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Rapid synthesis of graft copolymers from natural cellulose fibers

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ABSTRACT

Cellulose is the most abundant natural polysaccharide polymer, which is used as such or its derivatives in a number of advanced applications, such as in paper, packaging, biosorption, and biomedical. In present communication, in an effort to develop a proficient way to rapidly synthesize poly(methyl acrylate)-graft-cellulose (PMA-g-cellulose) copolymers, rapid graft copolymerization synthesis was carried out under microwave conditions using ferrous ammonium sulfate–potassium per sulfate (FAS–KPS) as redox initiator. Different reaction parameters such as microwave radiation power, ratio of monomer, solvent and initiator concentrations were optimized to get the highest percentage of grafting. Grafting percentage was found to increase with increase in microwave power up to 70%, and maximum 36.73% grafting was obtained after optimization of all parameters. Fourier transforms infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA/DTA/DTG) analysis were used to confirm the graft copolymerization of poly(methyl acrylate) (PMA) onto the mercerized cellulose. The grafted cellulosic polymers were subsequently subjected to the evaluation of different physico-chemical properties in order to access their application in everyday life, in a direction toward green environment. The grafted copolymers demonstrated increased chemical resistance, and higher thermal stability.

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1. Introduction

During the last few years, intense research efforts have been made to replace the traditional materials with polymers (Thakur, Ding, Ma, Lee, & Lu, 2012; Thakur, Lin, Tan, & Lee, 2012; Thakur, Tan, Lin, & Lee, 2011). In this direction development of polymeric materials from renewable raw materials has increased noticeably during the last few years (Bharti, Mishra, & Sen, 2013; Qiu, Ren, & Hu, 2012). Using renewable polymeric materials, more eco-friendliness can be achieved relative to the conventional toxic synthetic polymer composites materials (Abdel-Halim, 2012; Oza, Meena, & Siddhanta, 2012; Unlu, Oztekin, & Atici, 2012). In order to accomplish this objective, researchers all around the globe are focusing their research efforts on the effective utilization of various kind of natural biodegradable polymers (Abdel-Halim & Al-Deyab, 2012; Akar, Altinisik, & Seki, 2012; Thakur, Thakur, & Gupta 2013). Among various materials found in nature, cellulose is the first polymer found most abundantly in nature (Cheema, El-Shafei, & Hauser, 2013; Nazi, Malek, & Kotek, 2012; Wu, 2012). Cellulose is an essential component of all the natural fibers and responsible for most of the properties of the natural fibers (Bao, Ma, & Sun, 2012; Dhakal, Zhang, & Bennett, 2012). Natural lignocellulosic fibers have been the indispensable component of human life since centuries back and are regarded as most valuable polymers due to their applications in everyday life (Dhakal, Zhang, Guthrie, & Bennett 2013). Properties of natural fibers such as eco-friendliness, biodegradability, easy availability, toxicologically harmless, lower cost carbon dioxide (CO_2) neutral, enhanced energy recovery, and non-corrosive nature make these as most valuable material in a number of applications especially in polymer composites. The molecular weight of cellulose present in different fibers also varies upon the type and inherent properties of the particular fibers. Generally, the molecular weights of native cellulose have been found to be at least 570,000 for degree of polymerization of 3500 (Gralén & Svedberg, 1943). Different kinds of lignocellulosic natural fibers are also characterized by an enormous degree of variability and diversity in their properties depending upon the nature and place of their origin (Dhakal, Zhang, Reis, Surip, & Bennett, 2012). Due to these reasons, the study and development of polymer composite materials especially using natural fibers as reinforcement have received great attention during the last two decades (Dhakal, Zhang, Bennett, & Reis, 2012; Thakur & Singha, 2011a). Indeed, the prime commercial interest in production of different kinds of products is

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driven by the renewable nature; low cost as well as biodegradability (Dhakal, Zhang, & Richardson, 2009). However the poor physico-chemical properties such as higher water and moisture absorption; lower chemical resistance and poor compatibility with most of the polymer matrices restrict their applications (Khoathane, Vorster, & Sadiku, 2008; Thakur & Singha, 2011b). In order to overcome the disadvantages of different kinds of natural polymers, various kinds of surface modification techniques are employed to change their specific properties (Eissa, Khosravi, & Cimecioglu, 2012; Khoathane, Sadiku, & Wambua, 2012; Thakur, Singha, & Misra, 2011; Zhong, Chai, & Fu, 2012). Among these techniques, graft copolymerization is one of the most promising methods to improve the physico-chemical properties of natural and synthetic polymers (Ofomaja, Ngema, & Naidoo, 2012; Teli & Sheikh, 2012; Thakur et al., 2012a). Different polymers demonstrate a particular extent of degree of grafting (the relative percentage increase in the molecular weight of parent polymer w.r.t. the incorporation of new copolymer), depending upon the reaction condition. Furthermore it improves the adhesion of the fiber-matrices in a composite which in turn changes the overall mechanical properties of the composites. Various natural fibers such as flax, sisal, hibiscus sabdariffa, pine needles and hemp have been traditionally used as reinforcement in biocomposites applications. Among these natural fibers, cellulosic Grewia optiva is another potential fiber obtained from Grewia optiva plant (Thakur et al., 2012a). It is naturally found in Himalayan region of India and China along with many other countries. It is a stiff fiber and has been traditionally used for preparation of ropes, carpets, basket and marine applications. These fibers are smooth, straight and fairly coarse. Recently we have demonstrated the successful modification of these fibers using methyl acrylate as reaction monomer in air as reaction medium (Thakur et al., 2012a). In continuation with our previous efforts, the current work presents the graft copolymerization of cellulosic Grewia optiva fibers with methyl acrylate under microwave radiation in an effort to rapidly modify these cellulosic fibers to provide an efficient way to save time and energy. The materials are prepared via free radical polymerization using redox initiator (Thakur et al., 2012b). The microwave radiation induced graft copolymerization synthesis is more advantageous on traditional thermal grafting as a result of more enhancement of reaction speed (Kamel, 2012; Mishra, Rani, & Sen, 2012). Furthermore microwave irradiation can heat the reaction system rapidly and evenly leading to uniform grafting and higher graft yield (Rani, Sen, Mishra, & Jha, 2012; Rani, Mishra, Sen, & Jha, 2012). The obtained poly(methyl acrylate) grafted cellulosic Grewia optiva fibers were characterized by Fourier transform infrared spectrometry (FT-IR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA/DTA/DTG). Physico-chemical properties of these grafted cellulosic polymers were also tested in different solvents and chemicals.

