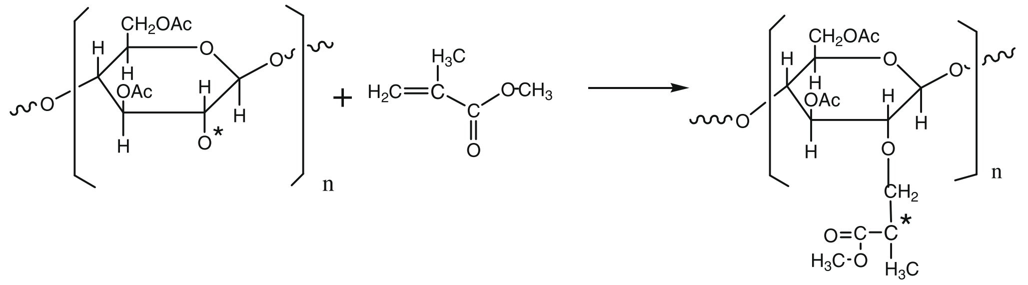
(7)


Monomer
OH*

(8)


n
n+1

(9)



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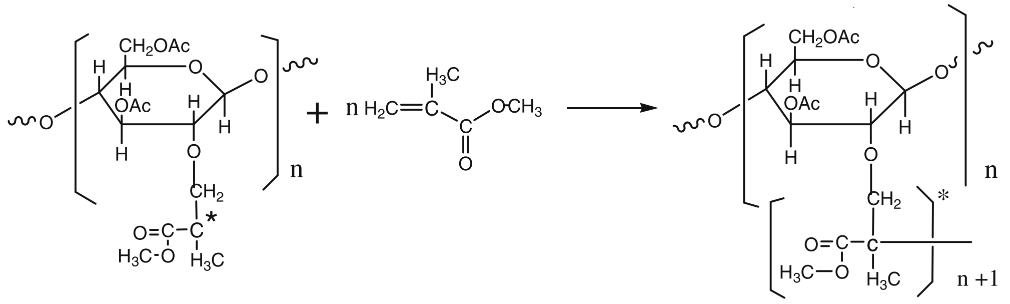

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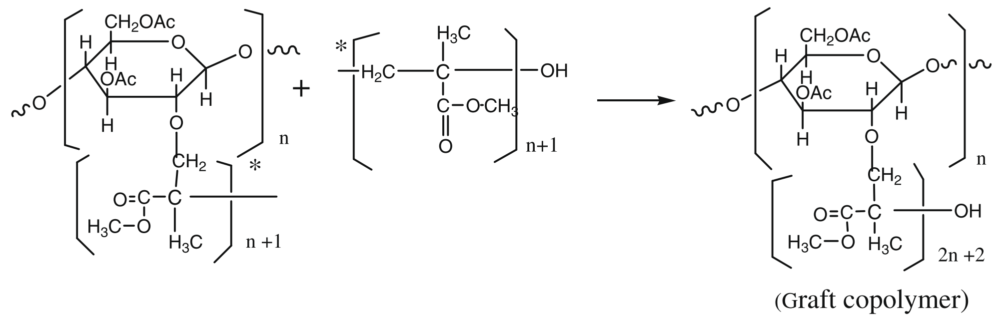

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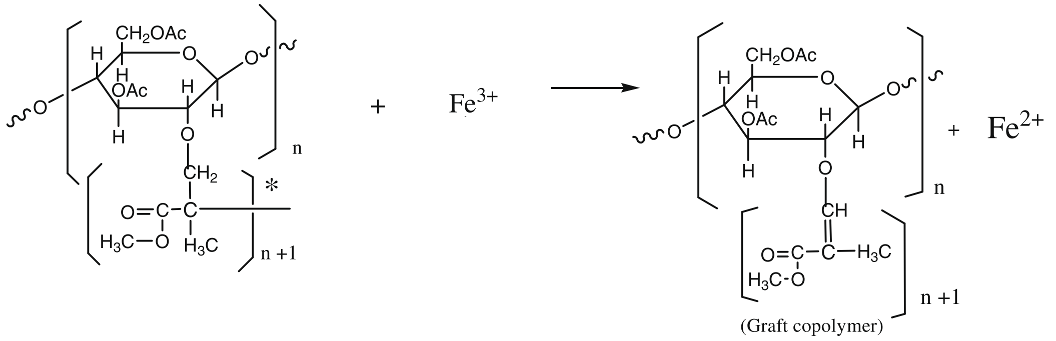
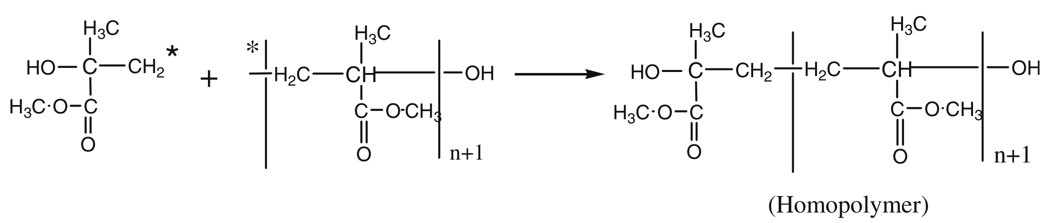


