

A COMPARATIVE STUDY ON FUNCTIONALIZATION OF CELLULOSIC BIOFIBER BY GRAFT COPOLYMERIZATION OF ACRYLIC ACID IN AIR AND UNDER MICROWAVE RADIATION

Amar S. Singha* and Ashvinder K. Rana

Graft copolymerization of *Grewia optiva* fiber with acrylic acid (AAc) was carried out by using a Ce(IV) redox initiator under two different conditions, i.e. in air and under the influence of microwave radiation. Different reaction conditions affecting grafting percentage (P_g) for both methods were optimized and compared. Optimized reaction parameters for maximum P_g (7.86%) for graft copolymerization of AAc onto *Grewia optiva* fiber in air were 90 min reaction time, a temperature of 45° C, 1.82×10^{-2} mol/L CAN, 2.88×10^{-1} mol/L nitric acid, and 3.50×10^{-1} mol/L AAc. However, the maximum P_g (5.56%) for graft copolymerization in the case of MWR were 15 min reaction time, 110 W power, 2.73×10^{-2} mol/L CAN, 2.88×10^{-1} mol/L nitric acid, and 2.91×10^{-1} mol/L AAc. Both raw and graft copolymerized fibers were subjected to the evaluation of some of their properties such as swelling, moisture absorbance, and chemical resistance behavior. The AAc-graft copolymerized *Grewia optiva* showed 19.23% more swelling when compared with that of raw fiber. Further morphological and structural changes, thermal stability, and the crystallinity of raw, *Grewia optiva*-g-poly(AAc) in air, and *Grewia optiva*-g-poly(AAc) under MWR fibers were also studied by SEM, FTIR, TGA, and XRD techniques.

Keywords: Acrylic acid; Swelling behavior; Microwave radiation; *Grewia optiva*; Thermal stability

Contact information: Applied Chemistry Research Laboratory, Department of Chemistry, National Institute of Technology Hamirpur 177005 (H.P) India. * Corresponding author: singhaamar36@gmail.com

INTRODUCTION

Grewia optiva, a natural cellulosic fiber, has distinctive characteristics and is widely used by residents of Hamirpur state, India, for making low cost items such as ropes, bags, socks, boots, mats, etc. The bio-degradability and compatibility of *Grewia optiva* fiber in main sewage system enables it to also be used in the manufacture of disposable items. Cellulose in general is widely applied in many fields because of its renewability, biocompatibility, and natural abundance. With the goal of using this fiber for various applications such as sanitary napkins, apparel, home furnishing, industrial uses, and as a component of soil for agriculture (Lie et al. 2007; Zhang et al. 2007), attempts have been made to modify the fiber surface chemically.

Graft copolymerization is an effective technique used to improve the inherent properties of natural fibers. The role of the initiator is very important, as it determines the path of the grafting process. Graft copolymerization of vinyl monomers can be initiated

through the generation of free radicals on a polymeric backbone by direct oxidation of the backbone by certain transition metal ions such as Ce(IV), Cr(VI), V(V), Co(III), and Mn(III)/sulphuric acid (Taghizadeh and Mehrdad 2006; Giri et al. 1989; Gao et al. 1996; Samal et al. 2003).

Das et al. (2010) reported grafting of acrylonitrile onto silk fibre by using KMnO_4 as an initiator. There are also other types of initiators that behave in a contrary fashion, such as $\text{H}_2\text{O}_2/\text{FAS}$ (Fanta et al. 1970), FAS/KPS (Kalia et al. 2008), peroxy disulphate/ascorbic acid, etc. These initiators firstly react with themselves to produce free radicals, which subsequently react with a polymeric backbone to produce free radicals centred on the polymeric backbone.

Apart from the initiator discussed above, the hydrazine redox system (Gaylord and Tomono 1975), as well as persulfate and metal acetylacetonate (Misra and Pande 1973) have also been reported as chain initiators used in the graft copolymerization process of macromolecules. Graft copolymerization of vinyl monomers onto cellulose/natural fibers by using ceric ammonium nitrate as an initiator has been studied by many researchers (Huang and Chandramouli 2003; Taghizadeh and Darvishi 2001).