2. Experimental

2.1. Materials and methods

Cellulosic Grewia optiva fibers used in the present investigation were obtained from the local resources of Himalayan region. The monomer methyl acrylate (MA); redox initiator ferrous ammonium sulphate (FAS) and potassium per sulphate (KPS); sodium hydroxide (NaOH) and acetone were used as received for graft copolymer synthesis. Graft copolymerization onto cellulosic Grewia optiva fibers was carried out in the following manner: in order to initiate the graft copolymerization synthesis onto cellulosic fibers, purification of raw Grewia optiva fibers followed by chemical modification through mercerization was carried out as per standard method reported in our earlier studies (Thakur et al., 2012a). Graft copolymerization reaction was carried out by immersing a known amount (1 g) of mercerized cellulosic Grewia optiva fibers in distilled aqueous solution for 24 h (Thakur, Singha, & Thakur, 2012a, 2012b, 2012c) followed by addition of celebrated amount of redox initiator (FAS-H_2O_2). This solution was stirring for 5–10 min so as to create free radical sites on the cellulosic backbone. Subsequently to start the copolymerization, methyl acrylate monomer (MA) was added into the reaction flask containing the mercerized cellulosic Grewia optiva fibers in the microwave oven. The reaction was carried out at different time intervals to optimize dissimilar conditions of solvent, time, initiator and monomer concentration for maximum percentage of grafting (Table 1). After the graft copolymerization reaction, the samples were filtered, washed with distilled water several times and then air dried. The dried cellulosic Grewia optiva fibers were then extracted with acetone in a Soxhlet extraction apparatus for 72 h to remove the homo-polymer formed and then equilibrated in distilled water for 24 h to remove unreacted chemicals. This step was essential to remove all the unreacted monomer from the grafted fibers. The fibers were then dried at 35–40 °C in hot air oven till the fibers attained constant weight. The percentage grafting (P_g) was calculated as per procedure reported earlier (Thakur et al., 2012a, 2012b, 2012c).

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

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

2.2. Structural characterization of poly(methyl acrylate)-g-cellulosic Grewia optiva polymers

The chemical structure of the cellulosic Grewia optiva fibers before and after graft copolymerisation synthesis with methyl acrylate (MA) monomer was characterized using Fourier transform infra red spectroscopy (FT-IR) using PERKIN ELMER RXI Spectrophotometer in order to confirm the synthesis of graft copolymers. The spectrum was recorded in the range of 400–4000 cm^{-1}. The morphological features of the cellulosic Grewia optiva fibers prior to and after graft copolymerisation were observed by using scanning electron microscopy machine (LEO 435 VP). Thermo gravimetric analyses (TGA/DTA/DTG) of the plain and grafted cellulosic Grewia optiva fibers with known weight were carried out in nitrogen atmosphere on a thermal analyzer (Perkin Elmer). The samples were heated from room temperature to 900 °C/min at a heating rate of 10 °C/min.

2.3. Physico-chemical characterization of raw and poly(methyl acrylate)-g-cellulosic Grewia optiva polymers

2.3.1. Swelling behavior

Swelling studies of the raw and grafted cellulosic Grewia optiva fibers were carried out in different solvents such as dimethyl formamide; water; methanol and isobutyl alcohol as per standard method (Thakur et al., 2012a, 2012b, 2012c). In brief bundles of fibers of known weight (2 g) were kept together and placed inside beakers containing different solvents at room temperature (23 °C). After a particular time the fibers were taken out and the weights of fibers were noted. Then the percent swelling was calculated from the increase in initial weight in the following manner (Thakur et al., 2012a, 2012b, 2012c):

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

where W_f is the final weight of fibers; W_i is the weight of raw fibers.

Table 1
Optimization of various reaction parameters for optimum graft copolymerization onto cellulosic Grewia optiva fibers under microwave radiation.

Sr. no.	Solvent (mL)	Monomer (mol/L × 10^{-1})	FAS:KPS (mmol/L)	Time (s)	% MW	% Grafting
1	80	2.35	1:1	300	60	6.71
2	95	2.35	1:1	300	60	8.12
3	110	2.35	1:1	300	60	10.95
4	125	2.35	1:1	300	60	8.97
5	140	2.35	1:1	300	60	8.62
6	110	2.10	1:1	300	60	8.99
7	110	1.85	1:1	300	60	8.22
8	110	2.90	1:1	300	60	14.60
9	110	3.05	1:1	300	60	18.17
10	110	3.30	1:1	300	60	15.63
11	110	3.45	1:0.150	300	60	14.30
12	110	3.05	1:0.200	300	60	15.88
13	110	3.05	1:0.250	300	60	25.75
14	110	3.05	1:0.500	200	60	22.78
15	110	3.05	1:0.250	250	60	23.93
16	110	3.05	1:0.250	350	60	30.70
17	110	3.05	1:0.250	400	60	27.42
18	110	3.05	1:0.250	450	60	25.91
19	110	3.05	1:0.250	500	60	22.96
20	110	3.05	1:0.250	350	60	28.12
21	110	3.05	1:0.250	350	50	24.37
22	110	3.05	1:0.250	350	70	36.73
23	110	3.05	1:0.250	350	80	33.03
24	110	3.05	1:0.250	350	90	28.10

