

Graft Copolymerization of Methyl Methacrylate onto Cellulosic Biofibers

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ABSTRACT: In this article, we have used the potassium persulfate to initiate the graft copolymerization of methyl methacrylate onto cellulosic biofibers in aqueous medium. Different reaction parameters, such as reaction time, initiator molar ratio, monomer concentration, amount of solvent, and reaction temperature, were optimized to get the maximum percentage of grafting (50.93%). The graft copolymers thus formed were characterized by Fourier transform infrared, scanning electron microscopy, X-ray diffraction, and thermogravimetric, differential thermal analysis, and derivative thermogravimetric techniques. A mechanism is proposed to explain the generation of radi-

cals and the initiation of graft copolymerization reactions. On grafting, percentage crystallinity decreases with reduction in its stiffness and hardness. The effect of grafting percentage on the physicochemical properties of raw as well as grafted fibers has also been investigated. The graft copolymers have been found to be more moisture resistant and also showed better chemical and thermal resistance.

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Key words: graft copolymerization; potassium persulfate; cellulosic biofibers; methyl methacrylate (MMA); physicochemical properties

INTRODUCTION

During the last two decades, polymer-based materials such as cellulosic fibers, poly (vinyl alcohol), poly(lactic acid), and rayon fibers have replaced a lot of conventional materials (glass fibers, carbon fibers, and Kevlar) in various applications.^{1–4} The ease of processing, cost reduction, and productivity are the most significant advantages that the polymers offer over other materials.^{5–7} Currently, most of the properties of the polymers are modified by using cellulosic fibers since cellulose and lignin contain hydroxyl groups, and the fibers can form bond with suitable polymer groups and also results in incorporating biodegradable properties in the resulting materials.^{8–10} Natural cellulosic fibers provide a wide range of applications in composite materials such as materials for construction, food packaging, and automotive parts.^{11–13} The strongest potential for cellulose products originates from the combination of the enormous properties such as low density, low health hazards, biodegradability, better wear

resistance, and a high degree of flexibility, low cost, renewability, and high specific strength.^{14–17} It is most likely that they will be a major chemical resource for the future. Although natural fibers have a number of advantages, these cellulosic fibers have few disadvantages with respect to their application as reinforcement in polymer composites.^{10,18–21} These fibers are very sensitive to moisture, chemicals, and water, and their properties are degraded when they come in contact with harsh environmental conditions.^{10,18–22} A variety of chemical treatments and modifications have been employed on cellulosic fibers before incorporation into finished products. Graft copolymerization is an effective technique used for modifying the properties of synthetic or natural polymers.^{22–24} In fact, the science and technology of multiphase polymer systems, particularly in graft copolymers, have received a great deal of attention for both academic and industrial interests in the last few decades. In most cases, the graft copolymers are made of monomer segments chemically bonded onto the backbone of a polymer. Modification of such cellulose polymers by grafting reactions provides a significant route to impart a new property or enhance existing properties. Grafting can be achieved by radiation or chemical methods.^{19–24} The chemical methods have some advantages, such as high radical yield and no degradation of cellulosic chain over radiation grafting. There are numerous studies on the grafting of various

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monomers such as acrylic acid, acrylonitrile, and acrylamide onto natural and synthetic fibers by this method.^{10,19,22}

Hibiscus sabdariffa, an edible medicinal plant, is mainly found in India, China, and Thailand. It is used in Ayurveda and traditional medicine.¹⁸ This species belong to the family Malvaceae with chromosome number $2n = 72$. It is an annual or perennial herb or woody based subshrub with a height of 2–2.5 m. It takes about six months to mature. The mature plant serves as a source of bast fibers. *Hibiscus sabdariffa* can be grown even in those areas where jute is not grown under wider climatic and soil conditions with much less care. It grows best in tropical and subtropical regions from sea level up to 3000 ft (900 m) with a rainfall of about 72 in. (182 cm) during its growing season. It can be grown as a summer crop in temperate regions. *Hibiscus sabdariffa* is usually propagated by seed but can grow readily from cuttings also. The fibers obtained from *Hibiscus sabdariffa* are similar in appearance to other type of fibers studied earlier, such as cotton, jute, flax, ramie, and hemp.^{12,13} *Hibiscus sabdariffa* is mainly composed of cellulose (55–71%), hemicellulose (11–14%), and lignin (9–14%).¹⁸ A part of the lignin and hemicellulose is linked chemically through ester linkages formed by the carboxyl groups of lignin.^{18–20} This in turn affects the physical properties of cellulosic *Hibiscus sabdariffa* fibers. As a vinyl monomer, methyl methacrylate (MMA) has the potential to graft onto cellulose fibers using different initiating systems, such as ionic and radical initiators. The aim of this research is to modify natural cellulosic *Hibiscus sabdariffa* fibers to improve and increase the consistency of their performance in different potential applications. Fiber modification consisted of solvent extraction and sodium hydroxide (NaOH) treatment to remove wax and lignin before graft copolymerization. In this study, MMA, which has a hydrophobic character, was selected as monomer and grafted onto cellulosic fibers by using potassium persulfate (KPS) as an initiator. The effects of graft copolymerization parameters on the percentage of grafting were investigated, and the changes in the properties of grafted fibers, such as water absorption, moisture absorption, chemical resistance, and thermal stability were reported.

EXPERIMENTAL

Materials

Hibiscus sabdariffa fibers were collected from local resources of Himalayan region. The chemicals and solvents such as NaOH, acetone, ethanol, and KPS were of Analar grade and used without further purification. Purified MMA was used as vinyl monomer

for graft copolymerization of the cellulosic *Hibiscus sabdariffa* fibers. Purification of natural *Hibiscus sabdariffa* fibers, MMA, and separation of homopolymer from the grafted fibers were carried out according to the procedure reported somewhere else.^{18–22} Briefly, the purified *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. These untreated fibers were subsequently subjected to extraction with acetone for 72 h in 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

Generally, the first step in chemical treatment of natural fibers is the mercerization process (pretreatment process). Mercerization of the cellulosic fibers was carried out per standard method reported earlier in some of our studies.¹⁸ Lignocellulosic *Hibiscus sabdariffa* fibers were immersed in NaOH solution of different concentration (2–10%) for different time intervals at room temperature for the optimization of time.¹⁸ 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 these natural fibers was given with 2% acetic acid 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.

