

Synthesis of Graft Copolymers of Binary Vinyl monomer Mixtures onto Acetylated *Saccharum spontaneum* L and Characterization

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ABSTRACT: Methylmethacrylate (MMA) + acrylamide (AAM), MMA + acrylonitrile (AN), and MMA + acrylic acid (AA) binary vinyl monomer mixtures were graft copolymerization onto acetylated *Saccharum spontaneum* L, was carried out and maximum graft yield (185.6 %) was found with MMA+AAM binary mixture. Synthesized graft co-polymers were characterized with FT-IR spectrophotometry, scanning electron microscopy (SEM), thermal analysis TGA/DTA/DTG, and X-ray diffraction (XRD) techniques. Thermal stability of Ss-g-poly(MMA + AAM) was found to be more than that of natural, acetylated S.

spontaneum fiber and other graft copolymers. Although on grafting, percentage crystallinity and crystallinity index were found to decrease but graft copolymers were found to exhibit more moisture, chemical, and thermal resistance. Also, it can be observed that the surface of the grafted fibers is highly rough in comparison with the ungrafted fiber. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2060–2071, 2011

Key words: acetylated *Saccharum spontaneum* L; graft copolymer; thermal resistance; moisture absorbance

INTRODUCTION

Cellulose as a biopolymer is the most abundant organic compound in nature and estimated to be at levels approaching 10¹¹ tons annually. Cellulose has the advantages over the other materials due to radiation stability, low cost of preparation and low density.¹ However, cellulose containing materials like natural fibers have been found to be vulnerable to moisture sensitivity and least chemical resistance. Cellulose consists of interconnected anhydroglucose units, each of which contains three hydroxyl groups. The properties of cellulose, such as its swell ability in different solvents, moisture sensitivity and least chemical resistance can be modified through converting the hydroxyl groups to other functionalities. Usually this can be done either by esterification, etherification or by grafting.

Introduction of acetyl groups by acetylation onto cellulose reduced the bond strength between cellulose molecules and resulted in increased swelling^{2,3} thereby leading to increased rate of graft copolymer-

ization. Graft copolymerization of vinyl monomer onto polymeric materials, including cellulose and cellulosic derivatives has been studied all over the world.^{4–10} Shen et al. graft copolymerized methyl methacrylate onto cellulose diacetate¹¹ and methyl methacrylate and styrene onto ethyl cellulose.¹² Vlcek et al.¹³ graft copolymerized styrene, methyl methacrylate and butyl acrylate onto cellulose diacetate. Chauhan et al.¹⁴ graft copolymerized a binary mixture of styrene and maleic anhydride onto cellulose extracted from *Pinus roxburghii* needles. The grafting reaction was initiated with gamma rays. Grafting parameters and reaction rate achieved maximum values with 1 : 1M ratio of styrene and maleic anhydride. Graft copolymerization of methacrylate (MA), ethyl acrylate (EA), and ethyl methacrylate on carboxymethyl cellulose using ceric ion in aqueous medium at 35°C has been carried-out by Okieimen and Ogbeifun.¹⁵ It has been observed that the frequencies of monomer grafting were not of the same order of magnitude even though the reaction conditions were the same.

Saccharum spontaneum L grows as a wasteland/lowland ecoregion weed and 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 is a first growing biomass with flowers containing fibers. These fibers are distinctly different in appearance from other type fibers studied earlier such as cotton,

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jute, flax, ramie, hemp, etc. These fibers are white/purplish silky and have better strength and fineness.^{16,17} Nature of the back-bone plays an important role in graft copolymerization. The reactivity of the monomers is also equally important in grafting process. The reactivity of monomers depends upon different factor viz. polarity, steric influences, swell ability of back-bone, chemical nature of monomers as well as the concentration of monomers. The graft copolymerization of vinyl monomer methylmethacrylate (MMA) using ferrous ammonium sulfate (FAS) -potassium persulfate (KPS) redox initiator onto the *Saccharum spontaneum* L fiber for more moisture resistant, higher chemical and thermal resistance has been reported earlier by the present authors.¹⁸⁻²¹ Different reaction parameters such as temperature, time, initiator molar ratio, monomer concentration, pH and solvent were optimized.

Graft copolymerization of monomeric mixture is a more complex phenomenon than the grafting of the individual monomers due to the difference in monomer reactivity ratios. In continuation to our earlier work of chemical modification through graft copolymerization with MMA, modification through graft copolymerization with different vinyl monomer mixtures onto acetylated *Saccharum spontaneum* L fiber was carried out and the effect on the hydrophobicity, thermal, and chemical resistance has been reported in the present article.

EXPERIMENTAL

Materials

Purification of materials

S. spontaneum-L fiber (Average dimension i.e., Fineness: 0.9 denier) was purified through soxhlet extraction in acetone for 72 h.²² Methylmethacrylate (MMA) (s. d. fine Chemicals Ltd, Mumbai, India) was purified by washing with 5% NaOH and subsequently drying over anhydrous Na₂SO₄ followed by distillation. Acrylamide (AAM), acrylonitrile (AN) and acrylic acid (AA) were used as received. FAS (s. d. fine Chemicals Ltd, Mumbai, India) was recrystallized from hot water and KPS (s. d. fine Chemicals Ltd, Mumbai, India) was used as received.

METHODS

Acetylation of *S. spontaneum*-L fiber

Acetylation of *S. spontaneum*-L fiber was carried-out as per the standard method.²³

Characterization

IR spectra of the samples were recorded with a Perkin-Elmer Fourier Transform Infrared (FTIR)

spectrophotometer 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 K α (1.5418 Å) radiation, N-filter, and scintillation counter detector at 45 KV and 35 mA on rotation between 5 and 40° (2 θ -scale) at 1 s step size and increment of 0.01° with 1.0 mm of divergent and anti-scattering slit. The small particle size of each sample was made and was put into sample holder which was made of PMMA with a round central cavity. Crystallinity index (C. I.) which measures the orientation of the cellulose crystals with respect to fiber axis was determined by using the wide angle X-ray diffraction counts at 2 θ -scale close to 22° and 18°. The counter reading at the peak intensity at 22° represent the crystalline material and the peak intensity at 18° corresponds to the amorphous material in cellulose.²⁴ Percentage Crystallinity (% Cr) and Crystallinity index (C. I.) were calculated as follows²⁵:

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

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

where I_{22} and I_{18} are the crystalline and amorphous intensities at 2 θ -scale close to 22° and 18°, respectively. Thermogravimetric analysis, differential thermal analysis, and differential thermogravimetric analysis of the samples were carried-out within the temperature range of 25–700°C at a heating rate of 5°C/min in air on a thermal analyzer (Perkin-Elmer, Pyris Diamond).

