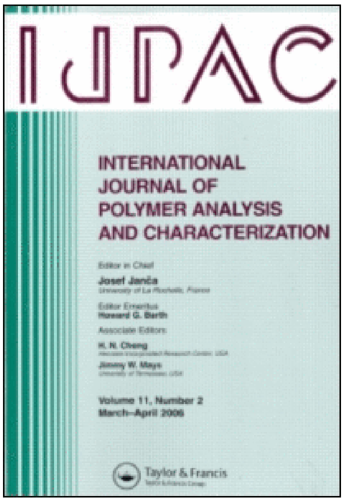

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KPS-INITIATED GRAFT COPOLYMERIZATION ONTO MODIFIED CELLULOSIC BIOFIBERS

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The graft copolymerization of cellulosic biofibers with methyl acrylate (MA) using potassium persulfate (KPS) as initiator has been reported. Various reaction parameters such as monomer, initiator concentration, reaction temperature, time, and amount of solvent were optimized to get the maximum grafting yield. The effect of percentage grafting on the physicochemical properties of raw as well as grafted fibers has been investigated. Morphological, thermal, and IR spectroscopic studies of the grafted as well as ungrafted fibers have also been carried out.

***Keywords*:** Biofibers; Graft copolymerization; Morphological and spectroscopic studies; Thermal

INTRODUCTION

From ancient times, materials based on lignocellulosic natural fibers have found a number of applications to meet the needs of humans.[1–4] The most important constituents of natural fibers are cellulose, hemicelluloses, lignin, and pectin. The properties of each constituent contribute to the overall properties of the natural fibers. Cellulose is one of the most generous polymers present in the fibers as a principal component of cell walls, microorganisms, etc.[5–7] Indeed, cellulose constitutes a ubiquitous and distinctively renewable natural resource that can be found from a range of sources all over the world. It has been used for a variety of products, including textiles, paper, packaging, and building materials. At present, a large number of industries throughout the world are initiating the design and engineering of new products with eco-friendly advantages.[8–11] Sustainable development and eco-efficiency are of key importance to the mainstream of international companies. In this perspective, biodegradability, eco-friendliness, easy availability, and light weight have become important considerations in the fabrication of new products. The problem of nonbiodegradability and the unaffordable cost of synthetic polymers can be efficiently reduced and managed by the development of novel materials based on alternative cost-effective eco-friendly biopolymers.[12–15] These alternative materials can be effectively used in management of the environment system.

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Various researchers all over the world are focusing their attention on the use of lignocellulose fibers in place of synthetic fibers in assorted fields, especially as reinforcing fillers.[16–22] However, greater attention is being given to the synthesis of green composites, which can help in resolving future environmental problems.[23–25]

Although natural fibers have a number of advantages, these fibers have a few disadvantages also.[26–28] These fibers are very sensitive to moisture, chemicals, and water, and their properties are degraded when they come in contact with harsh environmental conditions. Among various methods to modify the properties of cellulosic fibers, grafting is a well-established technique used to cause more or less extensive modification of properties and textile performance of natural and synthetic fibers.[29,30] It is one of the most conventional methods of incorporating desired functional groups onto the cellulosic backbone. A graft copolymer is formed when growing polymer chains are attached to the polymeric backbone by means of chemical bonds.[31,32] Vinyl monomers have also been extensively used for grafting of various synthetic and natural polymers. Modification by grafting of vinyl monomer on cellulosic fibers increases the properties and utility of cellulose-based materials.[33–35] Grafting also helps to improve properties such as solubility since cellulosic fibers are difficult to dissolve in common solvents because of their high crystallinity, and they degrade before reaching their melting temperature due to the strong hydrogen bonding present in the cellulose molecules.

A literature survey has revealed scanty information on improving the existing properties of cellulosic *Hibiscus sabdariffa* fibers through graft copolymerization technique. In this study, the most recent results on *Hibiscus sabdariffa* fiber grafting with methyl acrylate (MA) monomer and potassium persulfate (KPS) initiator systems are reported. The yield of grafting has been studied as functions of monomer and initiator concentration, temperature, time, solvent, and other factors. The physicochemical, thermal, and morphological properties of grafted *Hibiscus sabdariffa* fibers have also been investigated. The results thus obtained seem highly promising for improving *Hibiscus sabdariffa* grafting properties at the industrial level.