Synthesis and purification of graft copolymers

A known amount (0.5 g) of the chemically modified *Hibiscus sabdariffa* fibers was immersed in a definite amount of distilled water for 24 h prior to graft copolymerization reaction to activate the reactive sites on the fibers surface.^{10,19,22} The graft copolymerization reaction was carried out in a 250-mL reaction flask kept in a water bath over a hot plate cum magnetic stirrer. A known amount of initiator (KPS) and monomer (MMA) was then added into

TABLE I
Optimization of Various Reaction Parameters for Optimum Graft Copolymerization of Methyl Methacrylate onto *Hibiscus sabdariffa* Fibers

| Sr. No. | Solvent (mL) | Monomer ($\times 10^{-1}$ mol/L) | KPS (mmol/L) | Time (min) | Temperature | % Grafting |
|---------|--------------|-----------------------------------|--------------|------------|-------------|--------------|
| 1. | 60 | 2.40 | 7.00 | 100 | 35 | 05.47 |
| 2. | 75 | 2.40 | 7.00 | 100 | 35 | 11.36 |
| 3. | 90 | 2.40 | 7.00 | 100 | 35 | 16.71 |
| 4. | 105 | 2.40 | 7.00 | 100 | 35 | 14.99 |
| 5. | 120 | 2.40 | 7.00 | 100 | 35 | 14.23 |
| 6. | 90 | 1.95 | 7.00 | 100 | 35 | 14.72 |
| 7. | 90 | 2.05 | 7.00 | 100 | 35 | 15.90 |
| 8. | 90 | 2.15 | 7.00 | 100 | 35 | 18.43 |
| 9. | 90 | 2.25 | 7.00 | 100 | 35 | 21.97 |
| 10. | 90 | 2.35 | 7.00 | 100 | 35 | 18.72 |
| 11. | 90 | 2.25 | 6.50 | 100 | 35 | 20.92 |
| 12. | 90 | 2.25 | 6.75 | 100 | 35 | 21.37 |
| 13. | 90 | 2.25 | 7.25 | 100 | 35 | 35.89 |
| 14. | 90 | 2.25 | 7.50 | 100 | 35 | 32.48 |
| 15. | 90 | 2.25 | 8.00 | 100 | 35 | 30.00 |
| 16. | 90 | 2.25 | 7.25 | 050 | 35 | 29.63 |
| 17. | 90 | 2.25 | 7.25 | 075 | 35 | 32.17 |
| 18. | 90 | 2.25 | 7.25 | 125 | 35 | 43.61 |
| 19. | 90 | 2.25 | 7.25 | 150 | 35 | 41.94 |
| 20. | 90 | 2.25 | 7.25 | 175 | 35 | 38.75 |
| 21. | 90 | 2.25 | 7.25 | 125 | 40 | 46.55 |
| 22. | 90 | 2.25 | 7.25 | 125 | 45 | 50.93 |
| 23. | 90 | 2.25 | 7.25 | 125 | 50 | 48.88 |
| 24. | 90 | 2.25 | 7.25 | 125 | 55 | 46.96 |

Optimized conditions are: solvent = 90 mL, monomer = 2.25×10^{-1} mol/L, KPS = 7.25 mmol/L, time = 125 min, and temperature = 45°C.

the flask containing fibers. The reaction mixture was then stirred at preset temperature for a particular time interval. Optimum conditions of solvent, monomer concentration, initiator (KPS ratio), time, and temperature were evaluated for maximum percentage of grafting (Table I). The homopolymer formed during graft copolymerization was removed by extraction with acetone in a soxhlet extraction apparatus for 72 h.^{19,22} The graft copolymers free from homopolymer were then dried in a hot air oven to a constant weight. The percentage grafting (P_g) was calculated per procedure reported earlier.^{19,22}

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

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

Characterization of grafted and raw *Hibiscus sabdariffa* fibers

Infrared spectroscopy. To verify changes in the structure of cellulosic fibers before and after graft copolymerization, the infrared (IR) spectra of the raw and grafted *Hibiscus sabdariffa* fibers were obtained. The Perkin-Elmer system RXI was used to characterize these fibers. The FTIR spectra were obtained with eight scans per sample over the range of 4000–500 cm^{-1} with 2 cm^{-1} resolution.

Scanning electron microscopy. Scanning electron microscopic (SEM) studies of raw/grafted *Hibiscus sabdariffa* fibers were carried out on Electron Microscopy Machine (LEO 435 VP). The excitation energy used was 5 keV. Fibers were mounted on the specimen holders with the help of electroconductive tape. To achieve good electric conductivity, all samples were first carbon sputtered followed by sputtering a gold-palladium mixture before examination. SEM micrographs of the samples show the morphology of the raw and grafted fibers. These micrographs clearly show the difference between raw and grafted cellulosic fibers.

X-ray diffraction studies. X-ray diffraction (XRD) studies were performed on a Bruker D8 Advance X-ray diffractometer, using Cu $K\alpha$ (1.5418 E) radiation, a Ni filters, and a scintillation counter as a detector at 40 KV and 40 mA on rotation from 5° to 50° at 2θ scale. Each sample was finely powdered into small particle size and homogeneously mixed before being subjected to X-ray analysis. The finely powdered sample was evenly distributed in the cavity of the sample holder with the help of a glass slide. The glass slide was carefully removed without disturbing the surface of the sample. The randomly oriented powdered sample with uniform surface was exposed to X-rays from all possible planes. The angle of

scattering of the diffracted beam was measured with respect to the incident beam of X-rays and relative intensity was obtained. Crystallinity index (C.I.) was determined by using the wide-angle XRD counts at 2θ close to 22° and 18° . The counter reading of peak intensity close to 22° and 15° is said to represent the crystalline material and amorphous material in cellulose, respectively.¹⁹ Percent crystallinity and crystallinity index (C.I.) were calculated using the following formulas:

$$\text{Percent crystallinity (\%Cr)} = (I_{22}/(I_{22} + I_{15})) \times 100$$

$$\text{Crystallinity index (\%C.I.)} = ((I_{22} - I_{15})/I_{22}) \times 100.$$

Thermal analysis. Thermal analysis of natural and synthetic polymers gives us good account of their thermal stability.^{18–20,22} Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetric (DTG) studies of samples were carried out in air atmosphere on a thermal analyzer (Perkin–Elmer) at a heating rate of $10^\circ\text{C}/\text{min}$. TGA was used to characterize the decomposition and thermal stability of materials under a variety of conditions and to examine the kinetics of the physicochemical processes occurring in the sample. Basically, in this method a change in thermal stability is examined in terms of percentage weight loss as a function of temperature.^{18–20} The mass change characteristics of a material are strongly dependent on the experimental conditions such as sample mass, volume and physical form, the shape and nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber and the scanning rate all have important influences on the characteristics of the recorded TG curve. At the same time, DTA involves comparing the precise temperature difference between a sample and an inert reference material while heating both. In thermal analysis, from time to time, overlapping reactions are difficult to resolve, and in some cases, resolution can be improved by hindering escape of evolved gas from the sample by placing a loosely fitting lid on the crucible, changing the packing or form of the sample, choosing a different crucible, or by varying the heating rate. Altering the experimental conditions may change the relative rates of the overlapping reactions and led to the better resolution. In DTG, the mass change with respect to temperature (dm/dT) is plotted against temperature. A point of inflection in the mass change step becomes a minimum in the derivative curve and for an interval of constant mass dm/dT is zero, a peak in the DTG curve occurs when the rate of mass change is a maximum. DTG peaks are characterized by the peak maximum (T_{max}) and the peak on set temperature (T_e). The area under DTG

curve is proportional to the mass change and the height of the peak at any temperature gives the rate of the mass change at that temperature. However, a DTG curve contains no more information than the original TG curve. DTG curves are frequently preferred when comparing results with DTA curves because of the visual similarity.

Physicochemical studies on raw and grafted *Hibiscus sabdariffa* fibers

For the effective utilization of natural fibers in different applications, particularly as reinforcement in polymer matrix based composite, meticulous interest lies in their behavior against different weathering conditions.^{10,18–22} The effect of environmental conditions on the natural fibers and polymer biocomposites has been studied by a number of researchers and has been the subject of much debate recently. The commercial viability of the grafted cellulosic fibers and natural fibers reinforced composites lies in their physical and chemical properties. Keeping in mind the commercial viability, a comprehensive study on swelling behavior in different solvents, moisture absorbance at different humidity levels, and chemical resistance behavior against 1N HCl and 1N NaOH of grafted/raw cellulosic fibers has been carried out to assess the potential application of these lignocellulosic fibers as reinforcing material in a number of engineering parts. Three specimens of each sample were used for the measurement of the earlier-mentioned properties, and average results have been reported.

Swelling behavior. To assess the applications of grafted fibers in everyday life, these were subjected to study in different solvents. Swelling (in different solvents such as dimethyl formamide, water, methanol, and isobutyl alcohol) studies of grafted and ungrafted fibers were carried out per methods reported somewhere else.^{18–22} The percent swelling was calculated from the increase in initial weight in the following manner:

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

where W_f is the final weight of raw/grafted fiber (after swelling), and W_i is the initial weight of raw/grafted fiber.

Water uptake behavior. Water uptake studies of the grafted as well as ungrafted fibers were carried out using the concept of capillary action.^{18,19,22} Wicks of fibers of 3-mm diameter and 50-mm length were prepared, and an initial ink mark was drawn at one end. The wicks were then dipped (5 mm) 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.

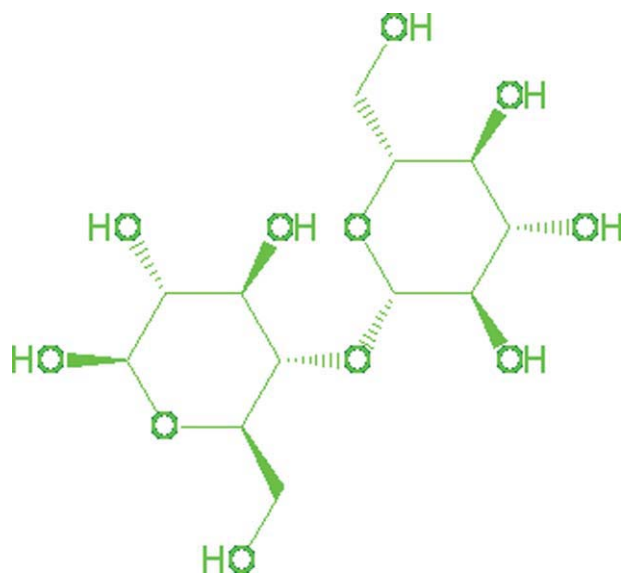


Figure 1 Structure of cellobiose (repeating unit of the cellulose polymer). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

$$P_w = ((T_f - D)/T_f) \times 100$$

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

Moisture absorbance behavior. Moisture absorbance studies were made in a humidity chamber. Known weights of dry grafted and raw fibers were placed in the humidity chamber for particular time interval (2 h) 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 (% M_{abs}) was calculated from the increase in initial weight in the following manner:

$$\begin{aligned} \text{\% Moisture absorbance (\%}M_{\text{abs}}\text{)} \\ = ((W_f - W_i)/W_i) \times 100 \end{aligned}$$

where W_f is the final weight of raw/grafted fibers, and W_i is the initial weight of raw/grafted fibers.

Chemical resistance behavior. Chemical resistance studies were carried out on grafted as well as raw fibers using acids (HCl) and bases (NaOH) of one normal (1N) 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 toward acid and base in terms of

percentage weight loss was studied as in the following manner:

$$\begin{aligned} \text{Percent chemical resistance } (P_{\text{cr}}) \\ = ((T_w - W_{\text{aci}})/T_w) \times 100 \end{aligned}$$

where T_w is the total weight, and W_{aci} is the weight after certain interval.

RESULTS AND DISCUSSION

In natural fibers such as *Hibiscus sabdariffa* fibers, the native cellulose molecule consists of linear glucan chains with repeating (1→4) β-glucopyranose units.^{10,18–22} Cellobiose is the dimer of cellulose, and it is the repeating unit of the polymer (Fig. 1). The degree of polymerization is determined by the number of single anhydroglucose units, and it varies depending on the origin of cellulose. It has been observed that in natural polymeric materials containing cellulose, C₂, C₃ and C₆—OH groups, and C—H sites are the active centers onto polymeric backbone.^{18–22} The presence of these three reactive hydroxyl groups on each unit of cellulose biofibers makes it susceptible to get modified through free radical graft copolymerization.^{1,2,10,18–22} *Hibiscus sabdariffa* fibers were chosen as the cellulose fibers because of their potential applications such as reinforcement in polymer composites and as support matrix in the removal of toxic metal ions, green hydrogels supports by suitable functionalization as cation (Fe³⁺) and anion (NO³⁻) adsorbents in near future.²⁵

During graft copolymerization process, an initiator helps in generating the free radicals that are responsible for creating active sites on the polymeric backbone. Along with graft copolymerization reaction, homopolymerization and various other side reactions also take place.^{1,2,10,19,22} Among various chemical initiator systems, KPS is a well-known initiator and has been used for graft copolymerization of MMA onto *Hibiscus sabdariffa* vinyl monomer polymerization. Hydroxyl radical formed from the reaction of SO₄^{-*} has initiated the process of polymerization by generating the free radicals on the *Hibiscus sabdariffa* fibers and MMA monomer. During termination reaction, grafting of poly (MMA) onto *Hibiscus sabdariffa* fibers has occurred and has formed the grafted copolymers. The detailed mechanism for the synthesis of *Hibiscus sabdariffa*-g-PMMA is given in Scheme 1.