(13)



(14)

25 ml. But further increase in solvent volume resulted in declined percentage grafting. This generally occurs on the setting up of various hydrogen abstraction reactions. This could also be due to decreased SO_4^{-*} and OH^* free radical concentration (Eq. (2b)).

3.2.4. Effect of molar ratio of initiator

It has been observed that under the influence of microwave radiations, small amount of initiator (FAS:KPS = 1:0.250) was involved for getting the maximum %GY as compared to conventional method. It could be due to the fact that MW radiations were also involved in the initiation of grafting reaction (Eqs. (3) and (5)). 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 (Table 1). This could be due to the fact that in the beginning Fe^{2+} gets oxidized to Fe^{3+} on reaction with KPS resulted in generation of more 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 resulted in generation of more Fe^{3+} ions which participated in termination reaction with reduction to Fe^{2+}. It was also observed that formation of homopolymer was considerably less at lower initiator concentration while there was a significant homopolymer formation beyond the critical ratio. This was due to the fact that the excess Fe^{2+} ions concentration beyond optimum concentration resulted in generation of poly(MMA) chains along with excess Fe^{3+} concentration ions which ultimately resulted in termination of growing chains (Eqs. (1) and (13)).

3.2.5. Effect of monomer concentration

It was observed that with increase in concentration of MMA, %GY increased continuously and reached maximum value (62.4%) at 2.94×10^{-3} mol/L (Table 1). 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 back-bone and give rise to graft copolymerization. This lead to depletion in the available MMA concentration as well as a reduction in the active sites on the *S. sponteneum* back-bone as graft copolymerization proceeded further. However, at higher monomer concentration, the primary radicals attacked the monomer instead of reacting with the back-bone polymer, thereby; initiating homopolymerization reaction and thus the low graft yield was observed beyond optimum monomer concentration.

3.2.6. Effect of MW power

Grafting was found to increase with increase in MW power upto 80% and further increase in MW power resulted in decreased %GY (Table 1). This behavior could be explained on the basis that as the