EXPERIMENTAL SECTION

Materials

Hibiscus sabdariffa fibers were collected from local resources in the Himalayan region. Reagent-grade chemicals namely, sodium hydroxide (NaOH), acetone, methyl acrylate (MA), and potassium persulfate (KPS) were used for graft copolymerization of the cellulosic biofibers. Purification of natural *Hibiscus sabdariffa* fibers, methyl acrylate, grafting reactions, and separation of homopolymer from the grafted fiber were carried out according to the procedure reported elsewhere.[29] The chemicals used were purified where necessary. The modified *Hibiscus sabdariffa* fibers were prepared in the following manner:

Cellulosic *Hibiscus sabdariffa* fibers were at the outset thoroughly washed with detergent powder and then soaked in distilled water for 3 h. Then these fibers were dried for 48 h in air at room temperature followed by drying at 100°C for 24 h to adjust the moisture content to 1–2% and then stored in a vacuum desiccator. These dried fibers were designated as untreated fibers. The untreated fibers were subsequently subjected to extraction with acetone for 72 h in a Soxhlet apparatus followed by washing with double distilled water and air drying to remove waxes and water-soluble ingredients prior to chemical treatments. Deionized water was used as a graft copolymer reaction medium.

Methods

Chemical modification of *Hibiscus sabdariffa* fibers. Chemical modification of *Hibiscus sabdariffa* fibers was done by treating them with NaOH solution of different concentrations for the optimum mercerization. Mercerization of the fibers was carried out as per the standard method reported earlier in some of our studies.[5] After the completion of mercerization process, the fibers were taken out and thoroughly washed with doubled-distilled water for removal of any NaOH content. However, the final washing to the natural fibers was given with 2% acetic acid in order to neutralize the last traces of NaOH used. As a final point, the fibers were washed again with fresh distilled water and dried in an oven at 70°C to a constant weight. These fibers were then kept in an air drier for 24 h. Thus, chemically modified *Hibiscus sabdariffa* fibers were prepared.

Graft copolymerization procedure. A known amount of the chemically modified *Hibiscus sabdariffa* fibers was immersed in a definite amount of distilled water for 24 h. A known amount of initiator (KPS) and monomer (MA) was then added to the flask containing fiber. The reaction mixture was then stirred at a fixed temperature for a particular time interval. Optimum conditions of solvent, time, temperature, initiator (KPS ratio), and monomer concentration were evaluated for maximum graft yield (Table I). The homopolymer formed during graft copolymerization was removed by extraction with acetone in a Soxhlet extraction apparatus for 72 h. The graft copolymer free from homopolymer was then dried in a hot air oven to a constant weight. The percentage grafting (P_g) was calculated as per the procedure reported earlier.[29,30]

$$\text{Percent grafting } (P_g) = \frac{W_g - W}{W} \times 100$$

where W is the weight of raw fiber and W_g is the weight of grafted fiber.

Swelling, moisture absorbance, chemical resistance, and water uptake analysis studies.

Swelling behavior. Swelling (in different solvents such as dimethyl formamide, water, methanol, and isobutyl alcohol) studies of grafted and ungrafted fibers were carried out as per methods reported elsewhere.[29,30] The percent swelling was calculated from the increase in initial weight in the following manner:

$$\text{Percent swelling } (P_S) = \frac{W_f - W_i}{W_i} \times 100$$

Moisture absorbance behavior. Moisture absorbance studies were made in a humidity chamber. Known weights of dry grafted and raw fibers were placed in the

Table I. Optimization of various reaction parameters for optimum graft copolymerization of methyl acrylate onto *H. sabdariffa* fiber

Sr. no.	Solvent mL	Monomer mol/L × 10^{-1}	KPS mmol/L	Time (min)	Temperature	% Grafting
1	50	1.85	5.00	090	40	08.79
2	75	1.85	5.00	090	40	15.67
3	100	1.85	5.00	090	40	20.28
4	125	1.85	5.00	090	40	18.40
5	150	1.85	5.00	090	40	17.13
6	100	1.70	5.00	090	40	18.57
7	100	2.00	5.00	090	40	28.50
8	100	2.15	5.00	090	40	26.83
9	100	2.30	5.00	090	40	24.74
10	100	2.45	5.00	090	40	22.85
11	100	2.00	6.00	090	40	34.38
12	100	2.00	6.50	090	40	38.58
13	100	2.00	7.00	090	40	45.71
14	100	2.00	7.50	090	40	43.93
15	100	2.00	8.00	090	40	42.06
16	100	2.00	7.00	030	40	37.87
17	100	2.00	7.00	060	40	44.36
18	100	2.00	7.00	120	40	59.40
19	100	2.00	7.00	150	40	55.78
20	100	2.00	7.00	180	40	53.29
21	100	2.00	7.00	120	45	56.36
22	100	2.00	7.00	120	50	63.15
23	100	2.00	7.00	120	55	59.27
24	100	2.00	7.00	120	60	54.75