The ceric ion has been suggested for the first time as a very efficient redox system by Mino and Kaiseman (1958); the ion helps to reduce the extent of homopolymerization during graft copolymerization. Khan (2004) studied photoinduced graft copolymerization of methacrylic acid onto natural bio-degradable fiber and reported a 42% increase in its hydrophilic character. Xiao et al. (1998) studied graft copolymerization of acrylic acid onto swollen and unswollen ramie fibers and characterized the graft copolymer by IR spectra, scanning electron microscopy, differential thermal analysis, and thermogravimetric analysis. They also reported an increase in water absorption behavior after the surface modification. The change in the properties of rayon fibers due to grafting of the AAc by chemical means and γ -radiation method has been reported by Kaur et al. (2010). They reported that the graft copolymerization through the γ -radiation method is a better method of grafting, compared to the chemical method.

Sun et al. (2003) prepared and characterized the graft copolymers of carboxymethyl chitosan with methacrylic acid by FTIR, ^1H NMR spectroscopy, and elemental analysis. Graft copolymerization of AAc onto poly(ethylene terephthalate) fiber using a ceric ion initiator was studied by Chansook and Kiatkamjornwong (2003). Okieimen et al. (1989) also prepared a graft copolymer of acrylic acid with starch by using ceric ammonium nitrate as the initiator. Feng and Wang (2011) reported the synthesis of superabsorbent by a graft copolymerization reaction of cellulose from flax shive and acrylic acid using $\text{N,N}'$ -methylenebisacrylamide as a crosslinker and potassium persulfate as an initiator in an aqueous solution under microwave irradiation. Grafting of vinyl monomers onto natural fibers by using MW radiation has also been reported by Singha et al. (2012).

Since not much work has been reported on modification of *Grewia optiva* fiber through the graft copolymerization method, the present work is a comparative study on graft copolymerization of acrylic acid onto *Grewia optiva* fiber in air and under the influence of microwave radiation using ceric ammonium nitrate as an initiator.

EXPERIMENTAL

Materials

Acrylic acid (AAc) was purified by initially washing with 5% sodium hydroxide and then drying over anhydrous Na_2SO_4 . Finally, it was subjected to distillation, and the middle fraction of distillate was used for further studies. Ceric ammonium nitrate (CAN) obtained from Merck chemicals was used as initiator.

The samples were weighed on a Libror AEG-220 (Shimadzu) electronic balance. Microwave equipment (Grill Microwave Oven 20PGI) was used for graft copolymerization of acrylic acid onto *Grewia optiva* fibers. A humidity chamber of Swastika make was used to study the moisture absorbance behavior of the graft copolymers.

Sample Preparation

Grewia optiva tree branches were collected from the Palampur region in Himachal Pradesh, India. After keeping the collected branches at room temperature for 3 to 4 days, these were immersed in continuously flowing fresh water for about 40 days at a temperature ranging between 25 and 30°C. The branches were then taken out of water, and fibers were separated from sticks by dissolving cementing and gummy materials through beating gently.

The fibers thus obtained were first washed thoroughly with 2% detergent solution, which was followed by drying in a hot air oven at 70 °C for 24 hrs. The dried fibers were designated as untreated fibers. These fibers were further subjected to soxhlet extraction with acetone for 72 hrs, followed by washing with double distilled water and air drying to remove waxes and other water soluble impurities prior to various chemical treatments. The dried fibers were then cut into pieces of length 20 to 25 mm, and 0.5 g of fiber was used as sample in each grafting reaction.

Extraction of Cellulose, Hemicellulose, and Lignin Contents

Cellulose, hemicellulose, and lignin contents in this fiber were extracted out as per the procedure reported by Sarkar et al. (1948), and it was found that this fiber had 58 to 62% cellulose, 22 to 24% hemicellulose, and 14 to 16% lignin, approximately.

Graft Copolymerization of AAc in Air

Reactive sites onto *Grewia optiva* fiber were activated by preswelling in 100 mL of distilled water at room temperature for 24 hrs prior to carrying out graft copolymerization. After the activation of the reactive sites, the fiber samples were transferred to the reaction kettle containing 100 mL distilled water used as a solvent in the grafting reaction. A known amount of the CAN and nitric acid was added to the reaction flask, followed by the dropwise addition of monomer with continuous stirring of the reaction mixture. The reaction was carried out in air at 45 °C for 120 min with continuous stirring. Homo-polymer formed during the graft copolymerization was removed by extraction with hot water. The grafted samples were then dried in a hot air oven at 60 °C to a constant weight.