2.3.2. Moisture absorbance behavior

The moisture absorbance studies of the raw and grafted cellulosic Grewia optiva fibers were made in a humidity chamber. Dry grafted and raw cellulosic Grewia optiva fibers of known weight were placed in the humidity chamber for particular time interval under 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 studied as a function of weight gain and was calculated using the following manner (Thakur et al., 2012a, 2012b, 2012c):

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

where W_f is the weight of grafted fibers; W_i is the weight of raw fibers.

2.3.3. Chemical resistance behavior

The chemical resistance of raw and grafted cellulosic Grewia optiva fibers was studied as a function of weight loss as per standard method reported earlier (Thakur, Singha, et al., 2011; Thakur, Tan, et al., 2011; Thakur et al., 2012a). Known amount of the raw and grafted cellulosic Grewia optiva fibers were placed in beakers having fixed volume of 1 N HCl and 1 N NaOH and the weight of the samples were noted down after certain intervals. 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 (Thakur et al., 2012a, 2012b, 2012c):

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

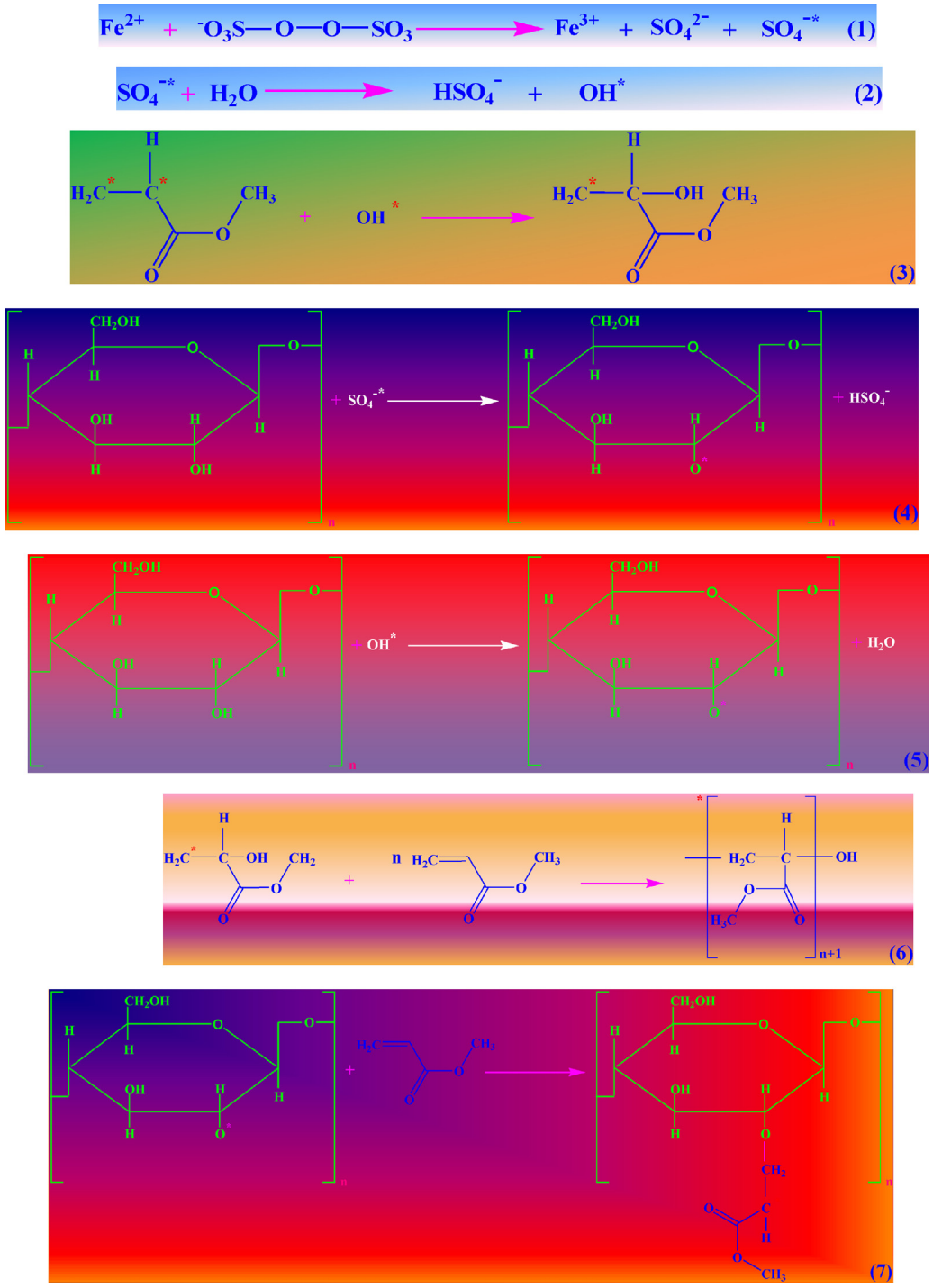
where T_w is the total weight and W_{aci} is the weight after certain interval.