Optimization of different reaction parameters for grafting of methylmethacrylate onto *Hibiscus sabdariffa* fibers

Percentage of grafting of methylmethacrylate onto *Hibiscus sabdariffa* fibers by chemical method has been determined as a function of various reaction

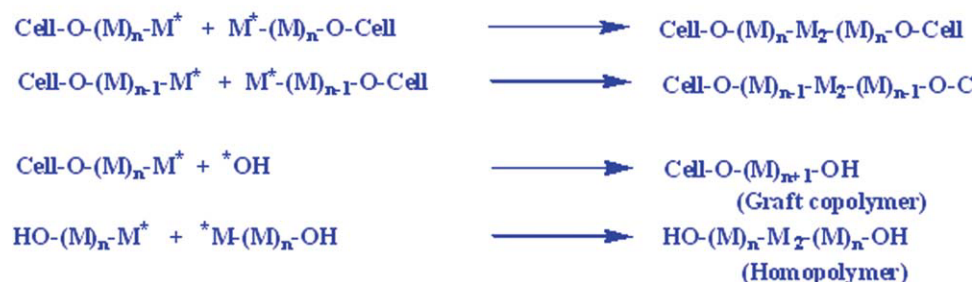
INITIATION



PROPAGATION



TERMINATION



Scheme 1 Mechanism of the graft copolymerization reactions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

parameters that seem to affect the grafting reaction, and the results are explained in light of the grafting mechanisms. Optimization of reaction parameters such as amount of solvent, monomer concentration, initiator (KPS ratio), time, and temperature were carried out for graft copolymerization of methylmethacrylate in air. Table I shows different values of percentage of grafting during optimization of the reaction parameters. The optimum conditions for maximum percentage of grafting (50.93%) as given in Table I were solvent = 90 mL, monomer = 2.25×10^{-1} mol/L, KPS initiator = 7.25 mM, time = 125 min, and temperature = 45°C.

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 the percentage of grafting of vinyl monomers on *Hibiscus sabdariffa* fibers. The effect of water on the percentage of grafting of methylmethacrylate onto *Hibiscus sabdariffa* seems to play an important role for two reasons: first, because of the hydrophilic nature of the backbone, and second, because of the solubility of the monomer in water. Water, which also has a zero solvent-transfer constant, does not involve any waste side reactions because of radical transfer.²⁶ Interaction of the hydroxyl groups of *Hibiscus sabdariffa* fibers with water through hydrogen bonding helps in swelling and opening of the fiber structure, making it accessible to the monomer and the growing polymeric chains.²⁶ To study the effect of amount of water during grafting of MMA, 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 MMA shows an initial jump in percentage of grafting with increasing amount of water, from 60 to 90 mL giving maximum (16.71%) grafting in 90 mL and then decreases sharply on further increase in the amount of water and becomes almost constant. The initial increase in grafting with the increasing amount of water helped in swelling of the backbone, thus exposing the active sites. The increase in solvent concentration after 90 mL resulted in decreased percentage of grafting probably due to the more dilution of reaction medium, which lowers the concentration of monomer radical per unit volume and hence less grafting takes place. The decrease in grafting beyond the optimum amount is attributed to the fact that in the presence of a higher amount of water, excessive solvation of the monomer occurs, which inhibits its accessibility to the active sites. Furthermore, excess water also affects the formation of the complex of both the cellulosic fibers and the monomer, thus decreasing the generation of the active sites on the cellulosic backbone and initiation of the monomer leading to a decrease in the percentage of grafting.²⁶

Effect of monomer concentration

Table I shows the effect of MMA concentration on grafting parameters. It is clear from the table that the percentage of grafting increases continuously with the increase in monomer concentration of MMA and reaches a maximum value (21.97%) at $(\text{MMA}) = 2.25 \times 10^{-1}$ moles. Further increase in the concentration of MMA leads to excessive homopolymerization, and it becomes difficult to extract homopolymer entangled in the *Hibiscus sabdariffa* fibers. Increase in grafting percentage with increasing monomer concentration is expected.^{10,19,22} At higher monomer concentrations, more monomer would be available in the polymer medium for reaction with cellulose thereby enhancing the grafting degree. However, decrease in percentage of grafting with further increase in concentrations beyond the optimum monomer concentration of MMA may be explained by the fact that at higher concentrations, formation of homopolymer in preference to grafting takes place leading to decrease in percentage of grafting. Further, formation of more homopolymer results in an increase in the viscosity of the reaction medium thereby restricting the mobility of the growing polymeric chains to the active sites, and hence a decrease in percentage of grafting is observed.

Effect of initiator concentration

The optimum molar concentration of initiator for the maximum percentage of grafting was found to be

7.25 mM (Table I). It has been observed that as the concentration of initiator increases, more and more radicals are generated on the backbone as well as on the monomer, which results in the increase in percentage of grafting. After reaching the optimum value (35.89%), percentage of grafting decreases with further increase in initiator concentration. It may be due to the fact that with further increase in the initiator concentration, chain termination reactions dominate the graft copolymerization, which leads to decrease in the percentage of grafting.

Effect of reaction time

The optimum reaction time has been found to be 125 min for graft copolymerization reaction. With the initial increase in time, percentage of grafting increases, reaches an optimum value (43.61%) at 125 min, and decreases with further increase in reaction time (Table I). This variation of percentage of grafting 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 percentage of grafting. 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 decreased percentage of grafting.

Effect of reaction temperature

Temperature plays an important role in every graft copolymerization reaction. The graft copolymerization had been recorded at different temperatures ranging from 35 to 55°C while keeping other parameters constant. The percentage of grafting increases with the initial increase in temperature, reaches the optimum value at 45°C, and then decreases with further rise in temperature. The earlier behavior of variation of percent grafting with temperature can be attributed to fact that with the initial rise in temperature, as the kinetic energy of the molecules increases more and more radicals drifted at faster rate onto the backbone, resulting in the increase in the percentage of grafting. However, after reaching the optimum temperature, with further increase in temperature, a considerable amount of homopolymer is formed, which results in an increase in the viscosity of the reaction mixture. It provides a hindrance for the radicals to move toward the active sites of the *Hibiscus sabdariffa* fibers resulting in the decrease in percent grafting.