Optimized conditions are: solvent, 100 mL; monomer, 2.00 × 10^{-1} mol/L; time, 120 min; KPS, 7 mmol/L; and temperature, 50°C.

humidity chamber for a particular time interval under different humidity levels ranging from 20% to 90%. Final weights of the samples exposed to different humidity levels were then noted. The percent moisture absorbance (%Mabs) was calculated from the increase in initial weight in the following manner:

$$\%\ \text{Moisture absorbance}\ (\%\ M_{abs}) = \frac{W_f - W_i}{W_i} \times 100$$

where W_f is the weight of grafted fiber and W_i is the weight of raw fiber.

Water uptake behavior. Water uptake studies of the grafted as well as ungrafted fibers were carried out using the concept of capillary action. Wicks of fibers of 0.7 mm diameter were prepared and an initial ink mark was drawn at one end. The wicks were then dipped into beakers containing water for a particular time interval. The rise of water in each wick was noted with the help of the ink mark.

Water uptake capacity of grafted and ungrafted fibers was calculated as follows:

$$P_w = \frac{T_f - D}{T_f} \times 100$$

where T_f is total fiber length and D is the distance traveled by water in the fiber wicks.

Chemical resistance behavior. Chemical resistance studies were carried out on grafted as well as raw fibers using acids (HCl) and bases (NaOH) of 1 N concentration. These studies were carried out in terms of weight loss. Known weights of both grafted and raw fibers were immersed in acids and bases for a particular time interval. Final weights of the samples subjected to the action of acids and bases were then noted.

The chemical resistance of grafted as well as ungrafted fibers towards acid and base in terms of percentage weight loss was studied as in the following manner:

$$\text{Percent chemical resistance } (P_{cr}) = \frac{T_w - W_{aci}}{T_w} \times 100$$

where T_w = total weight and W_{aci} = weight after certain interval.

Characterization of raw/grafted *Hibiscus sabdariffa* fibers.

Infrared spectroscopy (IR). IR spectra of the raw and surface-modified *Hibiscus sabdariffa* fibers were taken with KBr pellets on a PerkinElmer RXI Spectrophotometer from 4000 to 500 cm^{-1} with a resolution of 2 cm^{-1}.

Scanning electron microscopy (SEM). Scanning electron microscopic (SEM) studies of raw/grafted *Hibiscus sabdariffa* fibers were carried out on a LEO 435 VP electron microscopy machine. The excitation energy used was 5 keV. Fibers were mounted on the specimen holders with the help of electro-conductive tape.

Thermal analysis. Thermal analysis of natural and synthetic polymers gives us a good account of their thermal stability. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) studies of samples were carried out in nitrogen atmosphere on a thermal analyzer (PerkinElmer) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

It has been observed that in natural polymeric materials containing cellulose C_2, C_3, and C_6–OH groups and C–H sites are the active centers for grafting of polymeric chains onto polymeric backbone.[29–31] The native cellulose molecule consists of linear glucan chains with repeating (1→4) β-glucopyranose units. Cellobiose is the dimer of cellulose and it is the repeating unit of the polymer (Figure 1). The degree of polymerization is determined by the number of single anhydroglucose units, and it varies depending on the origin of cellulose. The mechanism of grafting methyl acrylate onto cellulose using potassium persulfate as the oxidizing initiator is explained in Scheme 1. It has been observed that the interaction of SO_4^{-*} with H_2O generates OH free radicals and these free radicals are responsible for carrying out graft copolymerization onto *Hibiscus sabdariffa* fibers.