3. Results and discussion

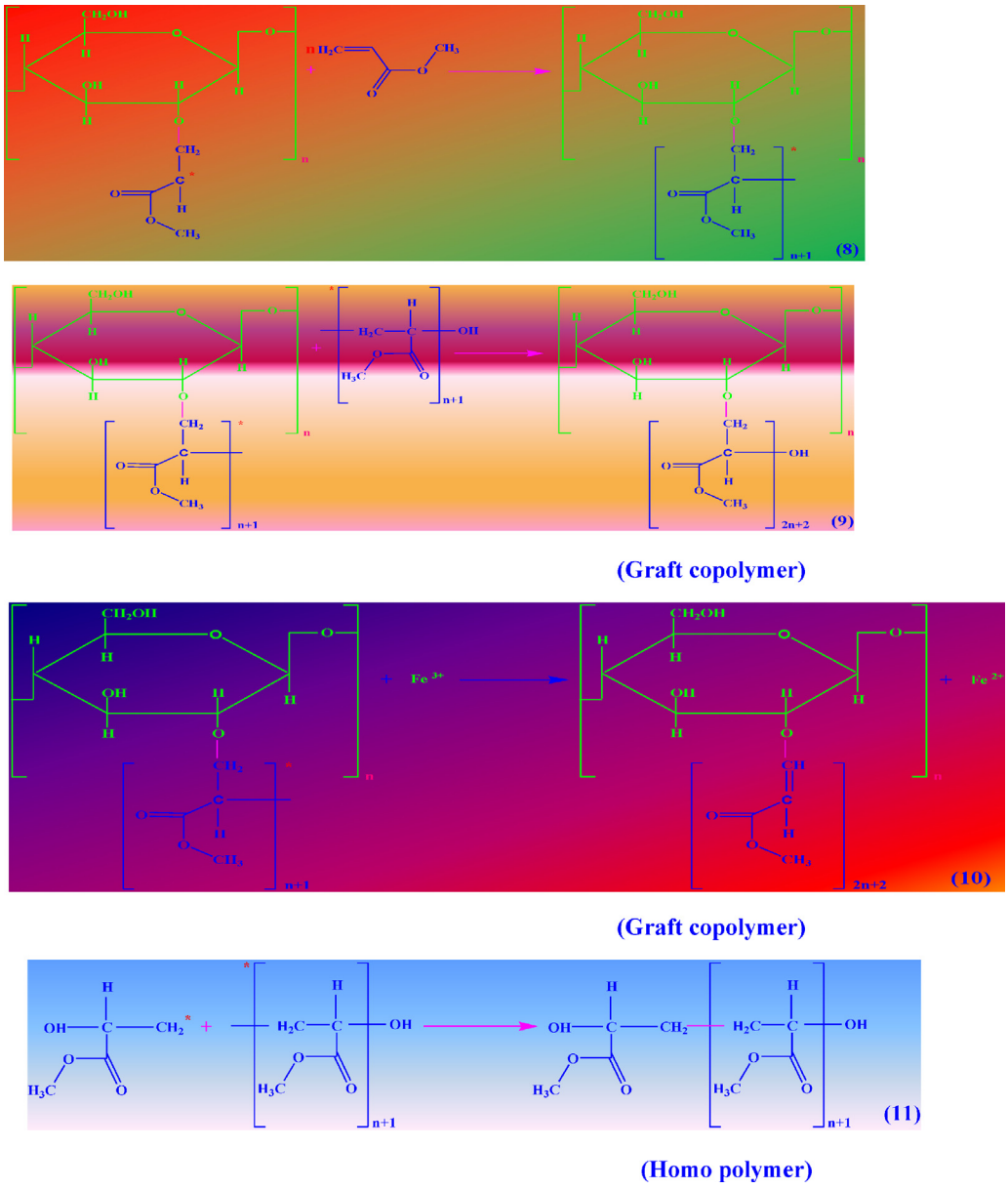
An initiator play the most significant role in any graft copolymerization reaction as it initiates the reaction by chemical means (Rani, Mishra, & Sen, 2013). The initiator creates a number of free radicals which are subsequently transformed to the polymeric backbone. The cellulosic Grewia optiva fibers consist of linear glucan chains with repeating (1→4)β-glucopyranose units and the presence of the reactive hydroxyl groups on each unit of cellulose makes cellulosic Grewia optiva fibers susceptible to get modified through free radical graft copolymerization (Thakur et al., 2012a, 2012b, 2012c). Free radicals onto the cellulosic polymeric backbone can be generated by direct/indirect method. In indirect methods radicals are generated through redox reactions. In cellulosic Grewia optiva fibers: C_2, C_3 and C_6—OH groups and C—H sites are the active centers for grafting of polymethyl acrylate (PMA) chains onto cellulosic backbone (Scheme 1). In the presence of methyl acrylate monomer, the free macroradicals are added to the double bond of the monomer which results in a covalent bond formation between monomer and the cellulosic Grewia optiva fibers with the creation of free radicals on to the methyl acrylate monomer ultimately resulting in the initiation of cellulosic chain which subsequently undergo copolymerization with the addition of methyl acrylate monomer molecules through the propagation and termination steps leading to the desired grafting copolymers (PMA-g-cellulose).