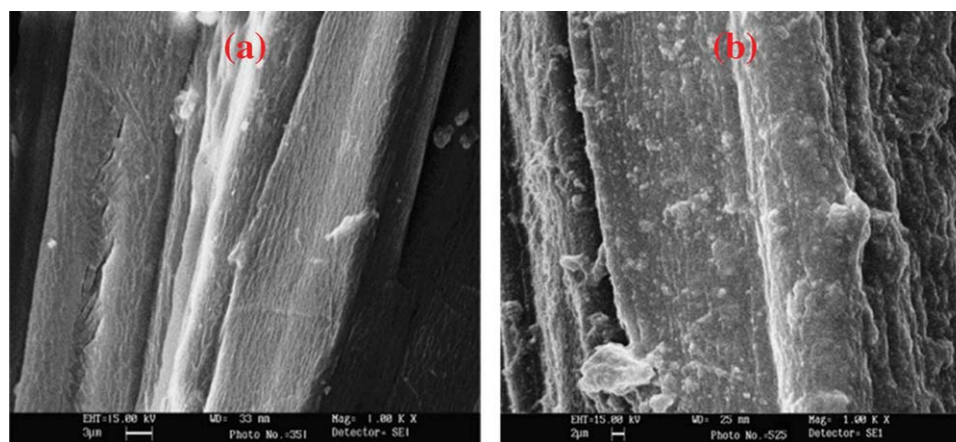


Figure 2 Scanning electron micrograph of (a) raw *Hibiscus sabdariffa* fibers and (b) poly (MMA)-grafted *Hibiscus sabdariffa* fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Evidence of grafting

Characterization by scanning electron microscopy

SEM was conducted to distinguish the morphological changes brought about by graft copolymerization reactions onto the candidate backbone polymer, i.e., *Hibiscus sabdariffa* fibers. Figure 2(a,b) reveals a clear cut distinction between the SEM of original *Hibiscus sabdariffa* fibers [Fig. 2(a)] and graft copolymer that there has been a sufficient deposition of poly (MA) onto *Hibiscus sabdariffa* fibers [Fig. 2(b)]. It can be observed that the surface of the grafted fibers is highly rough in comparison with the ungrafted fibers [Fig. 2(b)], which is attributed to the high graft density. Various researches in their innovative work have reported that the adhesion of the grafted fibers to other materials improved with an increase in the roughness of its surface because of an increase in surface area for bonding and mechanical interlocking.^{27,28} So the rougher surface on the grafted *Hibiscus sabdariffa* fibers is expected to be of benefit to improve the adhesion of grafted *Hibiscus sabdariffa* fibers to other polymers and, hence, improve the mechanical performance of the green composites.

Characterization by FTIR spectroscopy

FTIR spectra of polymeric networks have been recorded to study the modification of *Hibiscus sabdariffa* fibers and incorporation of poly (MMA) into the cellulosic backbone [Fig. 3(a,b)]. The FTIR spectrum of the raw *Hibiscus sabdariffa* fibers showed a broad peak at 3415.4 cm^{-1} because of bonded OH groups and at 2923.3 , 1426.5 , and 1031.0 cm^{-1} because of $-\text{CH}_2$, $\text{C}-\text{C}$, and $\text{C}-\text{O}$ stretching, respectively [Fig. 3(a)]. On grafting, FTIR bands due to characteristic functional groups incorporated into *Hibiscus sabdariffa* fibers have been witnessed besides the previously listed bands.¹⁰ In the case of *Hibiscus*

sabdariffa-g-poly (MMA), an additional peak at 1731.7 cm^{-1} was observed [Fig. 3(b)], which corresponds to carbonyl group ($>\text{C}=\text{O}$) of the PMMA chains, which was absent in raw fibers [Fig. 3(a)]

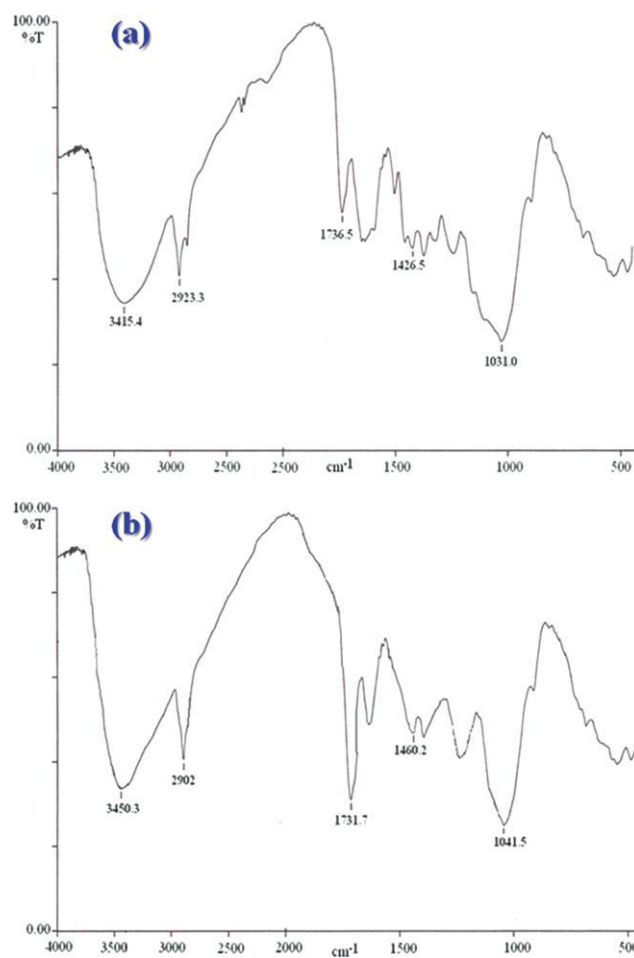


Figure 3 FTIR spectra of (a) raw *Hibiscus sabdariffa* fibers and (b) poly (MMA)-grafted *Hibiscus sabdariffa* fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Percentage Crystallinity (% Cr) and Crystallinity Index (C.I.) of Raw *Hibiscus sabdariffa* Fibers and *Hibiscus sabdariffa*-g-Poly (MMA) Fibers

| Sample 1 | $I_{C22.08}$ | $I_{A14.28}$ | % Cr | C.I. |
|--|--------------|--------------|-------|-------|
| Raw <i>H. sabdariffa</i> fiber | 93.78 | 45.39 | 67.38 | 51.59 |
| Sample 11 | $I_{C22.20}$ | $I_{A16.75}$ | % Cr | C.I. |
| MMA-grafted <i>H. sabdariffa</i> fiber | 97.26 | 59.87 | 63.15 | 38.44 |

followed by small shifts in the other characteristic peaks.¹⁰ The earlier results have provided evidences for grafting of MMA onto the *Hibiscus sabdariffa* through covalent bonds.