Graft copolymerization

Initially optimization of different reaction parameters like reaction time, temperature, pH, solvent, initiator, and monomer concentrations was carried-out for graft copolymerization of principal monomer (MMA) onto acetylated backbone, prior to carrying out grafting with binary mixture. Activation of acetylated *S. spontaneum*-L fiber (0.5 g) was done at room temperature by immersing in 125 mL of distilled water for 24 h. A definite molar ratio of FAS-KPS was added to the reaction flask followed by addition of binary monomer mixture with continuous stirring. Reaction was carried-out under optimized reaction conditions and removal of homopolymers was carried-out with different solvents. Percentage polymer loading (%PL), percentage graft yield (%GY) and percentage grafting efficiency (%GE) were calculated as per the following methods (Table I)²⁶:

TABLE I
Evaluation of Optimum Reaction Parameter for Grafting of Binary Vinyl Monomer Mixture onto Acetylated *S. spontaneum*

| Sr. No. | Binary mixtures | $\times 10^{-3}$ mol L ⁻¹ | %PL ^a | %GY ^b | %GE ^c |
|---------|-----------------|--------------------------------------|------------------|------------------|------------------|
| | [MMA]+[AA] | | | | |
| 1 | | 2.94+1.45 | 232.1 | 99.6 | 42.91 |
| 2 | | 2.94+2.18 | 241.4 | 115.4 | 47.80 |
| 3 | | 2.94+2.91 | 249.9 | 165.4 | 66.18 |
| 4 | | 2.94+3.69 | 222.7 | 138.7 | 62.28 |
| 5 | | 2.94+4.37 | 213.2 | 119.8 | 56.19 |
| | [MMA]+[AAm] | | | | |
| 1 | | 2.94+0.21 | 232.6 | 108.2 | 46.51 |
| 2 | | 2.94+0.28 | 242.7 | 123.6 | 50.92 |
| 3 | | 2.94+0.35 | 263.2 | 185.6 | 70.51 |
| 4 | | 2.94+0.42 | 221.9 | 152.3 | 68.63 |
| 5 | | 2.94+0.49 | 209.3 | 123.9 | 59.19 |
| | [MMA]+[AN] | | | | |
| 1 | | 2.94+1.51 | 224.5 | 95.3 | 42.44 |
| 2 | | 2.94+2.27 | 253.3 | 172.2 | 67.98 |
| 3 | | 2.94+3.03 | 237.9 | 152.7 | 64.18 |
| 4 | | 2.94+3.79 | 216.8 | 132.1 | 60.93 |
| 5 | | 2.94+4.56 | 198.2 | 119.3 | 60.19 |

^a Percentage polymer loading.

^b Percentage grafting.

^c Percent graft efficiency.

^d Percent homopolymer.

Percent polymer Loading (%PL)

$$= [(W_2 - W_1)/W_1] \times 100$$

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

Percent grafting yield (% GY)

$$= [(W_3 - W_1)/W_1] \times 100$$

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

Percent graft efficiency (% GE)

$$= [(W_3 - W_1)/(W_2 - W_1)] \times 100$$

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

Swelling behavior in different solvents

Totally, 250 mg of grafted and raw samples were immersed in a definite volume (100 mL) of water, methanol, *n*-butanol, dimethyl formamide at 25°C for a period of 24 h. Samples were removed from the solvent after filtration. Excess solvent was removed quickly with filter papers. Final weight of the sample was taken and the percent swelling was calculated as follows²⁷

$$\text{Percent swelling (PS)} = [(W_f - W_i)/W_i] \times 100$$

where W_i and W_f are the initial and final weights of samples, respectively.

Moisture absorption study

Moisture absorbance studies at various relative humidity levels were carried-out as per the method reported earlier.²⁷ 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 2 h and then the final weight (W_f) of the samples exposed to different relative humidities ranging from 20 to 100% were taken. The % moisture absorbance was calculated from the increase in initial weight in the following manner:

% of moisture absorbance (% M_{abs})

$$= [(W_f - W_i)/W_i] \times 100$$

Acid and base resistance

Acid and base resistance studies were carried-out as per the method reported earlier.²⁷ Acid and base resistance was studied by placing a known weight (W_i) of dry grafted and ungrafted samples in a fixed volume of 5N HCl and 5N NaOH and the final weight (W_f) of the samples were noted down after every 12 h interval until the constant weight was reached.