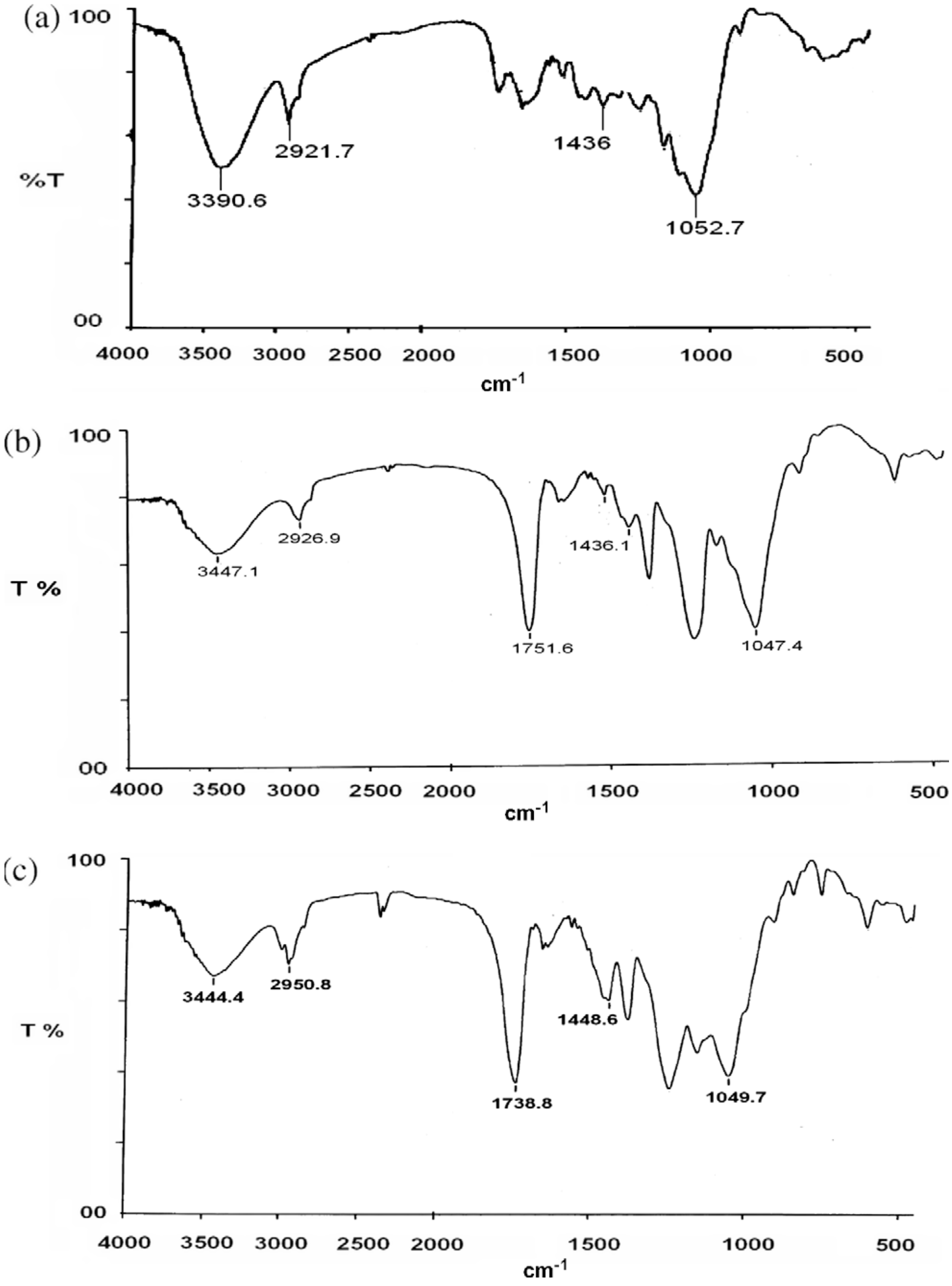


Fig. 1. IR spectra of (a) *S. spontaneum* fiber (b) acetylated fiber (c) Ss-g-poly(MMA).

power was increased, more macro radicals were generated, which resulted in increased graft yields. At MW power more than 80%, yield started decreasing which may be either due to more homopolymerization at high powers or disintegration of graft copolymers may take place at MW power greater than 80%.

3.3. Characterization of graft copolymers

3.3.1. Fourier transform-infrared (FT-IR) spectroscopy

Saccharum spontaneum L. fiber showed broad peaks at 3390.6 cm^{-1} due to hydrogen bonded (–OH). 2921.7 cm^{-1} due to C–H stretching and 1436, 1052.7 cm^{-1} arising from C–C and C–O stretching, respectively (Fig. 1a). 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 1751.6 cm^{-1} due to C=O and intensity of the broad peak due to hydrogen bonded –OH was found to decrease (Fig. 1b). On grafting, IR bands due to characteristic functional groups incorporated into acetylated *S. spontaneum* L. appeared at 1738.8 cm^{-1} due to C=O of MMA (Fig. 1c).

3.3.2. Scanning electron microscopy (SEM)

The changes in the topography and morphology of fiber surfaces were studied by SEM (Fig. 2a–c). It can be observed that the surface of the acetylated (Fig. 2b) and grafted (Fig. 2c) fibers is highly rough in comparison with the ungrafted fiber (Fig. 2a), which is attributed to the high graft density. Some researches 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. Therefore, the rough surfaces are expected to be beneficial for improvement of adhesion in case of graft copolymer and hence improve the mechanical performance of composites.