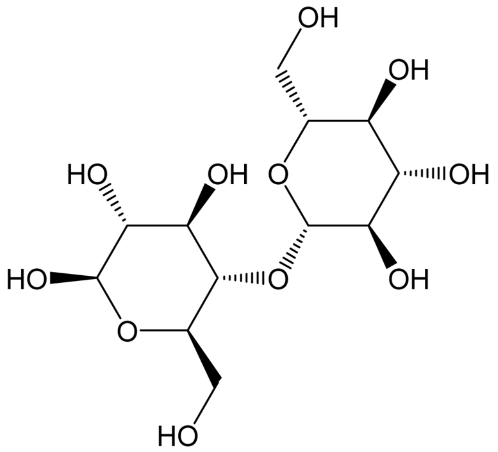


Figure 1. Structure of cellobiose (repeating unit of the cellulose polymer).

Optimization of Different Reaction Parameters for Grafting MA onto *Hibiscus sabdariffa* Fibers

The various reaction parameters that have been optimized to achieve the maximum graft yield are monomer concentration, initiator, reaction temperature, reaction time, and solvent. Table I shows different values of graft yields during optimization of the reaction parameters. The optimum conditions for maximum graft yield (63.15%) as given in Table I were: solvent, 100 mL; monomer, 2.00×10^{-1} mol/L, time, 120 min; temperature, 50°C; KPS monomer, 7 mmol/L.

Analysis of Different Parameters on Overall Graft Copolymerization of the Fibers

Effect of monomer concentration. The graft yield increases with the initial increase in monomer concentration, reaches the optimum value, and then decreases with further increase in the monomer concentration (Table I). The above behavior of the monomer concentration may be explained on the basis that initially more and more radicals reach onto the backbone, resulting in the increase in graft yield. However, with further increase in the monomer concentration, homopolymerization dominates over graft copolymerization, leading to decreased graft yield.

Effect of solvent. The presence of water as a reaction medium in the grafting reactions has been found to have a very important effect on percentage of grafting of vinyl monomers on *Hibiscus sabdariffa* fibers. To study the effect of amount of water during grafting of MA, graft copolymerization has been carried out as a function of amount of water, and the results are presented in Table I. It has been observed that percentage of grafting of MA shows an initial jump with increasing amount of water, from 50 to 100 mL, giving maximum (63.15%) grafting in 100 mL, and then decreases sharply on further increase in the amount of water and becomes almost constant.

INITIATION

$$^{-}O_3S\text{-O-O-}SO_3^{-} \longrightarrow 2SO_4^{-\,*} \tag{1}$$

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

$$\text{Cell-OH} + SO_4^{-*} \longrightarrow \text{Cell-O}^{*} + HSO_4^{-} \tag{3}$$

$$\text{Cell-OH} + {}^{*}OH \longrightarrow \text{Cell-O}^{*} + H_2O \tag{4}$$

$$M + {}^{*}OH \longrightarrow {}^{*}M\text{-OH} \tag{5}$$

$$M + SO_4^{-*} \longrightarrow {}^{*}M\text{-}SO_4^{-} \tag{6}$$

PROPAGATION

$$\text{Cell-O-(M)}_n\text{-M}^{*} + \text{M}^{*}\text{-(M)}_n\text{-O-Cell} \longrightarrow \underset{\text{(Graft copolymer)}}{\text{Cell-O-(M)}_n\text{-M}_2\text{-(M)}_n\text{-O-Cell}} \tag{11}$$

$$\text{Cell-O-(M)}_{n-1}\text{-M}^{*} + \text{M}^{*}\text{-(M)}_{n-1}\text{-O-Cell} \longrightarrow \underset{\text{(Graft copolymer)}}{\text{Cell-O-(M)}_{n-1}\text{-M}_2\text{-(M)}_{n-1}\text{-O-Cell}} \tag{12}$$

$$\text{Cell-O-(M)}_n\text{-M}^{*} + {}^{*}OH \longrightarrow \text{Cell-O-(M)}_{n+1}\text{-OH} \tag{13}$$

$$\text{HO-(M)}_n\text{-M}^{*} + {}^{*}\text{M-(M)}_n\text{-OH} \longrightarrow \underset{\text{(Homopolymer)}}{\text{HO-(M)}_n\text{-M}_2\text{-(M)}_n\text{-OH}} \tag{14}$$

TERMINATION

$$\text{Cell-OH} + {}^{*}\text{M-OH} \longrightarrow \text{Cell-O-M}^{*} + H_2O \tag{7}$$

$$\text{Cell-O-M}^{*} + nM \longrightarrow \text{Cell-O-(M)}_n\text{-M}^{*} \tag{8}$$

$$\text{Cell-O}^{*} + nM \longrightarrow \text{Cell-O-(M)}_{n-1}\text{M}^{*} \tag{9}$$

$${}^{*}\text{M-OH} + nM \longrightarrow \text{HO-(M)}_n\text{-M}^{*} \tag{10}$$

Scheme 1. Mechanism of the graft copolymerization reactions.