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

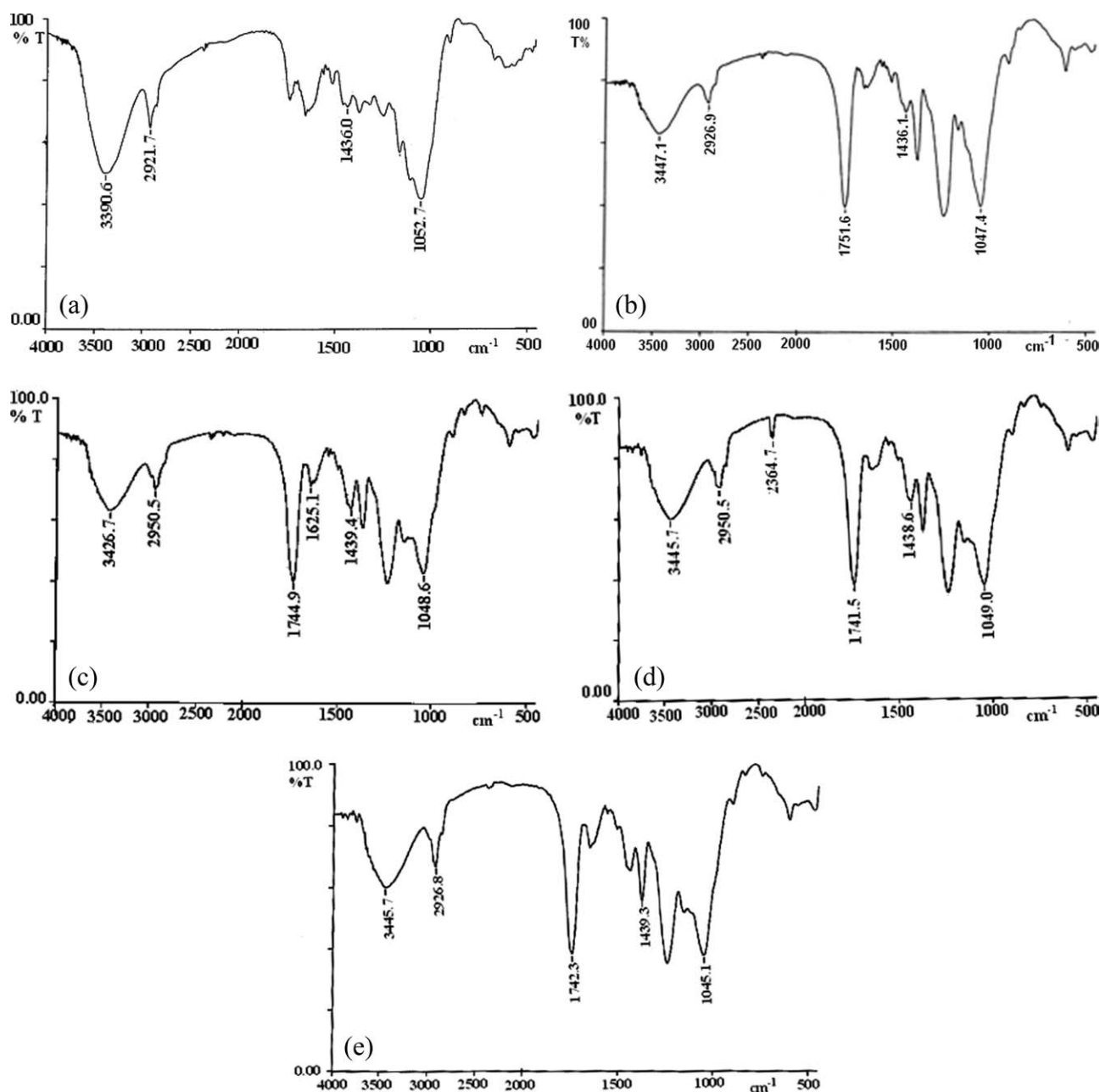


Figure 1 (a) IR spectra of *S. spontaneum* fiber; (b) IR spectra of acetylated *S. spontaneum* fiber; (c) IR spectra of Ss-g-poly(MMA+AAM); (d) IR spectra of Ss-g-poly(MMA+AN); (e) IR spectra of Ss-g-poly(MMA+AA).

RESULTS AND DISCUSSION

Characterization of graft copolymers

Fourier transform-infrared (FT-IR) spectroscopy

S. 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 cm^{-1} , 1052.7 cm^{-1} arising from C-C and C-O stretching, respectively, [Fig. 1(a)]. The introduction of acetyl moiety in the acetylated *S. spontaneum-L* fiber was confirmed by this spectral analysis. 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. 1(b)]. On grafting, IR bands due to characteristic functional groups incorporated into acetylated *S. Spontaneum-L* have been witnessed apart from the previously listed bands. Ss-g-poly(MMA+AAM) showed additional peaks 1744 m^{-1} (C=O of MMA) and 1625.1 cm^{-1} (C=O of AAM) [Fig. 1(c)]. Ss-g-poly(MMA+AN) showed additional peaks 1741.1 cm^{-1} (C=O of MMA) and 2365.1 cm^{-1} (C≡N

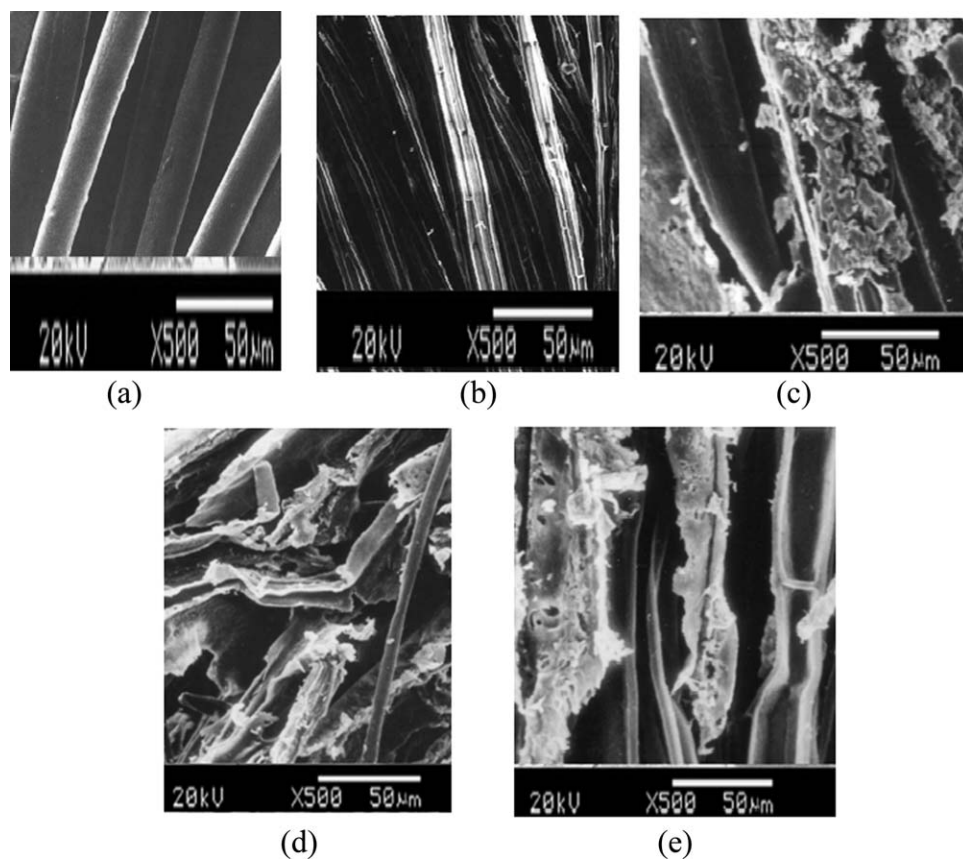


Figure 2 Scanning Electron Micrograph of (a), *S. spontaneum* fiber; (b), acetylated *S. spontaneum* fiber; (c), Ss-g-poly(MMA+AAM); (d), Ss-g-poly(MMA+AN); (e), Ss-g-poly(MMA+AA).

stretching of AN) [Fig. 1(d)]. Ss-g-poly(MMA+AA) showed additional peaks 1742.3 cm^{-1} (C=O of MMA) and 2926.8 cm^{-1} (OH of AA) [Fig. 1(e)].

Scanning electron microscopy

The changes in the topography and morphology of fiber surfaces were studied by scanning electron microscopy (SEM). It can be observed that the surface of the grafted fibers is highly rough in comparison with the ungrafted fiber [Fig. 2(a–e)], which is attributed to high graft density. 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.^{28–30}

X-ray diffraction studies

As is evident from Figure 3 percentage crystallinity and crystallinity index were found lower in acetylated *S. spontaneum* fiber than the raw fiber. Moreover, percentage crystallinity and crystallinity index was found to decrease with increase in percentage grafting. Since incorporation of monomer moiety in the backbone impairs the natural crystallinity of the

fiber, therefore, graft copolymerization of different monomer mixtures onto *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.³¹ Since crystallinity index (C. I.) is the quantitative measure of the orientation of the crystal lattice to the fiber axis, therefore, lower crystallinity index in case of graft copolymers stands for poor order of crystal lattice in the fiber.^{18–21}

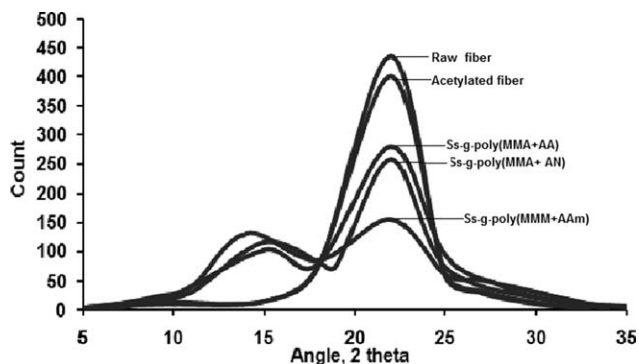


Figure 3 X-ray diffraction studies.