3.3.3. XRD studies

Percentage crystallinity and crystallinity index were found to decrease in acetylated *S. spontaneum* (Ss-2; %Cr, 84.2I & CI, 0.81) and grafted samples (Ss-3; %Cr, 83.69 & CI, 0.80 to Ss-6; %Cr, 71.77 & CI, 0.60) in comparison to original back-bone (Ss-1; %Cr, 85.32 & CI, 0.82) (Fig. 3). Since incorporation of acetyl group

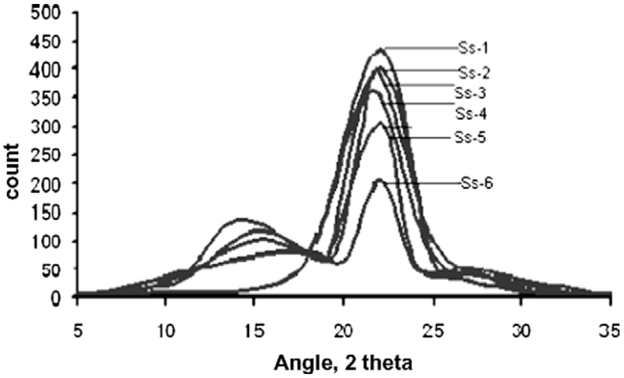


Fig. 3. X-ray diffraction studies.

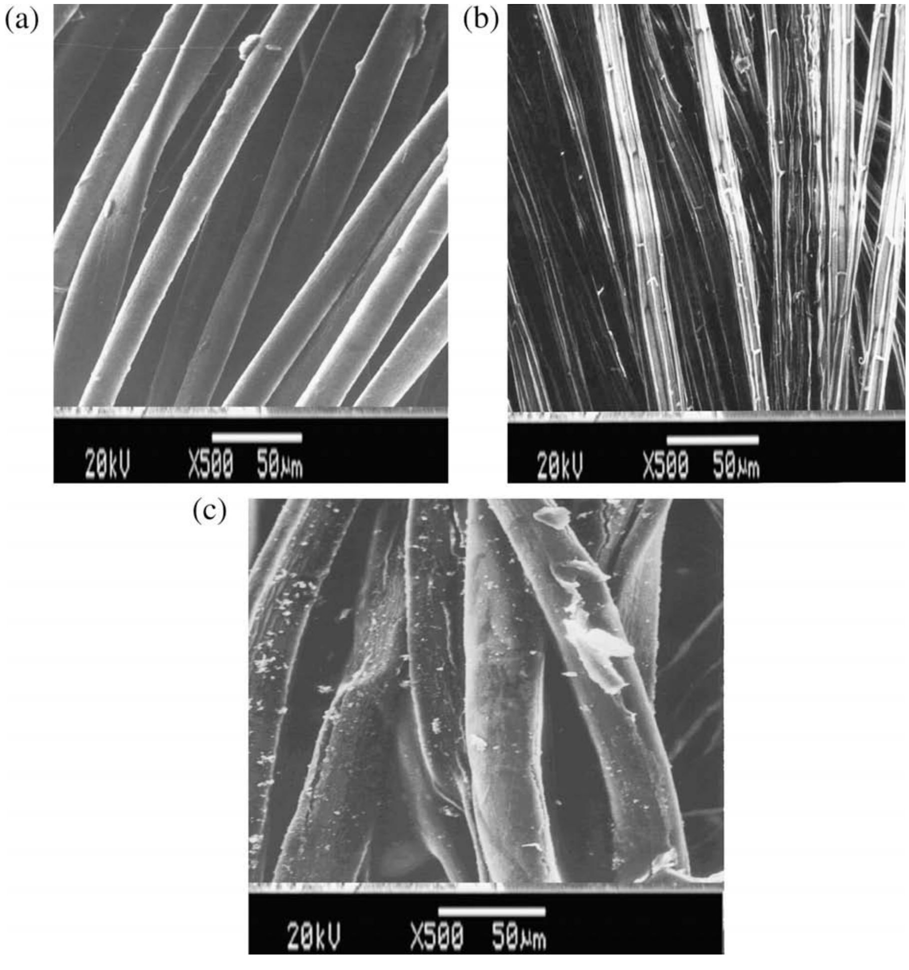


Fig. 2. SEM of (a) *S. spontaneum* fiber (b) acetylated fiber (c) Ss-g-poly(MMA).

and monomer moiety in the back-bone impairs the natural crystallinity of the fiber, therefore, graft co-polymerization of MMA onto acetylated *S. spontaneum* fiber resulted in impaired crystallinity, and increased amorphous region of the fiber. Thus with increased in percentage grafting, the percentage crystallinity and crystallinity index decreased along with reduction in stiffness and hardness.