Different reaction parameters such as monomer concentration, initiator, microwave power, reaction time and solvent have been optimized to get the maximum percentage of grafting (Thakur et al., 2012a, 2012b, 2012c). Table 1 shows different values of percentage of grafting during optimization of the reaction parameters. The optimum conditions for maximum graft yield (36.73%) as given in Table 1 were: solvent – 110 mL; monomer – (3.05×10^{-1} mol/L), time – 350 s; FAS:KPS – 1:0.250 mmol/L and microwave power = 70%. The effect of the addition of methyl acrylate (MA) monomer on the percentage of grafting parameters is shown in Table 1. It has been observed that percentage of grafting increases with the initial increase in monomer concentration reaches the optimum value and then slightly decreases with further increase in the monomer concentration (Table 1). This behavior of increase in grafting with increase in monomer concentration can be explained by the fact that initially more and more radicals reach into the cellulosic Grewia optiva polymer backbone resulting in an increase in percentage of grafting. However, decrease in percentage of grafting beyond optimum value is most probably

due to preferential domination of homopolymerization over graft copolymerization. Table 1 demonstrates the effect of redox initiator FAS:KPS on to grafting parameters. An increase in FAS:KPS amount resulted in an increase in number of free radical active sites on the cellulosic back bone polymer where graft copolymerization reaction takes place. The optimum molar ratio for the maximum graft yield was found to be 1:0.250 (Table 1). However, a further increase in initiator concentration beyond the optimum value has been found to decrease percentage of grafting which may be attributed to the formation of more Fe^{3+} ions at higher molar ratio, which results in the termination of growing (Thakur et al., 2012a, 2012b, 2012c). Solvent has also been found to play an important role in most of the graft copolymerization reactions (Thakur et al., 2012a, 2012b, 2012c). In our study we have used water as solvent. Table 1 shows the effect of amount of water during grafting of methyl acrylate (MA) onto cellulosic Grewia optiva fibers. It has been observed that percentage of grafting of methyl acrylate (MA) shows an initial jump in percentage of grafting with increasing amount of water, from 80 to 110 mL giving maximum (8.92%) grafting in 110 mL and then decreases on further increase in the amount of water and becomes almost constant. Time plays a significant role under any sets reaction conditions. In present study



Scheme 1. Mechanism for graft copolymerization onto Grewia optiva fibers.



Scheme 1. (*Continued*).

where the reaction was carried out under microwave radiation the optimum reaction time has been found to be 350 s for graft copolymerization reaction. The percentage of grafting has been found to increase with the initial increase in time reaches an optimum value at 350 s, and decreases with further increase in reaction time (Table 1). This behavior of decrease in grafting with further increase in time beyond the optimum value may be due the mutual destruction of growing polymeric chains, leading to homopolymerization of the reaction monomer radicals and backbiting by the active radicals. Graft copolymerization reaction in the presence of MWR took very less time to completion because of the passage of electromagnetic waves in the solution, which oscillates the speed of the chain carrier free radicals and ultimately leads to the formation of small molecular chain graft copolymer (Rani et al., 2013; Thakur, Thakur, & Gupta, 2013). The graft copolymerization of methyl acrylate (MA) monomer onto the cellulosic Grewia optiva fibers was carried out at different microwave powers. Grafting was found to increase with increase in microwave power up to 70%, and further increase in microwave power resulted in decreased/no grafting. This behavior could be explained by an increase in the grafting percentage as power is increased, thus generating more macro radicals. Beyond optimum value grafting percentage starts decreasing. This behavior may be due either to more homopolymerization at high powers or to the decomposition of graft copolymers, which may take place at microwave power higher than 70%.

3.1. Analysis of physico-chemical properties of grafted poly(methyl acrylate)-g-cellulosic Grewia optiva polymers

The percent swelling of raw and poly(methyl acrylate) grafted Cellulosic Grewia optiva fibers carried out under different solvents is shown in Fig. 1. The raw cellulosic Grewia optiva fibers possess hydrophilic —OH groups at C_2, C_3 and C_6 of the glucose unit and these have greater affinity for water molecules resulting in more swelling of the raw fibers in the polar solvents. The swelling behavior of raw cellulosic Grewia optiva fibers in different solvents follows the trend as $H_2O > CH_3OH >$ iso-BuOH > DMF. However poly(methyl acrylate) grafted cellulosic Grewia optiva fibers

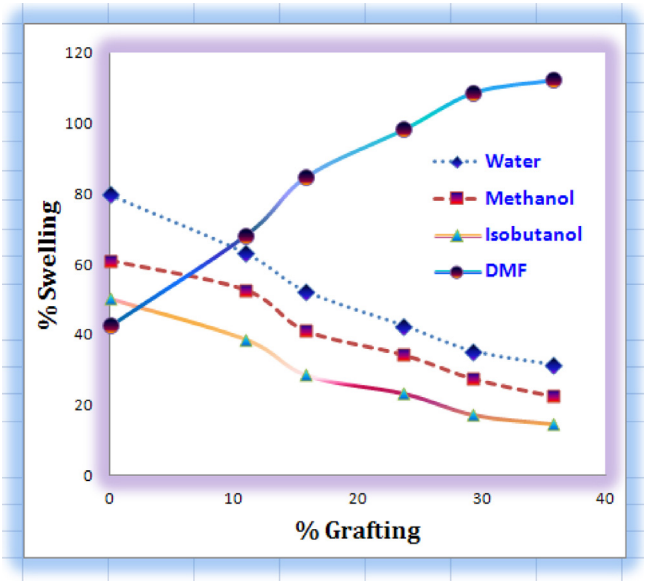


Fig. 1. Swelling behavior of raw and grafted cellulosic Grewia optiva fibers in different solvents.

show a reversal swelling behavior varies as a function of percentage of grafting (P_g) and follow the trend; DMF > CH_3OH > H_2O > iso-BuOH. This reversal in swelling behavior can be attributed to the blockage of active sites on polymeric substrate by poly MA chains which cause change in the sorption of the different solvents (Thakur et al., 2012a, 2012b, 2012c). Fig. 2 shows the moisture absorbance behavior of raw and poly(methyl acrylate) grafted cellulosic Grewia optiva fibers at different humidity levels as a function of P_g. The raw cellulosic Grewia optiva fibers show more M_{abs} as compared to poly(methyl acrylate) grafted cellulosic Grewia optiva fibers and this behavior of grafted fibers may be due to attachment of poly(methyl acrylate) chains grafted onto the cellulosic Grewia optiva fibers which shows lesser affinity toward water (Thakur et al., 2012a, 2012b, 2012c). The acid and base resistance of the raw and poly(methyl acrylate) grafted cellulosic Grewia optiva fiber