Characterization by XRD

As is evident from Table II, percentage crystallinity and crystallinity index were found to decrease with optimum percentage grafting of poly (MMA) onto *Hibiscus sabdariffa* fibers. Since incorporation of monomer moiety in the cellulosic backbone impairs the natural crystallinity of the cellulosic fiber, the graft copolymerization of MMA onto *Hibiscus sabdariffa* fibers resulted in impaired crystallinity and increased amorphous region of the fiber (Table II). Thus, with optimum percentage grafting, the percentage crystallinity and crystallinity index decreased along with reduction in stiffness and hardness.^{10,19,22} Since crystallinity index (C.I.) is the quantitative measure of the orientation of the crystal lattice to the fiber axis, the lower crystallinity index in case of graft copolymers stands for poor order of crystal lattice in the fibers. Thus, the misorientation of the crystal lattice to the fiber axis during grafting resulted in graft copolymers with low crystallinity and crystallinity index. This clearly indicates that the cellulose crystals are better oriented in the raw *Hibiscus sabdariffa* fibers followed by *Hibiscus sabdariffa*-g-poly (MMA) fibers.

Characterization by thermal analysis

Thermal behavior of raw fibers and grafted fibers was studied as a function of % weight loss with the increase in temperature [Fig. 4(a,b)]. In case of raw *Hibiscus sabdariffa* fibers [Fig. 4(a)], in the beginning, depolymerization, dehydration, and glucosan formation took place between the temperature ranges of 25.0°C and 200.0°C followed by the cleavage of C—H, C—C, and C—O bonds.^{10,19,22,29} For raw fibers, the initial decomposition (IDT) temperature has been found to be 200°C (8.45% wt. loss) and the final decomposition temperature (FDT) to be 510°C (87.57% wt. loss). In case of MMA grafted *Hibiscus sabdariffa* fibers [Fig. 4(b)], the IDT has been found to be 199°C (7.15% wt. loss) and the FDT to be 518°C (88.50% wt. loss). The TGA studies have been further supported by DTA evaluation. DTA of raw

fibers shows exothermic peaks at 350.0°C (7.8 μ V). The endotherm at 65°C can be attributed to formation and evaporation of volatile pyrolysis products in the raw *Hibiscus sabdariffa* fibers.²⁹ In case of graft copolymer, a continuous exothermic rise in temperature has been observed. An exothermic peak is observed at 422.17°C (3.8 μ V), which shows the loss of amorphous and crystalline structure of grafted fiber. This behavior appears due to the initial disturbance in the crystalline lattice of the polymer backbone (*Hibiscus sabdariffa*) during the graft copolymerization.

Further DTG analysis of grafted and ungrafted *Hibiscus sabdariffa* fibers was studied as a function of rate of weight loss (mg/min) versus temperature. In the case of raw *Hibiscus sabdariffa* fibers, decomposition at 57°C, 287°C, and 397°C was found with 0.100 mg/min, 0.451 mg/min, and 1.123 mg/min weight loss, respectively, due to the oxidative reactions which are mainly responsible for acceleration in the rates of weight loss and depolymerization of cellulose in air at temperatures below 300°C.²⁹ The oxidative reactions include production of hydroperoxide, carbonyl, and carboxyl groups. At temperatures above 300°C, the rate of thermal degradation is independent of the oxidative reactions, and the peak at 397°C may be due to the oxidation of the some of the charred residue.²⁹ However, in the case of *Hibiscus sabdariffa*-g-poly (MMA), the decomposition was observed at 412°C with 0.8 mg/min weight loss. Thus, it could be concluded from the DTG studies that the rate of thermal decomposition was higher in the case of *Hibiscus sabdariffa*, whereas in the case of *Hibiscus sabdariffa*-g-poly (MMA) fibers, the rate of thermal decomposition is lower. The enhanced thermal resistance of graft copolymer was due to the incorporation of more covalent bonding through inclusion of poly (MMA) chains onto the polymer backbone.

Analysis of swelling, moisture absorbance, water uptake, and chemical resistance behavior

Swelling behavior of raw fibers and their graft copolymers

Swelling behavior of grafted and ungrafted cellulosic fibers was studied in different solvents, such as dimethyl formamide, water, methanol and isobutyl