3.3.4. TGA, DTA and DTG analysis of ungrafted, acetylated and grafted S. spontaneum

TGA of ungrafted, acetylated and grafted *S. spontaneum* were studied as a function of wt.% loss vs temperature. During thermal analysis, initially the samples got degraded by dehydration, glycogen formation and depolymerization. In case of *S. spontaneum*, two-stage decomposition was found in the temperature range

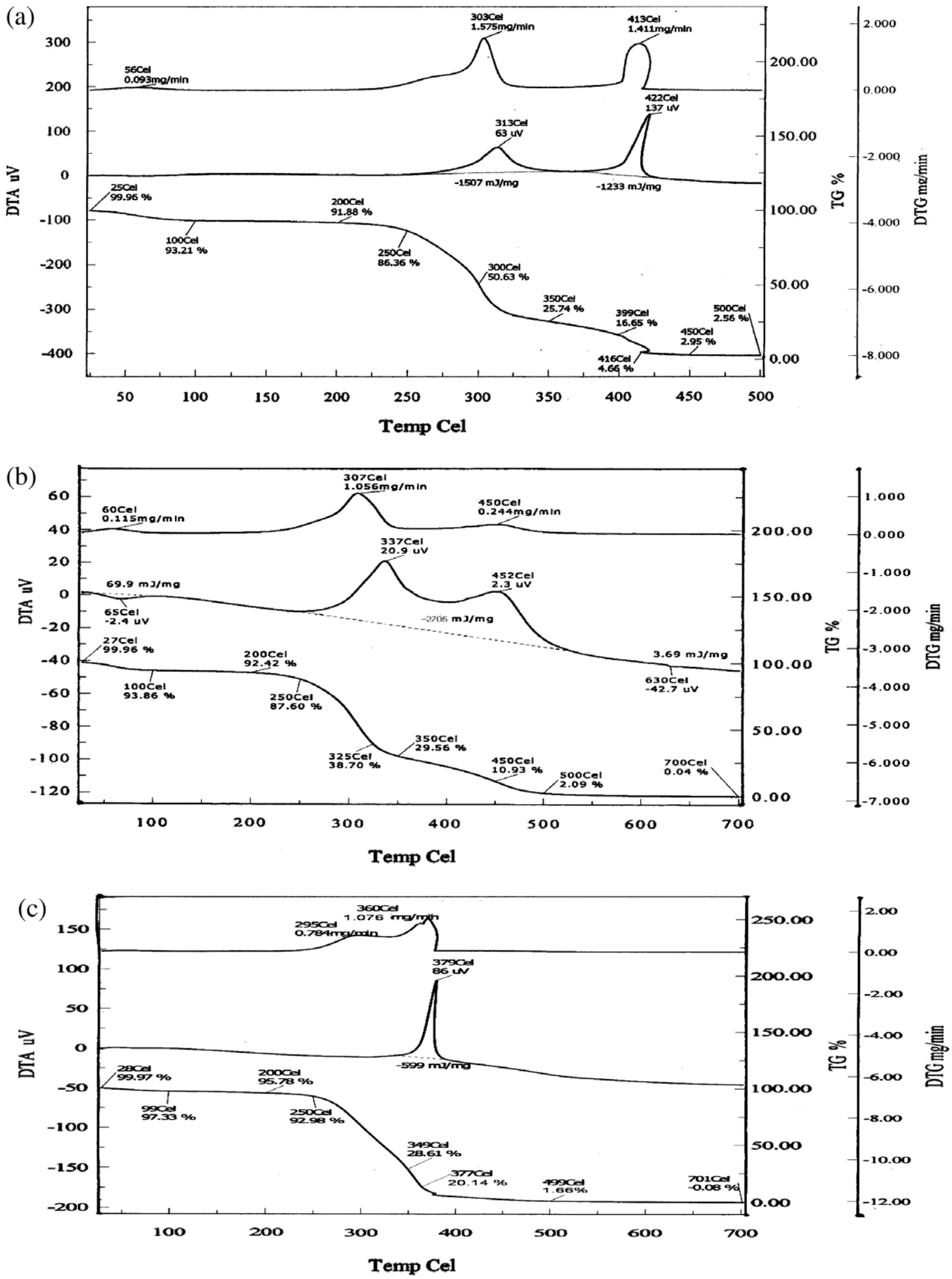


Fig. 4. TGA, DTA and DTG curves of (a) *S. spontaneum* fiber (b) acetylated fiber (c) Ss-g-poly(MMA).

from 225 to 320 °C with 60% weight loss and 320–416 °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 case of acetylated *S. spontaneum*, also two-stage decomposition was found in the temperature range from 250 to 325 °C with 48.90% weight loss and 325–500 °C with 36.61% weight loss.

Ss-g-poly(MMA) showed single stage decomposition. After the initial loss of moisture, decomposition continued beyond 250–499 °C with 91.32% 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 back-bone polymer through covalent bonding, thereby resulting in reinforcement of amorphous region.