The increase in solvent concentration after 100 mL resulted in decreased graft yield, probably due to the greater dilution of reaction medium, which lowers the concentration of monomer radical per unit volume and hence less grafting takes place.

Effect of initiator. The optimum molar concentration of initiator for maximum graft yield was found to be 7 mmol/L (Table I). It has been observed that as the concentration of initiator increases, more and more radicals are generated, which results in the increase in graft yield. After reaching the optimum value, graft yield decreases with further increase in initiator concentration (Table I). This may be due to the fact that with further increase in the initiator concentration chain termination reactions dominate the graft copolymerization, which leads to premature decay of the monomer radicals.

Effect of reaction time. The optimum reaction time has been found to be 120 min for graft copolymerization reaction. With the initial increase in time graft yield increases, reaches an optimum value at 120 min, and decreases with further increase in reaction time (Table I). This variation of percent graft yield with time can be explained on the basis that as the reaction time increases, more and more radicals move onto the backbone, resulting in the increased graft yield. After reaching the optimal value with further increase in reaction time, most of the active sites on the backbone are occupied by the radicals, and the formation of the homopolymer dominates the graft copolymerization. Moreover, viscosity of the reaction medium increases with time, which provides hindrance for radicals to move onto active sites of the backbone and results in the decrease in graft yield.

Effect of reaction temperature on grafting. Temperature plays an important role in every graft copolymerization reaction. The graft yield increases with the initial increase in temperature, reaches the optimum value at 50°C, and then decreases with further rise in temperature. The above behavior of variation of percent grafting with temperature can be attributed to the fact that with the initial rise in temperature, as the kinetic energy of the molecules increases, more and more radicals drifted at a faster rate onto the backbone, resulting in the increase in graft yield. However, after reaching the optimum temperature, with further increase in temperature a considerable amount of homopolymer is formed, which results in increase in the viscosity of the reaction mixture. This hinders the radicals from moving towards the active sites of the polymeric backbone, resulting in the decrease in percent grafting.

Analysis of Swelling, Moisture Absorbance, Water Uptake, and Chemical Resistance Behavior

Swelling behavior of raw fibers and their graft copolymers. Grafted and ungrafted *Hibiscus sabdariffa* fibers have been found to exhibit different swelling behavior in different solvents (Figure 2). The swelling behavior of ungrafted fiber in different solvents follows the trend $H_2O > CH_3OH >$ iso-BuOH > DMF due to greater affinity of water for OH groups present in the raw *Hibiscus sabdariffa* fibers. In the case of grafted fiber, swelling behavior varies as a function of P_g and follows the trend DMF $> CH_3OH > H_2O >$ iso-BuOH. This reversal in swelling behavior may be due to blockage of active sites on the polymeric substrate by poly MA chains, which causes change in the sorption of the different solvents. Since poly MA chains on grafted fiber are more solvolyzed by dipolar aprotic solvent (DMF) than by water or alcohol, more swelling took place in DMF than other solvents.

Moisture absorbance behavior of raw fibers and their graft copolymers. The moisture absorbance behavior at different humidity levels as a function of P_g has been depicted (Figure 3). It has been found that moisture absorbance (M_{abs}) decreases with the increase in P_g. The raw fiber shows more M_{abs} as compared to grafted fibers. This behavior of grafted fibers may be due to the attachment of poly MA chains grafted onto the fiber, which shows less affinity toward water.