Graft Copolymerization of AAc Under the Influence of Microwave Radiation (MWR)

Preswelled *Grewia Optiva* fiber was graft copolymerized under microwave radiation in a microwave oven at 110 W power. A known amount of the CAN and nitric acid was added to the reaction mixture followed by the dropwise addition of the monomer with continuous stirring of the reaction mixture. The reaction flask was then put in the microwave oven for 15 min in order to carry out graft copolymerization. Homopolymer formed during the graft copolymerization was removed, and samples were then dried in a hot-air oven at 60 °C to a constant weight.

The percent grafting (P_g) and percent efficiency (P_e) were calculated as per an earlier reported method (Singha and Rana 2011). Optimum conditions of time, temperature or MWR, CAN concentration, nitric acid, and monomer concentration were determined so as to get maximum graft yield. The optimum grafting conditions were obtained by applying the grafting reaction protocol as one condition was varied for a set of reaction conditions, keeping other reaction parameters constant.

Evaluation of Physical and Chemical Properties

Chemical resistance

The chemical resistance of raw and *Grewia optiva*-g-poly(AAc) fiber was studied as a function of percent weight loss of fiber when treated with different chemicals. A known amount 1.0 g (W_i) of raw and grafted fiber was treated with a definite volume of hydrochloric acid and sodium hydroxide of different strengths for a time interval of 24 hrs. The fibers were then washed 2 to 3 times with distilled water and finally dried in an oven at 70 °C to a constant weight to get the final weight (W_f). The percent weight loss was determined as per Singha and Rana's method (2011).

Swelling behavior

The swelling behavior of the raw and grafted *Grewia optiva*-g-poly(AAc) fiber was studied in different solvents such as water, butanol, dimethyl formamide (DMF), and carbon tetrachloride (CCl_4). Dry samples of grafted as well as raw fibers (1.0 g) were suspended in 100 mL of the solvents kept at 35 °C for 24 hrs. The solvent that adhered on the surface of the samples was removed by softly pressing between the folds of the filter paper. The samples were then weighed to get the final weight. The percent swelling was calculated as per Singha and Rana's method (2011).

Moisture absorption

The moisture absorption study of grafted as well as raw fiber was performed at different humidity levels ranging from 20% to 80% for a fixed time period of 2 hrs. The percent moisture absorption was studied as a function of weight gain and was calculated according to Singha and Rana's method (2011).

Crystallinity Index (CI)

Finely powdered samples placed in the central cavity of the sample holder made of polymethylmethacrylate were used for X-ray diffraction. The crystallinity index (CI) was determined by using the wide angle X-ray diffraction counts at 2θ angle, close to 22°

and 15°. Crystallinity index measures the orientation of cellulose crystals with respect to the fiber axis. The counter reading of peak intensity close to 22° and 15° is said to represent the crystalline and amorphous contents in cellulose, respectively. Percent crystallinity and crystallinity index (CI) were calculated using the following equation (Mwaikambo and Ansell 2002),

$$\%C_r = \frac{I_C}{I_C + I_A} \times 100 \quad (1)$$

$$C.I = \frac{I_C - I_A}{I_C} \quad (2)$$

where I_C and I_A are the crystalline and amorphous intensities at 2θ scale close to 22° and 15° angles.