In 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). 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 (Fig. 4a). However, acetylated fiber showed broad exothermic decomposition at 337–452 °C (−2706 mJ/mg) (Fig. 4b) and Ss-g-poly(MMA) exhibited exothermic decomposition at 379 °C (−599 mJ/mg). In case of Ss-g-poly(MMA) exothermic peak arising at 359 °C corresponds to the thermal decomposition taking place in the temperature range between 250 and 499 °C in TGA (Fig. 4c).

DTG analysis of grafted, acetylated and ungrafted *S. spontaneum* were studied as a function of rate of weight loss (mg/min) vs temperature. In case of *S. spontaneum* decompositions at 303 and 413 °C were found at the rate of 1.575 mg/min and 1.411 mg/min weight loss, respectively. However, in case of acetylated fiber decomposition at 307 and 450 °C occurred with 1.056 and 0.224 mg/min weight loss, and in Ss-g-poly(MMA), decomposition was observed at 360 °C with 1.076 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 than acetylated and grafted fibers. The better thermal resistance of acetylated and graft copolymer were due to incorporation of more covalent bonding through inclusion of acetyl groups and poly(MMA) chains onto back-bone polymer (Fig. 4a–c).

3.3.5. Moisture absorbance study

It was found that graft co-polymerization of MMA onto acetylated *S. spontaneum* has a great impact on the moisture absorbance behavior (Fig. 5). 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, converting the fiber less sensitive towards moisture.

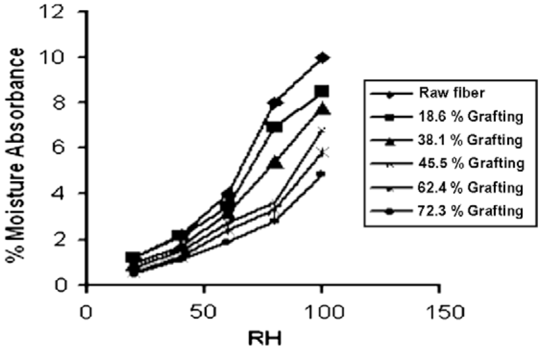


Fig. 5. Effect of grafting on moisture absorbance at different humidity levels.

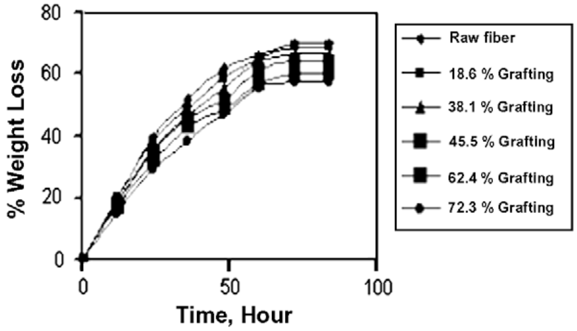


Fig. 6. Effect of grafting on acid resistance.

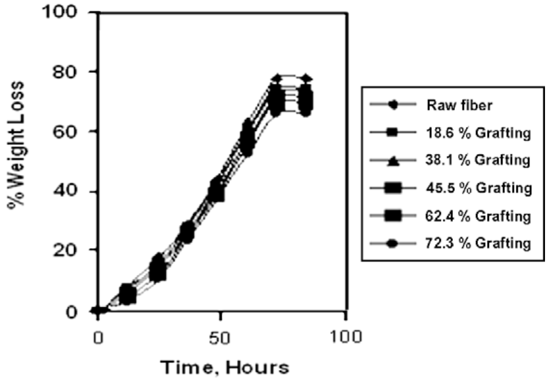


Fig. 7. Effect of grafting on base resistance.

3.3.6. Acid and base resistance study

It was observed that acid and base resistance of the acetylated fiber increased with increased in percent grafting (Figs. 6 and 7). This is due to the fact that poly(MMA) chains grafted onto acetylated *S. spontaneum* fiber have less affinity for acid and base as compared to hydroxyl and other functional groups present in ungrafted fiber. Therefore, the resistance of fiber towards acid and base increased with increased in incorporation of poly(MMA) chains onto acetylated back-bone.

4. 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. Though with increase in grafting, % crystallinity and crystallinity index decreased, but incorporation of poly(MMA) chains on back-bone polymer could result in higher acid, base and thermal resistance as well as decrease in moisture absorbance as compared to the acetylated 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 acetylated fiber.

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