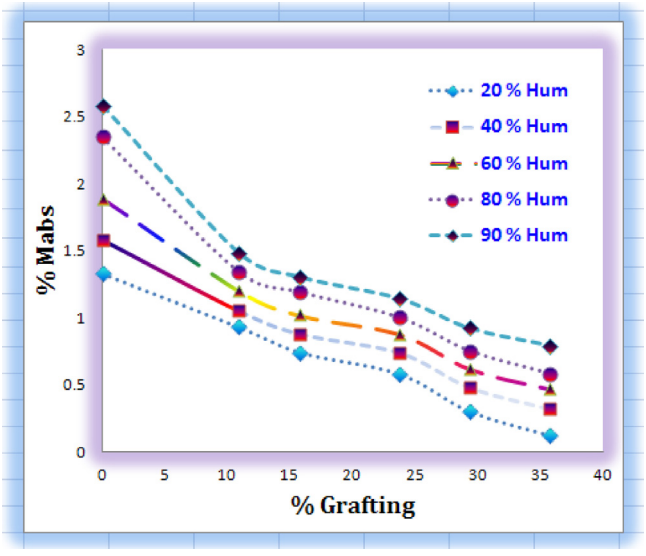


Fig. 2. Moisture absorbance behavior of raw and grafted cellulosic Grewia optiva fibers at different humidity levels.

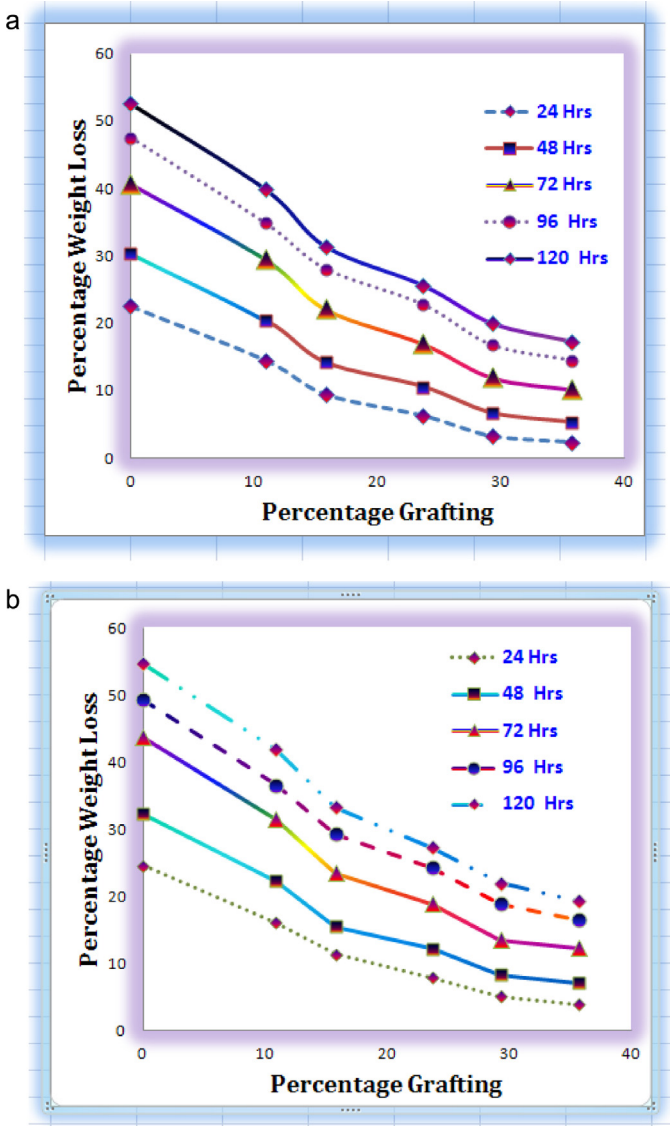


Fig. 3. (a) Acid resistance behavior of raw and grafted cellulosic Grewia optiva fibers in 1 N HCl at different time intervals and (b) base resistance behavior of raw and grafted cellulosic Grewia optiva fibers in 1 N NaOH at different time intervals.

in air was studied as a function of percent weight loss against acid/base solution of 1 N HCl and 1 N NaOH respectively. It has been observed that resistance toward chemicals increase with the increase in % grafting (Fig. 3a and b). 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 toward the chemicals.

3.2. Analysis and characterization of raw and poly(methyl acrylate)-g-cellulosic Grewia optiva polymers

The infra red spectra for raw and grafted cellulosic Grewia optiva fibers were obtained by using an FT-IR spectrophotometer (Fig. 4a and b). Poly(methyl acrylate) grafted cellulosic Grewia optiva fibers (Fig. 4b) resulted in significant differences in the infrared spectra. In the FT-IR spectra of raw cellulosic Grewia optiva fibers (Fig. 4a), the intense broad peak ranging from 3020 to 3700 cm^{-1} is due to the hydrogen bonded OH— vibration of the cellulose structure fiber. The large peak at 1590 and 780 cm^{-1} could be due to the presence of