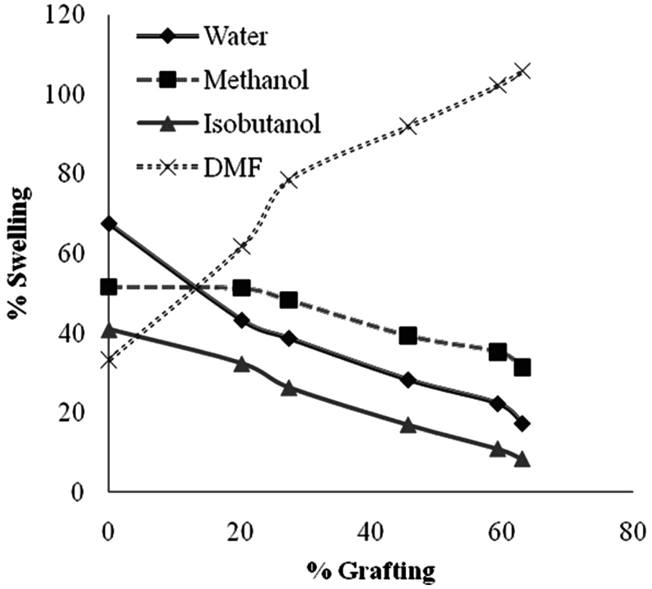


Figure 2. Swelling behavior of ungrafted and grafted *Hibiscus sabdariffa* fibers in different solvents.

Water uptake behavior of raw fibers and their graft copolymers. Water uptake studies of the raw and grafted fibers have been made by capillary action. Water uptake capacity of graft copolymers was found to decrease with increase in grafting (Figure 4). This behavior of grafted fibers may be attributed to the

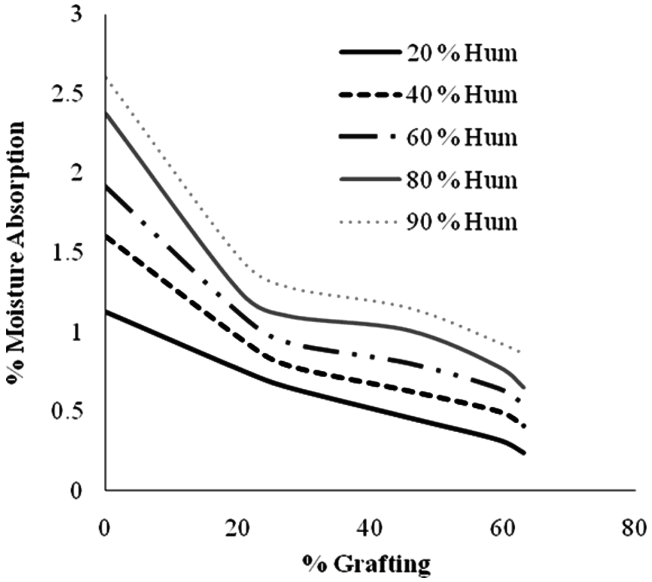


Figure 3. Moisture absorbance behavior of raw and grafted *Hibiscus sabdariffa* fibers at different humidity levels.

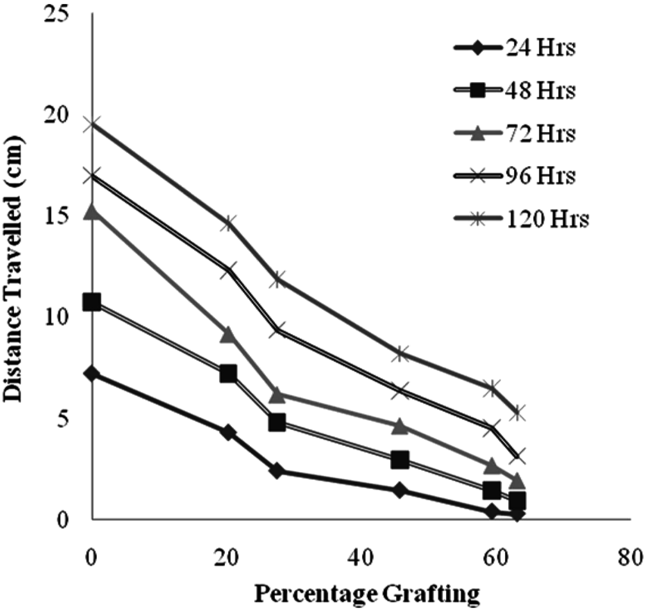


Figure 4. Water uptake behavior of raw and grafted *Hibiscus sabdariffa* fibers at different time intervals.

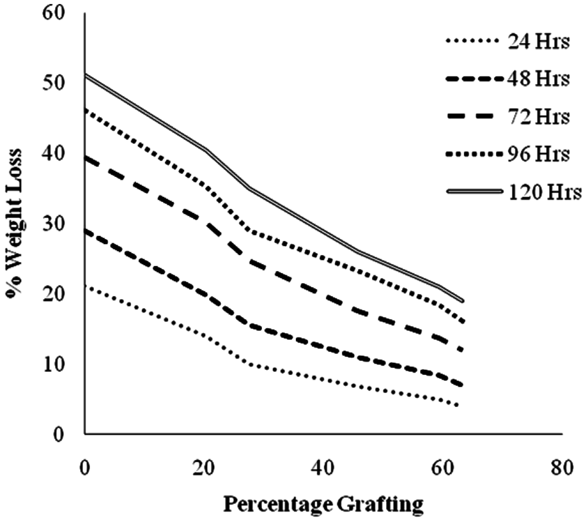
hydrophobicity of poly (MA) chains that are incorporated at active sites on the fiber surface as a result of graft copolymerization.