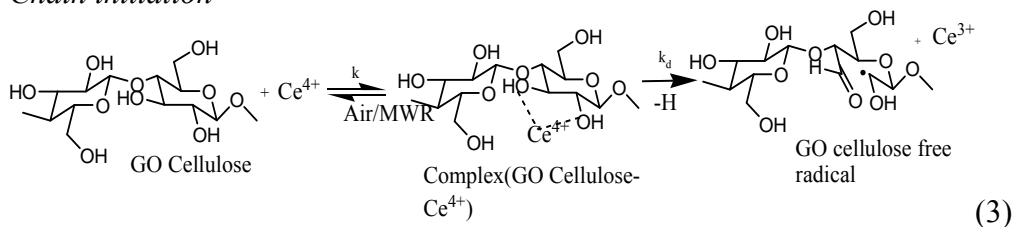
RESULTS AND DISCUSSION

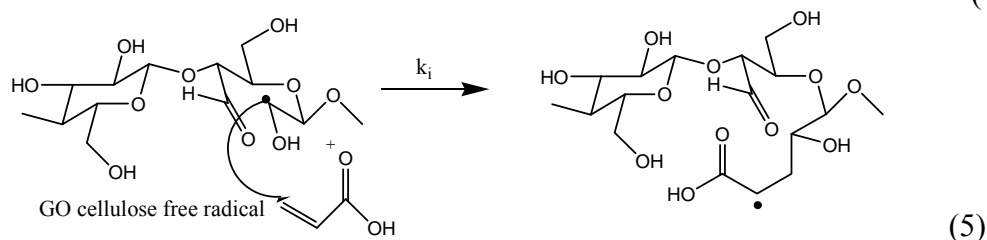
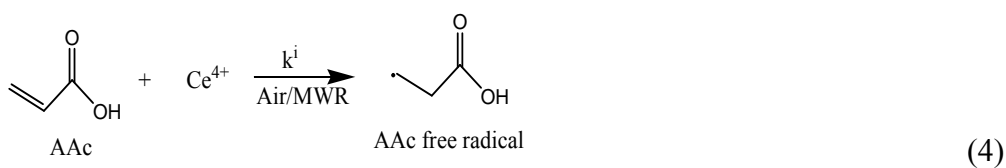
Reaction Mechanism

In the case of graft copolymerization onto natural fiber using Ce(IV) ion as an initiator, free radical active sites are generated directly on the cellulosic backbone without formation of intermediate radicals in the solvent. Thus, the procedure leads to a decrease in homopolymer formation. The grafting reaction generally proceeds through the formation of an intermediate metal-ion chelate complex. Such a complex is not restricted to a single site on the cellulose backbone; rather it involves both primary and secondary hydroxyl groups of glucose units in inducing free-radical formation on the cellulosic backbone. This has been confirmed by ESR studies (Misra et al. 1993). The grafting of acrylic acid onto the *Grewia Optiva* (GO) backbone in air and under the influence of microwave radiation is supposed to take place through the following mechanism (Scheme 1).

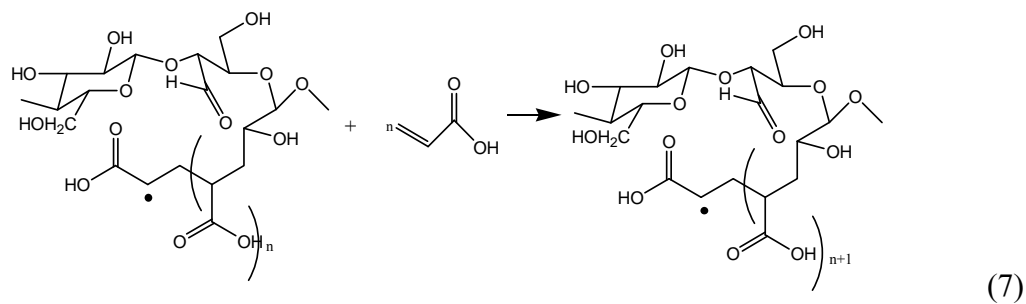
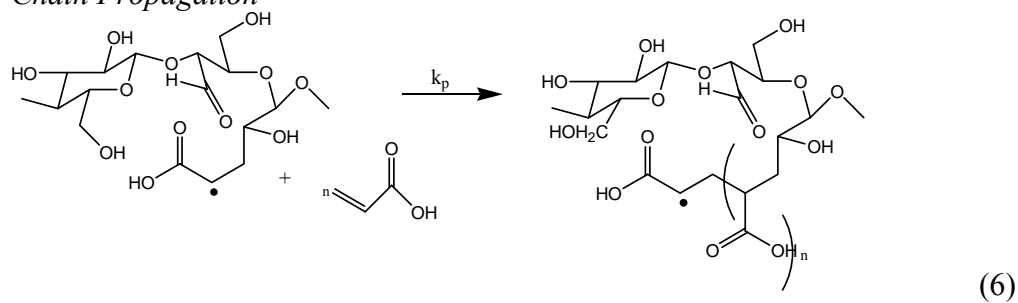
Ceric ions form complexes with the carbon chain of polymer backbone as well as with monomer (Eqs. 3 & 4) and generate free radicals (Kaur et al. 2010). Free radicals then result in the formation of graft copolymer [GOC-g-poly (AAc)] by reacting at the active sites of the polymeric backbone (Eqs. 5 & 6). Monomer may combine with the macro GOC-g-poly(AAc) radical to forms graft copolymer (Eq. 7). On the other hand the ceric ions and poly (AAc) free radicals combine with the GOC-g-poly (AAc) free radicals and CH free radicals respectively to cause termination of the reaction (Eqs. 8 & 9).