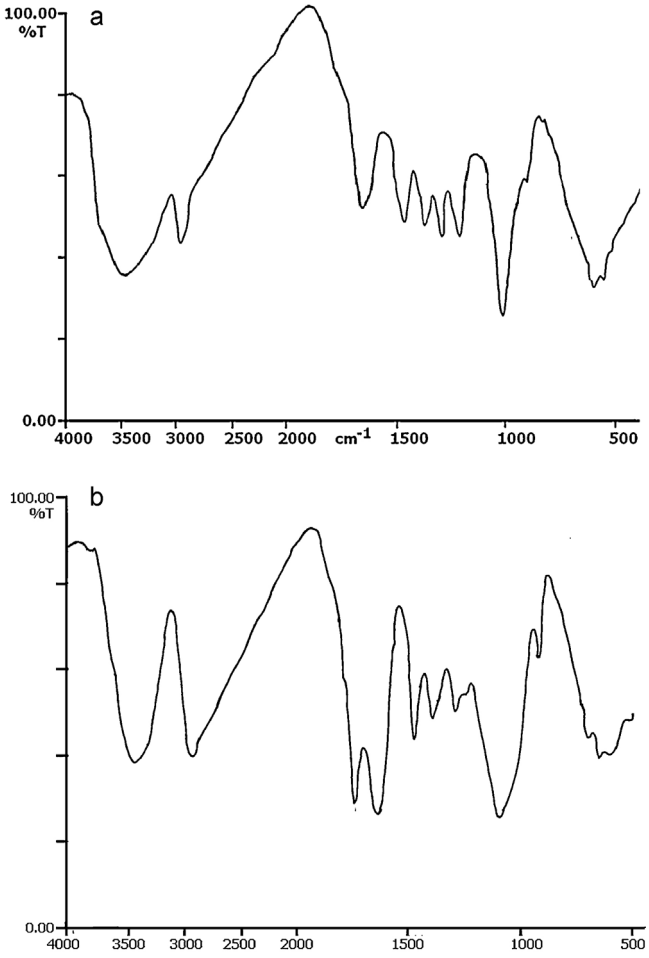


Fig. 4. (a) FT-IR spectrum of raw cellulosic Grewia optiva fibers and (b) FT-IR spectrums of grafted cellulosic Grewia optiva fibers.

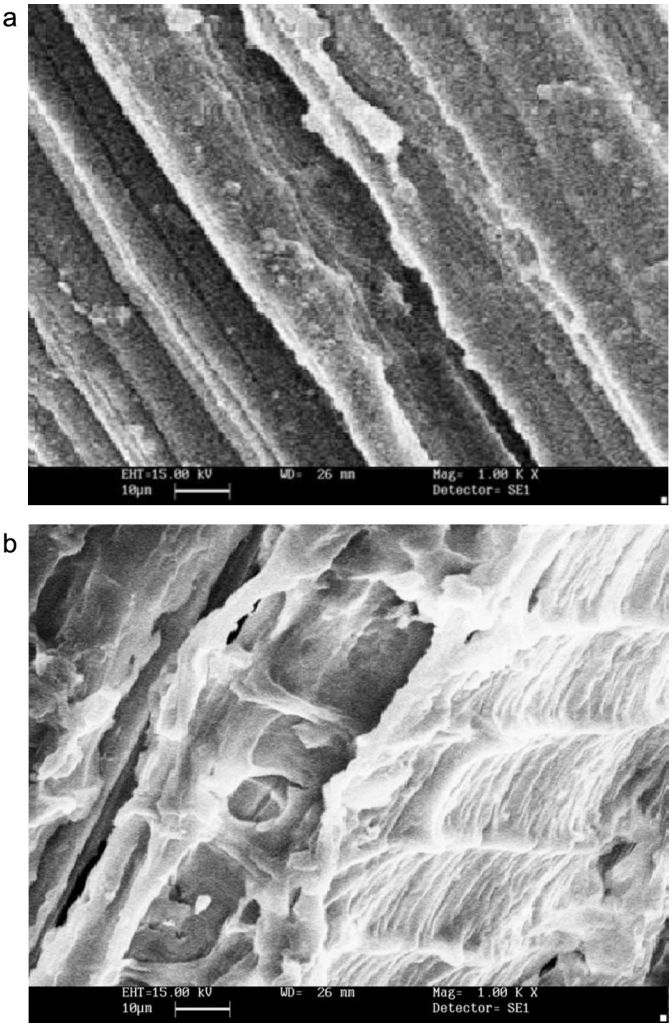


Fig. 5. (a) Scanning electron micrographs of raw cellulosic Grewia optiva fibers and (b) scanning electron micrographs of grafted cellulosic Grewia optiva fibers.

lignin in the raw cellulosic Grewia optiva fibers. Weaker peaks also occurred at 1372–1457 cm^{-1} due to C—H, —CH_2 and CH_3 bending. The peaks at 2330 cm^{-1} and 2921.3 cm^{-1} can be assigned to C—H stretching in cellulosic polymer chain and C—H stretching vibration of the aliphatic methylene group. The poly(methyl acrylate) grafted cellulosic Grewia optiva fibers (Fig. 4b) on the other hand showed additional characteristics absorption band at 1730 cm^{-1} along with the reduction in the intensity of the some of the basic peaks of cellulosic Grewia optiva fibers confirming the successful grafting of poly(methyl acrylate) chains into cellulosic Grewia optiva fibers (Thakur et al., 2012a, 2012b, 2012c). Scanning electron micrographs of the raw and grafted cellulosic Grewia optiva studied using scanning electron microscopy are shown in Fig. 5(a and b). As evident from the SEM results, the ungrafted Grewia optiva fibers demonstrate smoother surfaces and a more homogeneous appearance. On the other hand, the grafted copolymers demonstrate the rough and scaly tissue of the grafted Grewia optiva fibers. The comparison of the micrographs clearly shows that, the raw fiber present a network structure in which, the fibrils are bound together by hemicellulose and lignin. On the other hand, surface morphology of the cellulosic Grewia optiva fibers changes upon grafting (Fig. 5b) signifying that a considerable amount of poly(methyl acrylate) has been grafted onto the cellulosic Grewia optiva fibers (Thakur et al., 2012a, 2012b, 2012c).