Chemical resistance behavior of raw fibers and their graft copolymers. The chemical resistance of the raw as well as of the grafted fibers has been studied in terms of percent weight loss in 1 N HCl and 1 N NaOH respectively. It has been observed that resistance towards chemicals increases with the increase in % grafting (Figure 5). This may be due to blockage of active sites vulnerable to the chemical attack by poly (MA) on the polymeric backbone resulting in more resistance towards the chemicals.

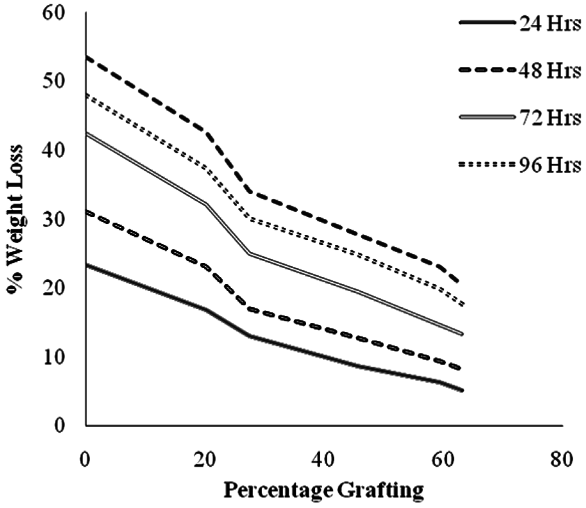
Evidence of Grafting

Characterization by FT-IR spectroscopy. The Fourier transform-infrared (FT-IR) spectrum of raw the *Hibiscus sabdariffa* fibers showed a broad peak at 3415.4 cm^{-1} due to bonded OH groups and at 2923.3, 1426.5, and 1031.0 cm^{-1} due to $-CH_2$, C–C, and C–O stretching respectively. However, in the case of *Hibiscus sabdariffa*-g-poly (MA) an additional peak at 1732.58 cm^{-1} was observed, which corresponds to carbonyl group ($>C=O$) of the PMA chains, which was absent in raw fiber. The above results have provided evidence for grafting of MA onto the *Hibiscus sabdariffa* through covalent bonds.

Characterization by scanning electron microscopy. The scanning electron micrographs of raw fibers and *Hibiscus sabdariffa*-g-poly (MA) show a clear-cut



(a)



(b)

Figure 5. (a) Acid resistance behavior of raw and grafted *Hibiscus sabdariffa* fibers in 1 N HCl at different time intervals; (b) Base resistance behavior of raw and grafted *Hibiscus sabdariffa* fibers in 1 N NaOH at different time intervals.

distinction between raw and grafted fibers (Figures 6 and 7), which provides evidence for the change in surface morphology of the fiber surface on grafting. From the scanning electron micrographs, it is clear that surface of raw *Hibiscus sabdariffa* fibers is smoother than that of the grafted fibers. This difference is due to the deposition of poly (MA) chains on the surface of raw *Hibiscus sabdariffa* fibers through graft copolymerization.