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

| Sample | %GY | At 20-scale | | % Cr | C. I. |
|--------------------|-------|-----------------|-----------------|-------|-------|
| | | I ₂₂ | I ₁₈ | | |
| Raw fiber | – | 436 | 75 | 85.32 | 0.82 |
| Acetylated fiber | – | 400 | 75 | 84.21 | 0.81 |
| Ss-g-poly(MMA+AA) | 165.4 | 281 | 80 | 77.83 | 0.71 |
| Ss-g-poly(MMA+AN) | 172.2 | 257 | 83 | 75.58 | 0.67 |
| Ss-g-poly(MMA+AAM) | 185.6 | 156 | 86 | 64.46 | 0.44 |

TGA, DTA, and DTG

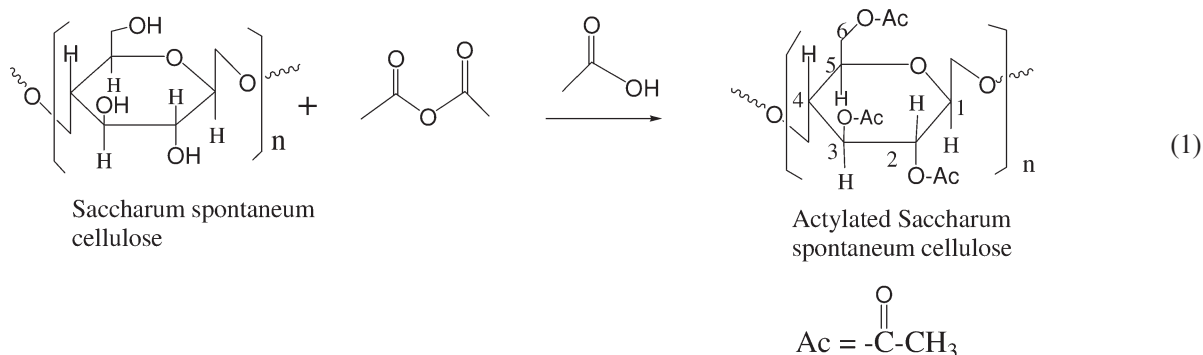
Thermogravimetric Analysis (TGA) of ungrafted, acetylated and grafted *S. spontaneum* were studied as a function of wt % loss versus temperature. Cellulosic *S. spontaneum* degrades by dehydration, glyco-gen formation and depolymerization. In case of *S. spontaneum*, two-stage decomposition was found 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 was attributed to loss by dehydration and volatilization processes, whereas the later stage was attributed to loss by depolymerization process [Fig. 4(a)]. In case of acetylated *S. spontaneum*, also two-stage decompositions were found in the temperature range from 250 to 325°C with 48.90% weight loss and 325–500°C with 36.61% weight loss [Fig. 4(b)]. However in case of Ss-g-poly(MMA+AAM), Ss-g-poly(MMA+AN), Ss-g-poly-(MMA+AA) showed single stage decomposition. The initial decomposition temperatures were 251, 250, and 250°C and the final decomposition temperatures were 555, 550, and 502°C with 78.51%, 84.83%, and 81.59% weight loss, respectively, [Fig. 4(c–e)]. 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(binary mixture) chains on backbone polymer through covalent bonding.

In case of Differential Thermal Analysis (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. 5(a)]. However, acetylated fiber showed broad exothermic decomposition at 337–452°C (–2706 mJ/mg) [Fig. 5(b)]. DTA studies of Ss-g-poly(MMA+AAM), Ss-g-poly(MMA+AN) and Ss-g-poly(MMA+AA) exhibited exothermic decomposition at 362°C (–678mJ/mg), 361°C (–853 mJ/mg) and 359°C (–1021mJ/mg), respectively [Fig. 4(c–e)].

Differential thermogravimetric (DTG) analysis of grafted, acetylated and ungrafted *S. spontaneum* were studied as a function of rate of weight loss (mg/min) versus temperature. In case of *S. spontaneum* decompositions at 303°C and 413°C were found with 1.575 mg/min and 1.411 mg/min weight loss, respectively, [Fig. 4(a)]. However, in case of acetylated fiber decomposition at 307°C and 450°C occurred with 1.056 mg/min and 0.224 mg/min weight loss [Fig. 5(b)]. In case of Ss-g-poly(MMA+AAM), Ss-g-poly(MMA+AN) and Ss-g-poly(MMA+AA), thermal decompositions were observed at 358°C, 352°C, and 352°C with 0.762 mg/min, 0.941 mg/min and 0.952 mg/min weight loss, respectively [Fig. 4(c–e)]. Thus it could be concluded from the DTG studies that the rate of thermal decomposition was higher in case of *S. spontaneum* than in case of grafted fibers. The better thermal resistance of graft copolymers were due to incorporation of more covalent bonding through inclusion of poly(MMA+AAM), poly(MMA+AN) and poly(MMA+AA) chains onto backbone polymer.^{26,32–34}

Mechanism

C₂, C₃, and C₆ hydroxyls of *S. spontaneum*-L (eq. 1) were acetylated using the standard method¹⁶.