Thermal properties of the unmodified and chemically modified raw and grafted cellulosic Grewia optiva biofibers were analyzed by thermogravimetric analysis. The changes observed when the unmodified cellulosic Grewia optiva fibers were compared to poly(methyl acrylate) grafted cellulosic Grewia optiva fibers confirm the successful surface modification of cellulosic Grewia optiva fibers supporting the results of FT-IR and SEM studies. The thermal decomposition of the samples was studied as a function of percent weight residue with increase in temperature. Generally in the case of natural cellulosic fibers, cellulose decomposes in the three stages. In the first stage the weight loss occurred in the range of 60–130 °C due to vaporization of water molecules adsorbed on the fiber surface. While the second stage of weight loss occurred due to the degradation by dehydration, glycogen formation and depolymerization in between 150 and 250 °C. The third stage of weight loss above 450 °C might be due to the further decomposition of the product of stage II leading to formation of tar through levoglucosan. For raw cellulosic Grewia optiva (GO) biofibers (Fig. 6a), the initial decomposition temperature (IDT) has been found to be 212 °C (% wt loss 3.7) and the final decomposition temperature (FDT) to be 518 °C (% wt loss 82.81). Poly(methyl acrylate)-g-cellulosic Grewia optiva biofibers also shows similar phase decomposition with higher thermal stability (Fig. 6b). These results clearly demonstrate that grafted cellulosic Grewia optiva biofibers are thermally more stable than raw biofibers. This might be due to the incorporation of poly(MA) chains through covalent

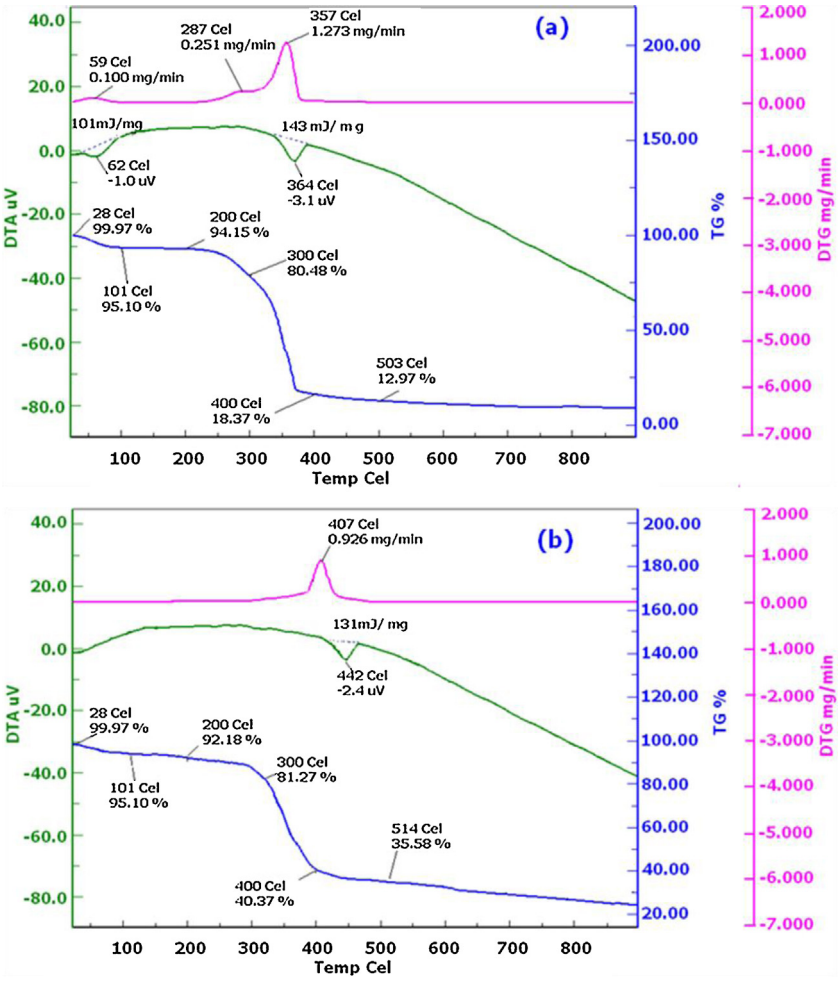


Fig. 6. (a) TGA/DTA/DTG curves of raw cellulosic Grewia optiva fibers and (b) TGA/DTA/DTG curve of grafted cellulosic Grewia optiva fibers.

bonding thereby possibly resulting in reinforcement of amorphous region.

4. Conclusions

- Cellulosic Grewia optiva copolymers could be rapidly grafted with the formation of poly(methyl acrylate) chains.
- FAS–KPS serves as potential redox initiator system for the graft copolymerization of poly(methyl acrylate) onto cellulosic Grewia optiva polymers.
- The presences of poly(methyl acrylate) chains onto the grafted cellulosic Grewia optiva polymers were ascertained by FT-IR/SEM/TGA/DTA/DTG studies.
- The evaluation of physico-chemical properties demonstrates that the successful incorporation of poly(methyl acrylate) chains onto cellulosic Grewia optiva polymers through graft copolymerization synthesis significantly reduces the affinity of fibers toward polar solvents.
- The blockage of reactive sites in the cellulosic backbone polymer leads to increased chemical resistance. The grafted fibers also exhibit higher thermal stability as compared to plain cellulosic Grewia optiva polymers.
- The grafted cellulosic Grewia optiva polymers can be used as potential reinforcement in polymer composites. In further communication we shall be reporting our results on the green composites prepared using grafted fibers as reinforcement.

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