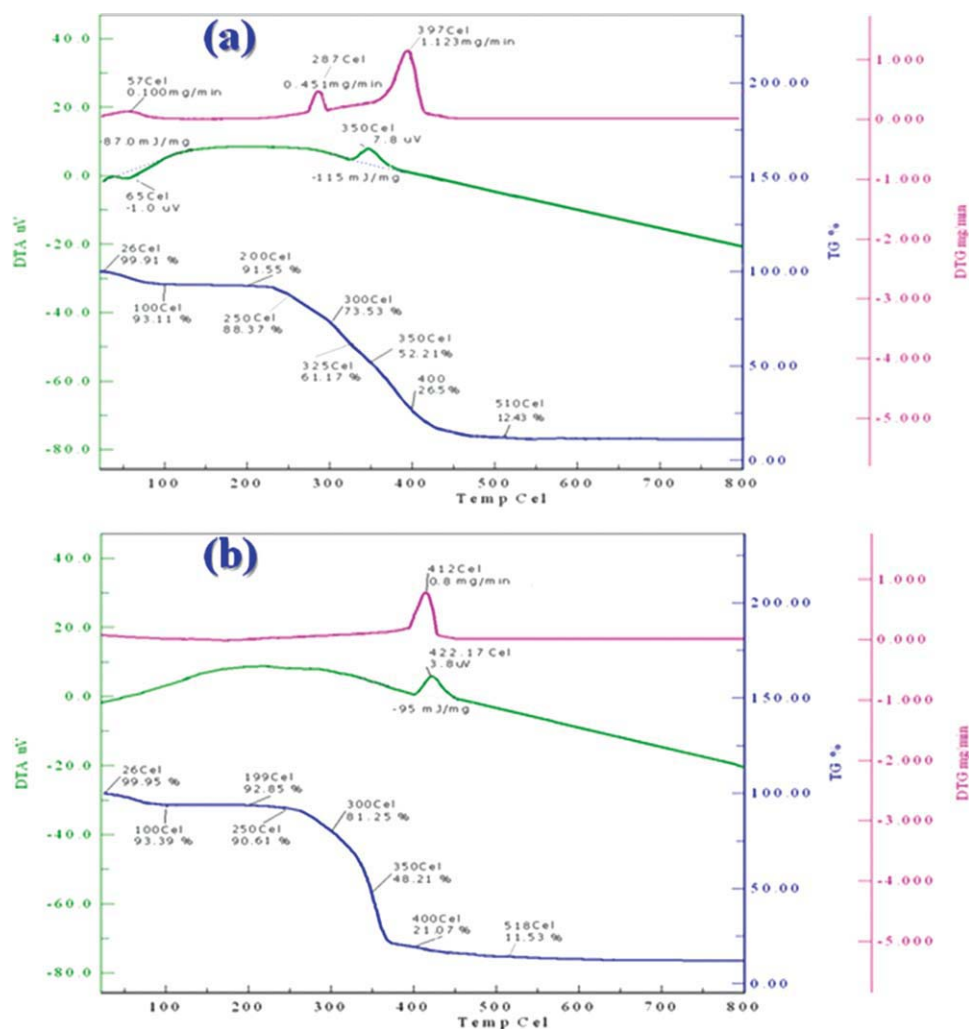


Figure 4 TGA/DTA/DTG thermogram of (a) raw *Hibiscus sabdariffa* fibers and (b) poly (MMA)-grafted *Hibiscus sabdariffa* fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

alcohol. Grafted and ungrafted *Hibiscus sabdariffa* fibers showed different swelling behavior in different solvents (Fig. 5). The swelling behavior of ungrafted fibers in different solvents follows the trend as $H_2O > CH_3OH > isoBuOH > DMF$. It has been observed that raw *Hibiscus sabdariffa* fibers showed maximum swelling in water and minimum swelling in dimethyl formamide.^{19,22} This trend in ungrafted fibers may be due to greater affinity of water for OH and CH_2OH groups present in the raw *Hibiscus sabdariffa* fibers, which results in more penetration of water into the polymeric backbone as compared with other solvents.^{19,22} In case of grafted fibers, swelling behavior varies as a function of P_g and follow the trend $DMF > CH_3OH > H_2O > isoBuOH$. In case of grafted fibers, water and alcohols cannot interact with the grafted fibers to the same extent as with raw fibers. This may be due to blockage of active sites on polymeric backbone by the polymeric chains of poly (MMA) grafted onto the fibers, which causes change in the sorption behavior of the

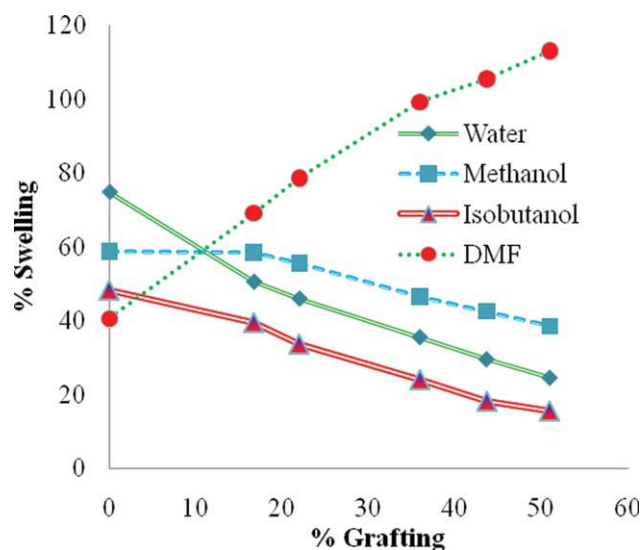


Figure 5 Swelling behavior of ungrafted and grafted *Hibiscus sabdariffa* fibers in different solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

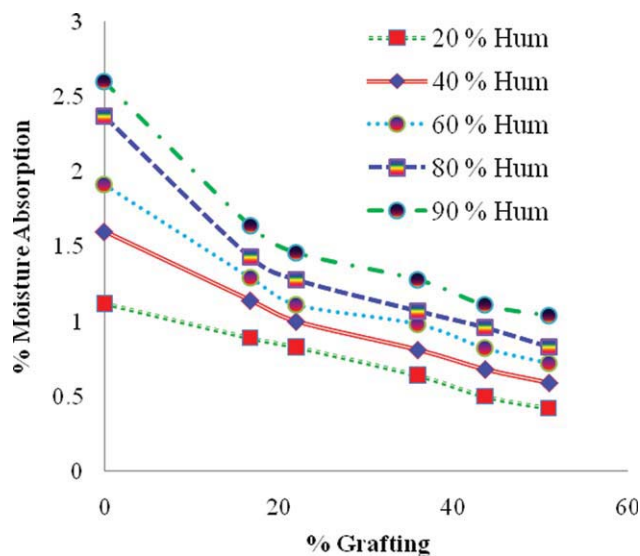


Figure 6 Moisture absorbance behavior of raw and grafted *Hibiscus sabdariffa* fibers at different humidity levels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

different solvents. Since poly (MMA) chains on grafted fibers get more solvolyzed by the dipolar aprotic solvent (dimethyl formamide) as compared with water or alcohol, so more swelling takes place in dimethyl formamide as compared with other solvents. Also, the other reason for more swelling in case of dimethyl formamide could be that grafting process leads to decrease in crystallinity and hence cellulose matrix opens up, which affects the size and voids where diffusion of solvent takes place to a considerable extent. In case of water and methanol, these voids fail to hold a large amount of these solvents. Hence, a different pattern for swelling is obtained in different solvents for grafted samples. Also, from the Figure 5, it is clear that grafted fibers shows least swelling in isobutyl alcohol. This could be caused by more steric hindrance because of alkyl group in isobutyl alcohol, as compared with methyl alcohol, and also because of low polarity index for isobutyl alcohol (4 D) as compared with methyl alcohol (5.1 D). It has also been observed that percent swelling depends upon the extent of grafting. Higher the percentage of grafting lower is the swelling in water.^{19,22}

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 (Fig. 6). It has been found that moisture absorbance (M_{abs}) decreases with the increase in P_g . The raw fibers show more M_{abs} as compared with grafted fibers. This behavior of grafted fibers may be due to

attachment of poly (MMA) chains grafted onto the fibers, which shows lesser affinity toward water.^{10,19,22}

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 (Fig. 7). This behavior of grafted fibers may be attributed to the hydrophobicity of poly (MMA) chains that are incorporated at active sites on the fibers surface as a result of graft copolymerization.¹⁰

Chemical resistance behavior of raw fibers and their graft copolymers

The chemical resistance of the raw as well of the grafted fibers has been studied in terms of percent weight loss in 1N HCl and 1N NaOH, respectively. It has been observed that resistance toward chemicals increases with the increase in % grafting [Fig. 8(a,b)]. This may be due to blockage of active sites vulnerable to the chemical attack by poly (MMA) on the polymeric backbone resulting in more resistance toward the chemicals.