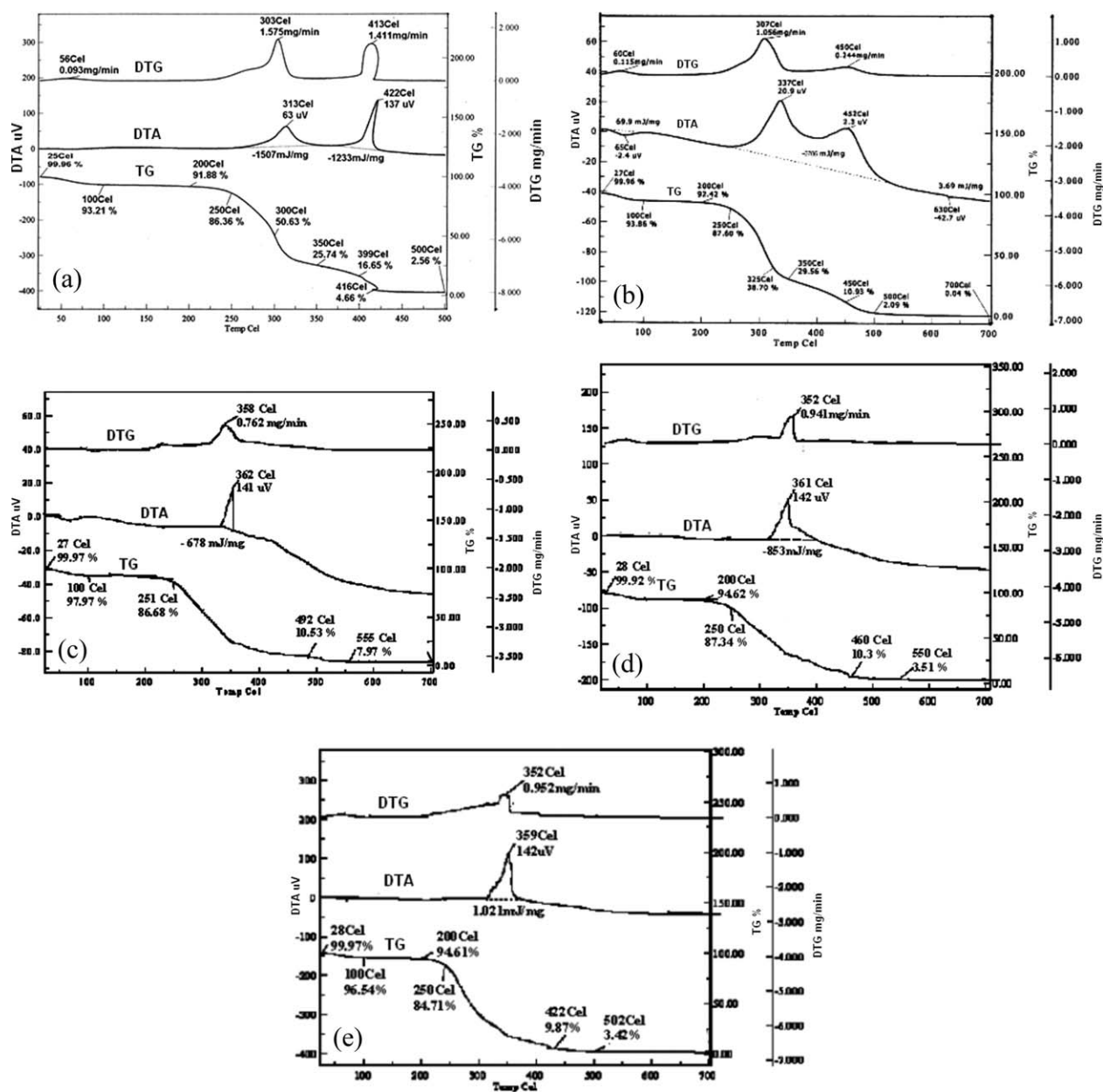


Figure 4 (a) TGA, DTA, and DTG curves of *S. spontaneum* fiber; (b) TGA, DTA, and DTG curves of acetylated *S. spontaneum* fiber; (c) TGA, DTA, and DTG curves of Ss-g-poly (MMA+AAm); (d) TGA, DTA, and DTG curves of Ss-g-poly (MMA+AN); (e) TGA, DTA, and DTG curves of Ss-g-poly (MMA+AA).

C₂, C₃, and C₆ esters and C–H groups are the active sites for the incorporation of polymeric chains onto acetylated *S. spontaneum*. Reaction of Fe²⁺ with KPS (eq. 2) generated SO₄⁻ ions. Interaction of SO₄⁻ with H₂O generated OH* (eq. 3) which are responsible for further chain propagation, thereby resulting in the formation of graft copolymer along with copolymer, homopolymer, and can be explained through the following mechanism:

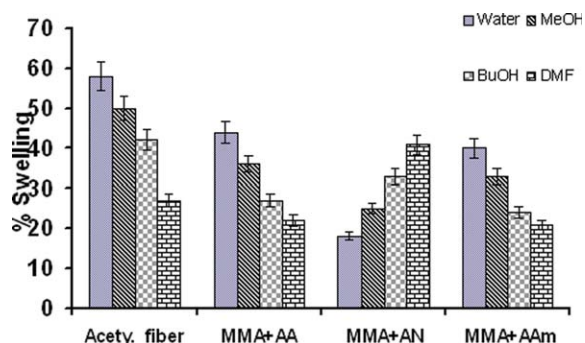
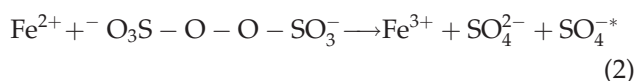
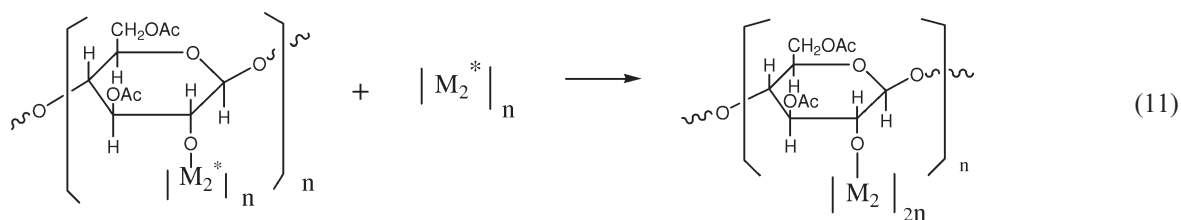
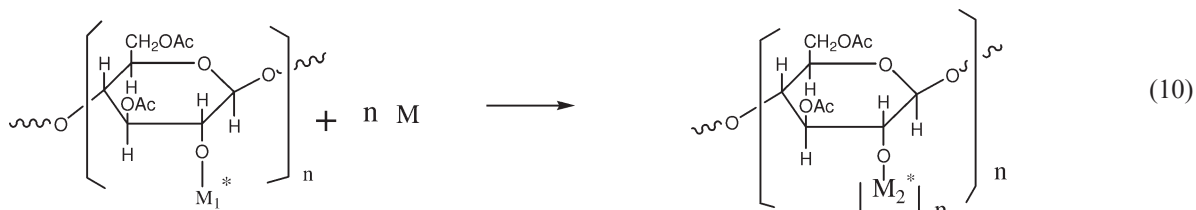
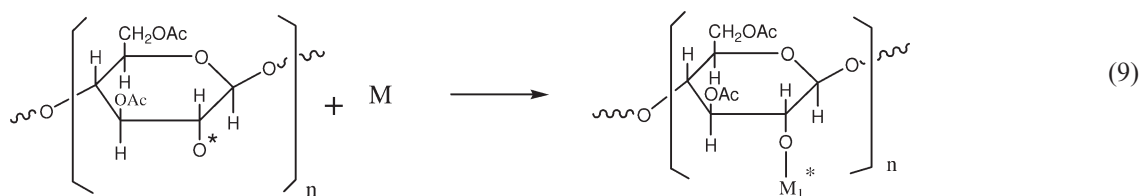
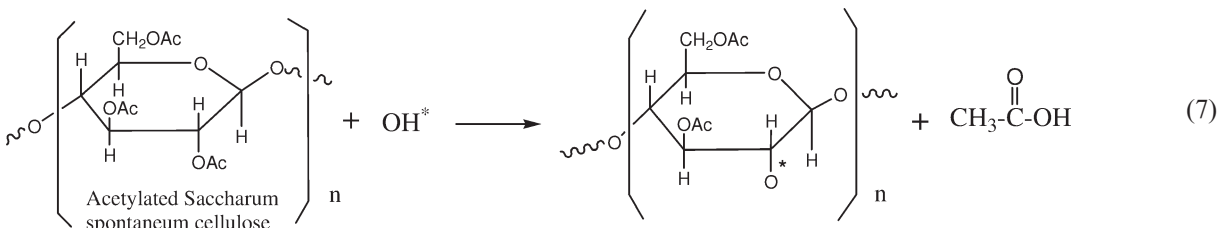
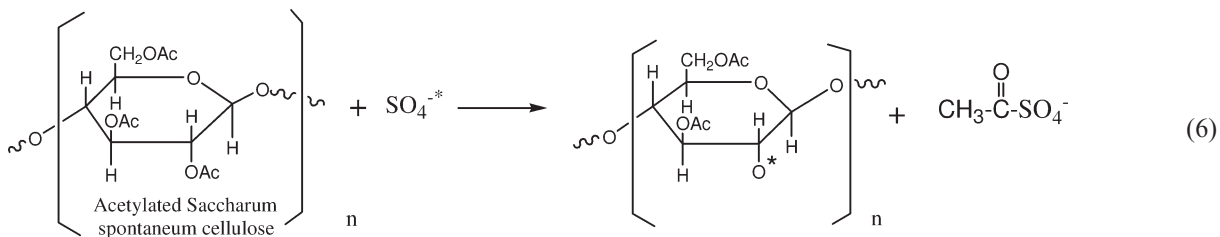
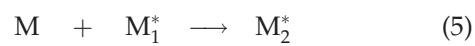
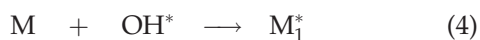
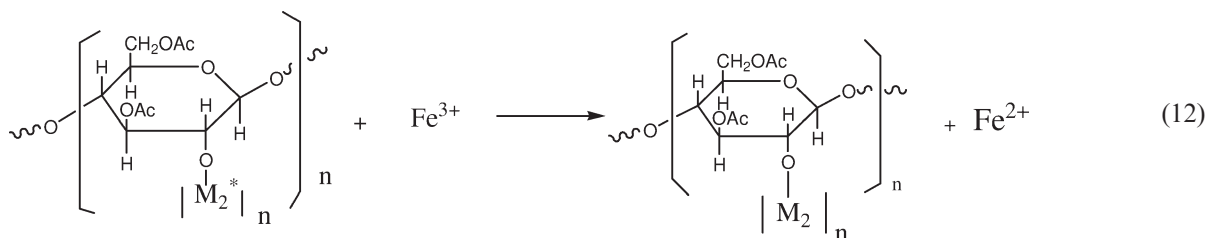


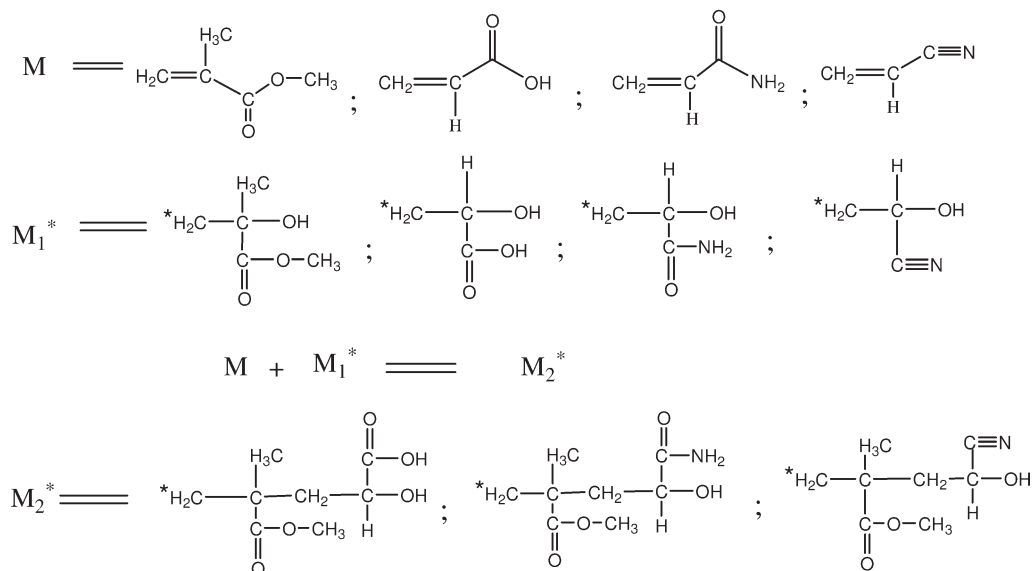
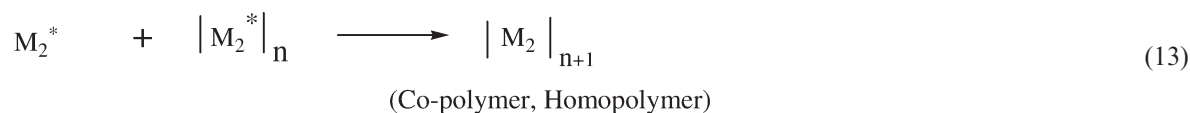
Figure 5 Effect of grafting on swelling behavior in different solvents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]



(Graft copolymer)



(Graft copolymer)



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, initiation of reaction by SO_4^{*-} (eq. 6) is unlikely to occur as the concentration of persulphate 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 acetyl group from the backbone polymer and generated the macro-radical on acetylated *S. spontaneum* fiber (eq. 7). Similarly, OH^* radicals reacted with monomer molecules resulting in free radical sites on the monomer (eq. 4) which further react with monomer moieties thereby resulting in active copolymer and homopolymer chains (eqs. 5, 8). Moreover, reaction between active back-bone and monomer gives active graft copolymer which further reacts with monomers and the grafting propagates (eqs. 9, 10). Termination of grafting might occurred by either process (eq. 11) or (eq. 12) 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+} was produced by the reaction between FAS with KPS (eq. 2), 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, attacked the growing graft copolymer chains, thereby resulting in termination of reaction with reduction of Fe^{3+} to Fe^{2+} (eq. 12). Reactions between

growing monomer chains also result in the termination of reaction and formation of copolymer and homopolymer (eq. 13). Hence, concentrations of initiator and monomer, variations of time, temperature, pH, and volume of the solvent affect the graft yield as these factors determine the relative population of various radical species generated in different steps during the course of reaction.