Chain initiation

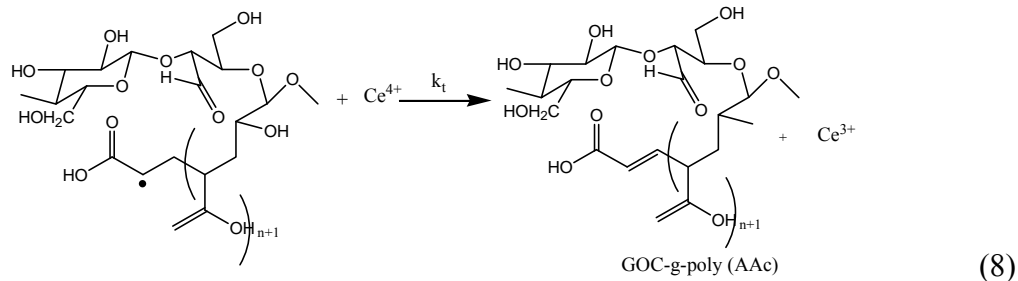


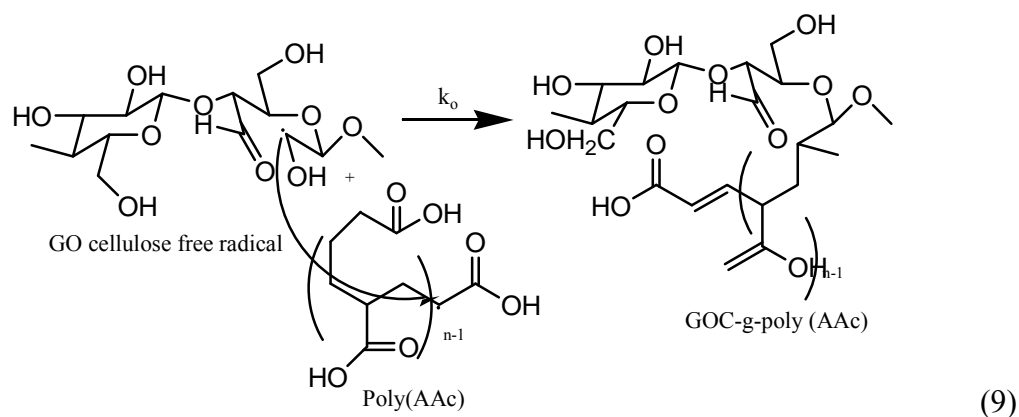


Chain Propagation



Chain Termination





Scheme 1. A possible mechanism for the graft copolymerization of the Acrylic acid onto *Grewia optiva* fiber

Effect of Time, Temperature, and Microwave Radiation

Time plays a very important role under both sets of conditions considered in this work (in air and under the influence of microwave radiation). The percentage of grafting and percent efficiency were studied as a function of time and the results are represented in Table 1. As shown in the table, P_g increased with an increase in time, giving maximum P_g (7.06%) at 120 min in air and at 15 min (2.76%) with microwave radiation (120 W). This probably happens because of the generation of more and more monomer radicals as time proceeds, which interact with the active sites on the polymeric backbone, resulting in increased P_g . However, beyond the optimum time P_g decreases due to irreversible termination by radical coupling. This may also be due to the mutual destruction of growing polymeric chains, leading to homopolymerization of the reaction monomer radicals and backbiting by the active radicals. Grafting in the presence of MWR took less time because of the passage of electromagnetic waves in the solution, which oscillates the speed of chain carrier free radicals and ultimately leads to the formation of small molecular chain graft copolymers.