CONCLUSIONS

Hibiscus sabdariffa fibers have been successfully modified through grafting using a chemical method.

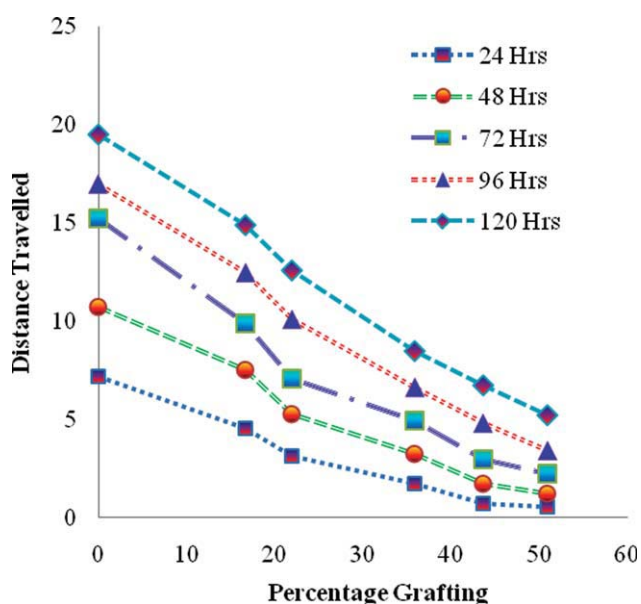


Figure 7 Water uptake behavior of raw and grafted *Hibiscus sabdariffa* fibers at different time intervals. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

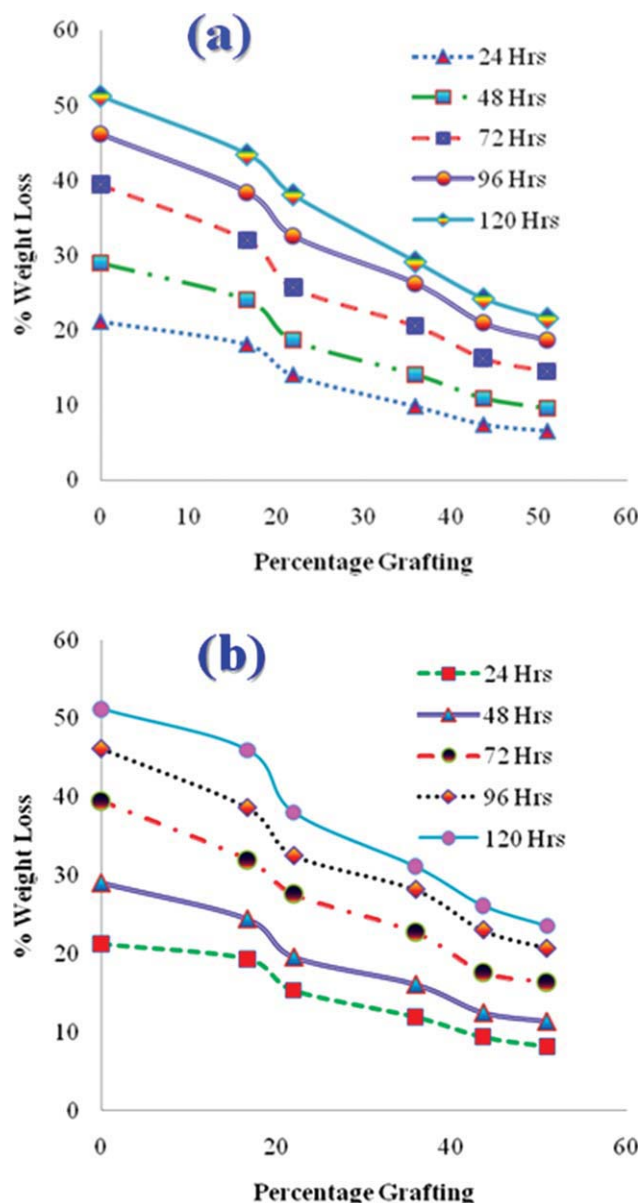


Figure 8 (a) Acid resistance behaviors of raw and grafted *Hibiscus sabdariffa* fibers in 1N HCl at different time intervals. (b) Base resistance behavior of raw and grafted *Hibiscus sabdariffa* fibers in 1N Na OH at different time intervals. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hibiscus sabdariffa-graft-poly MMA 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, time, and temperature on the percentage of grafting was investigated. The grafting effect increases with the increasing solvent concentration until a maximum is obtained, and the further increase of the solvent concentration caused a sharp decline of the grafting effect. The optimum conditions for maximum percentage of grafting

(50.93%) onto *Hibiscus sabdariffa* fibers has been found to be: solvent = 90 mL, monomer = 2.25×10^{-1} mol/L, KPS = 7.25 mM, time = 125 min, and temperature = 45°C. As seen from the experimental results, MMA monomer can be successfully grafted onto cellulosic *Hibiscus sabdariffa* fibers by the use of KPS initiator. Further, it has been observed that the factors such as temperature, initiator, and monomer concentration affect the percentage of grafting to a considerable extent. The thermal stability of the grafted cellulosic fibers obtained through free radical graft copolymerization method has been found to be better than that of the raw cellulosic fibers. The resistance to the swelling behavior of the grafted fibers in different solvents has also been found to be better than that of the raw fibers. Although the graft copolymerization synthesis decreases the crystallinity and crystallinity index of grafted cellulosic fibers, incorporation of poly (MMA) chains onto fibers polymer backbone could result in higher acid, base, and thermal resistance. The moisture absorption of the grafted fibers is also decreased compared with the raw fiber. Moreover, on grafting, the morphological changes with respect to surface morphology of the grafted copolymers have been found to exert different physical and chemical properties

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