Effect of concentration of binary vinyl monomer mixtures on percent grafting

Initially optimization of different reaction parameters was carried-out for getting maximum graft yield (152.6%) on graft copolymerization of MMA onto acetylated backbone (Table III). The different optimized parameters were: reaction time, 90 min; temperature, 40°C; pH, 7; solvent, 125 mL; FAS:KPS, 1 : 0.75; MMA, 2.94×10^{-3} mol/L. Graft copolymerization of binary vinyl monomer mixtures such as MMA + AAm, MMA + AN and MMA + AA onto acetylated *S. spontaneum* fiber using MMA (2.94×10^{-3} mol L⁻¹) as the principal monomer showed 185.6% (AAm; 0.35×10^{-3} mol L⁻¹), 172.2% (AN; 2.27×10^{-3} mol L⁻¹) and 165.4% (AA; 2.91×10^{-3} mol L⁻¹) graft yield, respectively (Table I).

Higher percentage graft yield observed in case of binary vinyl mixtures could be explained on the basis of monomer reactivity ratio. The reactivity ratios in case of different binary vinyl monomer mixtures have been found to be: MMA+AAm: $r_1 = 2.53$, $r_2 = 0.82$; MMA+AN: $r_1 = 1.09$, $r_2 = 0.15$;

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

| Sr. No. | Reaction time (min) | Reaction temp. (°C) | pH | Solvent (mL) | Molar ratio (FAS : KPS) | [MMA] × 10 ³ mol L ⁻¹ | % PL ^a | %GY ^b | %GE ^c | %HM ^d |
|---------|---------------------|---------------------|-----|--------------|-------------------------|---|-------------------|------------------|------------------|------------------|
| 1 | 60 | 45 | 7.0 | 100 | 1 : 1.00 | 2.45 | 180.4 | 80.2 | 44.4 | 55.6 |
| 2 | 90 | 45 | 7.0 | 100 | 1 : 1.00 | 2.45 | 206.4 | 99.6 | 48.2 | 51.8 |
| 3 | 120 | 45 | 7.0 | 100 | 1 : 1.00 | 2.45 | 208.2 | 65.0 | 31.2 | 68.8 |
| 4 | 150 | 45 | 7.0 | 100 | 1 : 1.00 | 2.45 | 198.4 | 55.6 | 28 | 72 |
| 5 | 180 | 45 | 7.0 | 100 | 1 : 1.00 | 2.45 | 192.4 | 42.1 | 21.8 | 78.2 |
| 6 | 90 | 30 | 7.0 | 100 | 1 : 1.00 | 2.45 | 190.4 | 59.2 | 31 | 69 |
| 7 | 90 | 35 | 7.0 | 100 | 1 : 1.00 | 2.45 | 202.0 | 82.1 | 40.6 | 59.4 |
| 8 | 90 | 40 | 7.0 | 100 | 1 : 1.00 | 2.45 | 228.4 | 100.2 | 43.8 | 56.2 |
| 9 | 90 | 45 | 7.0 | 100 | 1 : 1.00 | 2.45 | 200.6 | 87.6 | 43.6 | 56.4 |
| 10 | 90 | 50 | 7.0 | 100 | 1 : 1.00 | 2.45 | 198.4 | 62.6 | 31.5 | 68.5 |
| 11 | 90 | 55 | 7.0 | 100 | 1 : 1.00 | 2.45 | 196.2 | 51.0 | 25.9 | 74.1 |
| 12 | 90 | 40 | 2.0 | 100 | 1 : 1.00 | 2.45 | 182.4 | 47.0 | 25.7 | 74.3 |
| 13 | 90 | 40 | 4.0 | 100 | 1 : 1.00 | 2.45 | 160.4 | 65.0 | 40.5 | 59.5 |
| 14 | 90 | 40 | 7.0 | 100 | 1 : 1.00 | 2.45 | 216.4 | 102.4 | 47.3 | 52.7 |
| 15 | 90 | 40 | 8.0 | 100 | 1 : 1.00 | 2.45 | 198.6 | 68.0 | 34.2 | 65.8 |
| 16 | 90 | 40 | 9.0 | 100 | 1 : 1.00 | 2.45 | 190.4 | 47.2 | 24.7 | 75.3 |
| 17 | 90 | 40 | 7.0 | 50.0 | 1 : 1.00 | 2.45 | 182.4 | 75.0 | 41.1 | 58.9 |
| 18 | 90 | 40 | 7.0 | 75.0 | 1 : 1.00 | 2.45 | 204.2 | 86.0 | 42.1 | 57.9 |
| 19 | 90 | 40 | 7.0 | 100 | 1 : 1.00 | 2.45 | 220.2 | 101.1 | 45.9 | 54.1 |
| 20 | 90 | 40 | 7.0 | 125 | 1 : 1.00 | 2.45 | 236.2 | 135.6 | 57.4 | 42.6 |
| 21 | 90 | 40 | 7.0 | 150 | 1 : 1.00 | 2.45 | 199.2 | 89.2 | 44.7 | 55.3 |
| 22 | 90 | 40 | 7.0 | 175 | 1 : 1.00 | 2.45 | 195 | 75.0 | 38.4 | 61.6 |
| 23 | 90 | 40 | 7.0 | 125 | 1 : 0.50 | 2.45 | 168.4 | 30.0 | 17.8 | 82.2 |
| 24 | 90 | 40 | 7.0 | 125 | 1 : 0.75 | 2.45 | 242 | 139 | 57.4 | 42.6 |
| 25 | 90 | 40 | 7.0 | 125 | 1 : 1.00 | 2.45 | 224.2 | 96.1 | 42.8 | 57.2 |
| 26 | 90 | 40 | 7.0 | 125 | 1 : 1.25 | 2.45 | 186.4 | 67.4 | 36.1 | 63.9 |
| 27 | 90 | 40 | 7.0 | 125 | 1 : 1.50 | 2.45 | 184.2 | 52.1 | 28.2 | 71.8 |
| 28 | 90 | 40 | 7.0 | 125 | 1 : 0.75 | 1.47 | 146.2 | 39.7 | 26.9 | 73.1 |
| 29 | 90 | 40 | 7.0 | 125 | 1 : 0.75 | 1.96 | 168.2 | 59.5 | 35.5 | 64.7 |
| 30 | 90 | 40 | 7.0 | 125 | 1 : 0.75 | 2.45 | 184.6 | 102.4 | 55.4 | 44.6 |
| 31 | 90 | 40 | 7.0 | 125 | 1 : 0.75 | 2.94 | 222.4 | 152.6 | 68.6 | 31.4 |
| 32 | 90 | 40 | 7.0 | 125 | 1 : 0.75 | 3.43 | 204.2 | 78.7 | 38.5 | 61.5 |

^a Percent polymer loading.