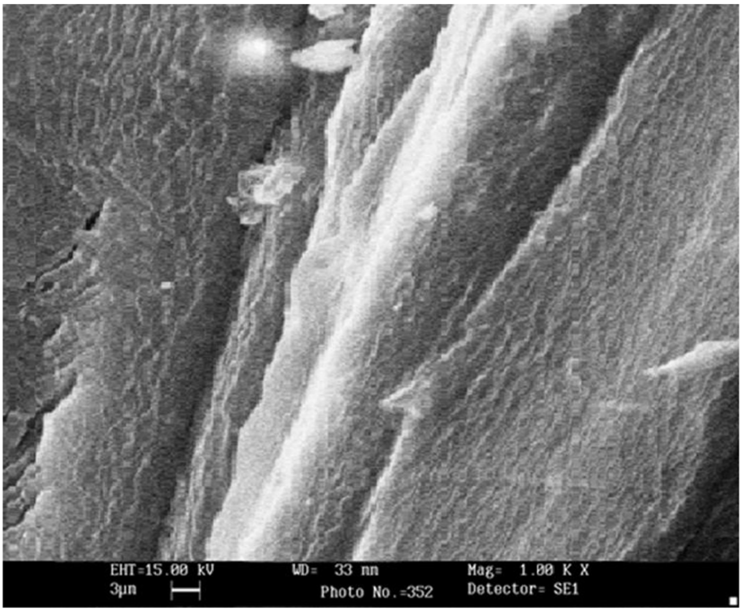


Figure 6. Scanning electron micrograph of raw *Hibiscus sabdariffa* fibers.

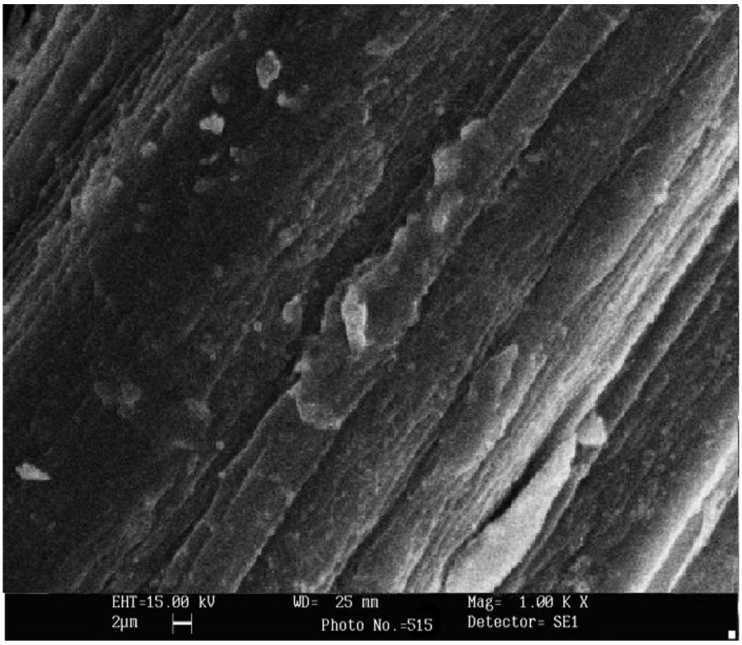


Figure 7. Scanning electron micrograph of MA grafted *Hibiscus sabdariffa* fibers.

Characterization by thermal analysis. Thermogravimetric analysis (TGA) of raw fiber and grafted fibers was studied as a function of % weight loss with increase in temperature. In the case of raw *Hibiscus sabdariffa* fibers, at the beginning of polymerization, dehydration and glucosan formation took place in the temperature range from 25.0° to 199.0°C followed by the cleavage of C–H, C–C, and C–O bonds. For raw fiber, the initial decomposition (IDT) temperature has been found to be 199°C (7.65% wt. loss) and the final decomposition temperature (FDT) to be 500°C (85.71% wt. loss). In the case of methyl acrylate (MA)-grafted *Hibiscus sabdariffa* fibers, the initial decomposition temperature (IDT) has been found to be 220°C (9.17% wt. loss) and the final decomposition temperature (FDT) to be 527°C (56.83% wt. loss). The TGA studies have been further supported by differential thermal analysis (DTA) evaluation. DTA of raw fiber shows exothermic peaks at 293.0°C (0.237 μV) and 355.0°C (1.126 μV). In the case of graft copolymer, a continuous exothermic rise in temperature has been observed. An exothermic peak is observed at 385.0°C (235 μV), which shows the loss of amorphous and crystalline structure of grafted fiber.

CONCLUSIONS

Hibiscus sabdariffa graft-poly methyl acrylate copolymers were synthesized by free-radical polymerization and were used to improve the stability and physicochemical properties of cellulosic biofibers. The effect of solvent, monomer, initiator, and other factors on the grafting yield was investigated. The grafting effect increases with increasing solvent concentration until a maximum is obtained, and the further increase of the solvent concentration caused a sharp decline of the grafting effect. As seen from the experimental results, MA monomer can be successfully grafted onto cellulosic *Hibiscus sabdariffa* fibers by the use of KPS initiator. Further, it has been observed that factors such as temperature, initiator, and monomer concentration affect the graft yield to a considerable extent.

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