Table 1. Optimization of Grafting Time

Sr. No	<i>Grewia optiva</i> -g-poly(AAc) in Air ^a			<i>Grewia optiva</i> -g-poly(AAc) Under the Influence of MWR ^b		
	Grafting Time (Min)	Percent Grafting (P_g)	Percent Efficiency (P_e)	Grafting Time (Min)	Percent Grafting (P_g)	Percent Efficiency (P_e)
1.	60	4.58	1.09	5	1.15	0.27
2.	90	5.80	1.38	10	2.02	0.47
3.	120	7.06	1.68	15	2.76	0.60
4.	150	6.04	1.43	20	1.66	0.39
5.	180	3.58	0.85	25	1.26	0.30

^a [CAN]: $1.82 \times 10^{-2} \text{ mol L}^{-1}$; [AAc]: $3.50 \times 10^{-1} \text{ mol L}^{-1}$; [HNO₃]: $2.88 \times 10^{-2} \text{ mol L}^{-1}$; Temp: 45°C.

^b [CAN]: $2.27 \times 10^{-2} \text{ mol L}^{-1}$; [HNO₃]: $2.88 \times 10^{-2} \text{ mol L}^{-1}$; [AAc]: $2.33 \times 10^{-1} \text{ mol L}^{-1}$; Power: 110 W.

The effect of temperature in air and MW radiation in a microwave oven is shown in Table 2. It can be seen that both P_g and P_e showed an increasing trend up to 45 °C. This was attributed to the fact that a high temperature can enhance the dynamic energy of the monomer molecules, which leads to an increase in the diffusion rate of monomer molecules from the reaction mixtures onto polymeric backbone, hence resulting in increased P_g and P_e . Beyond 45 °C P_g decreased, which may be due to an increase in the rate of chain transfer and chain termination reactions between monomer molecules and grafted chains. Also, combination of free monomer radicals at higher temperature may result in a decreased graft yield. While in case of graft copolymerization under MWR, the maximum P_g was obtained at a power 110 W, however no grafting was obtained beyond a power of 110 W. This is because the increased power caused burning of the fibers, and only a blackish color material was obtained.

Table 2. Optimization of Reaction Temperature and Microwave Radiation

Sr. No	<i>Grewia optiva</i> -g-poly(AAc) in Air ^a			<i>Grewia optiva</i> -g-poly(AAc) Under the Influence of MWR ^b		
	Grafting Temp (°C)	Percent Grafting (P_g)	Percent Efficiency (P_e)	MWR Power	Percent Grafting (P_g)	Percent Efficiency (P_e)
1.	25	4.08	0.97	110	2.76	0.60
2.	35	6.50	1.54	220	-	-
3.	45	7.06	1.68	350	-	-
4.	55	5.88	1.40	-	-	-
5.	65	4.92	1.17	-	-	-

^a [CAN]: 1.82×10^{-2} mol L⁻¹; [AAc]: 3.50×10^{-1} mol L⁻¹; [HNO₃]: 2.88×10^{-2} mol L⁻¹; Time: 120 min. ^b [CAN]: 2.27×10^{-2} mol L⁻¹; [HNO₃]: 2.88×10^{-2} mol L⁻¹; [AAc]: 2.33×10^{-1} mol L⁻¹; Time: 15 min.

Effect of CAN Concentration

Both P_g and P_e were studied as a function of CAN concentration, and those results are shown in Table 3. It was found that P_g increased with an increase in initiator concentration, giving maximum P_g (7.06%) at CAN = 1.82×10^{-2} mol/L in air and at CAN = 2.73×10^{-2} mol/L (5.24%) under MWR.

Table 3. Optimization of Initiator Concentration

Sr. No	<i>Grewia optiva</i> -g-poly(AAc) in Air ^a			<i>Grewia optiva</i> -g-poly(AAc) Under the Influence of MWR ^b		
	[CAN] x 10 ⁻² Mol/L	Percent Grafting (P_g)	Percent Efficiency (P_e)	[CAN] x 10 ⁻² Mol/L	Percent Grafting (P_g)	Percent Efficiency (P_e)
1.	0.91	6.06	1.44	1.82	2.28	0.54
2.	1.36	6.46	1.53	2.27	2.76	0.65
3.	1.82	7.06	1.68	2.73	5.24	1.24
4.	2.27	6.16	1.46	3.19	3.68	0.87
5.	2.73	5.62	1.33	3.64	3.10	0.81

^a [AAc]: 3.50×10^{-1} mol L⁻¹; [HNO₃]: 2.88×10^{-2} mol L⁻¹; Time: 120 min; Temp: 45°C. ^b [HNO₃]: 2.88×10^{-2} mol L⁻¹; [AAc]: 2.33×10^{-1} mol L⁻¹; Time: 15 min; Power: 110W.