^b Percent grafting.

^c Percent graft efficiency.

^d Percent homopolymer.

MMA+AA: $r_1 = 1.25$, $r_2 = 0.225$.³⁵ Since r_2 values in all the binary mixtures are small, therefore, it is quite evident that formation of copolymer between the two different monomeric moieties takes place which suppressed the comonomer homopolymerization. Similarly r_1 values clearly indicate the formation of copolymer between the different monomers in the binary mixtures which suppressed the formation of principal monomer homopolymerization, thereby resulting in higher graft yields.^{18,31} On the other hand, lower graft yield in case of principal monomer alone could be due to higher reactivity ratio of MMA with MMA thereby, resulting in more homopolymerization.

Higher percentage graft yield obtained in case of MMA+AAM and MMA+AN binary mixtures than in case of MMA+AA, could be due to the presence of a strong acceptor monomer in the binary mixtures MMA+AAM and MMA+AN. The low graft yield with MMA+AA binary mixture was due to the fact

that AA is more strongly associated with water, thereby resulting in decreased free radical sites and hence low graft yield.³¹

Swelling studies

It was found that graft copolymerizations of binary mixtures onto *S. spontaneum* had a great impact on the swelling behavior (Fig. 5). The swelling behavior studies were carried-out in different solvents like water, MeOH, BuOH, and DMF. It was observed that *S. spontaneum* fiber showed maximum swelling in water (62%) followed by MeOH (49%), BuOH (42%) and DMF (34%). However, different patterns were observed for graft copolymers varied with percentage grafting and nature of monomers. MMA-AAM (% GY; 185.6), MMA+AA (% GY; 165.4) in water and MMA+AN (% GY; 172.2) in DMF showed maximum swelling [Fig. 5(a)]. This is due to the fact that both MMA and AN are hydrophobic, therefore,

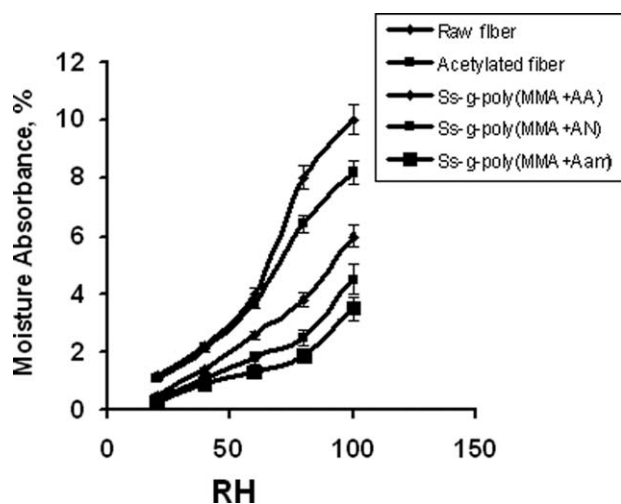


Figure 6 Effect of grafting on moisture absorbance at different humidity levels.

showed maximum swelling in DMF. Whereas AA, AAm are hydrophilic in nature and maximum swelling were observed in water.

Moisture absorbance study

It was found that graft copolymerizations of binary mixtures onto *S. spontaneum* had a great impact on the moisture absorption behavior (Fig. 6). With increase in graft yield, moisture absorbance was found to decrease. This could be due to the fact that the sites vulnerable for moisture absorption got blocked with poly(MMA+AAm), poly(MMA-AN), and poly(MMA+AA) chains to convert the fiber less sensitive towards moisture. In case of fibers grafted with poly (MMA+AN), it was less moisture sensitive than poly(MMA+AAm) and poly(MMA+AA) because poly(AN) is hydrophobic and poly (AAm) and poly(AA) are hydrophilic in nature.

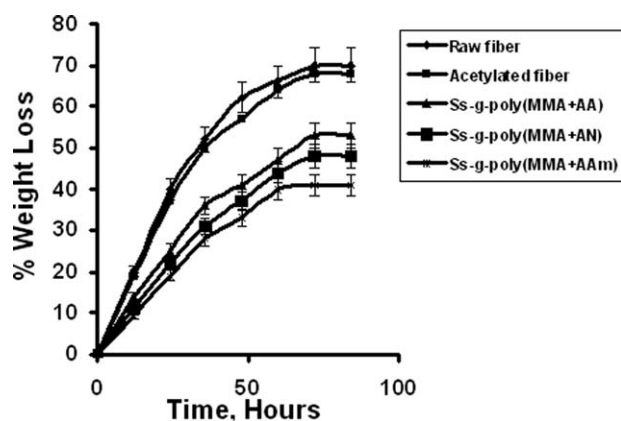


Figure 7 Effect of grafting on acid resistance.

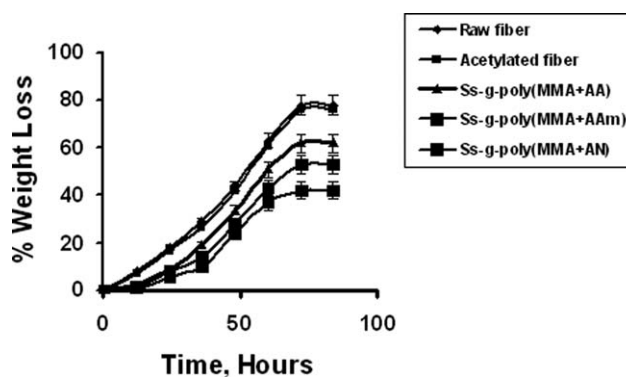


Figure 8 Effect of grafting on base resistance.

Acid and base resistance study

It was observed that acid and base resistance of the fiber increased with increase in percent grafting (Figs. 7 and 8). This is due to the fact that poly(MMA+AAm), poly(MMA+AN) and poly(MMA-AA) chains grafted onto acetylated *S. spontaneum* fiber have less affinity for acid and base. Therefore, the resistance of fiber towards acid and base increased with increase in incorporation of poly (binary vinyl) chains onto backbone.

CONCLUSIONS

The grafting of MMA+AAm, MMA+AN, and MMA+AA binary mixtures onto acetylated *S. spontaneum-L* fiber in presence of FAS-KPS as redox initiator has been found to have physicochemical, thermal as well as morphological impacts. Although with increase in grafting, % crystallinity and crystallinity index decreased, but incorporation of poly(MMA+AAm), poly(MMA+AN), and poly(MMA+AA) chains on backbone polymer could result in higher acid, base and thermal resistance as well as decrease in moisture absorbance as compared to the original and 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.

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