An initial increase in CAN resulted in an increase of free radical active sites on the polymeric backbone, where grafting takes place. However, a further increase in CAN concentration beyond the optimum value accelerates the dissociation rate of Ce (IV), which reduces the concentration of CAN participating in graft copolymerization. Additionally, a higher concentration of CAN makes it easier for Ce (IV) to be involved in a termination reaction, thereby causing a decrease in P_g (Scheme 1, Eq. 6).

Effect of Nitric Acid Concentration

Table 4 shows the effect of nitric acid on graft copolymerization of AAc onto *Grewia optiva* fiber in air and MWR. It can be observed from Table 4 that in both cases P_g increased with an increase in nitric acid concentration from 1.44×10^{-1} to 2.88×10^{-1} mol/L, giving maximum P_g of 7.06% in air and 5.24% under MWR. An initial increase in nitric acid concentration increased the concentration of Ce^{4+} that forms a complex with *Grewia optiva* fiber, thus increasing the number of reaction sites and P_g (Eqs. 8 & 9).

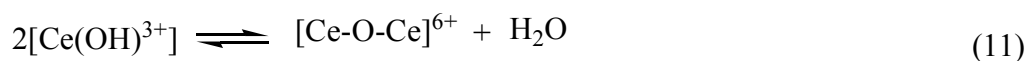
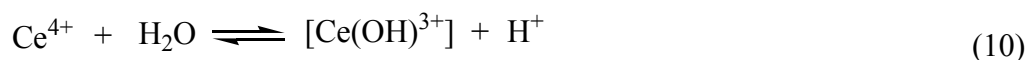


Table 4. Optimization of Nitric Acid Concentration

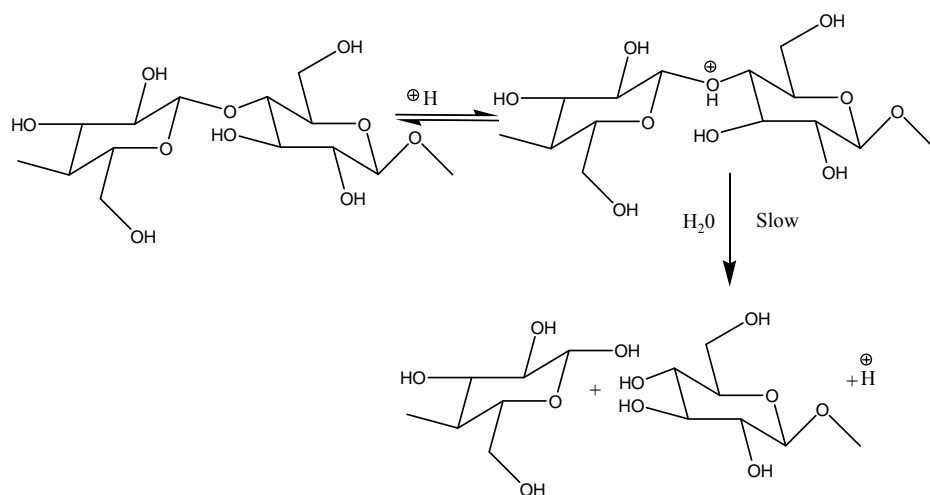
Sr. No	<i>Grewia optiva</i> -g-poly(AAc) in Air ^a			<i>Grewia optiva</i> -g-poly(AAc) Under the Influence of MWR ^b		
	[HNO ₃] x 10 ⁻¹ Mol/L	Percent Grafting (P_g)	Percent Efficiency (P_e)	[HNO ₃] x 10 ⁻¹ Mol/L	Percent Grafting (P_g)	Percent Efficiency (P_e)
1.	1.44	2.64	0.62	1.44	3.32	0.79
2.	2.16	4.64	1.10	2.16	3.52	0.83
3.	2.88	7.06	1.68	2.88	5.24	1.24
4.	3.6	5.10	1.27	3.6	4.32	1.02
5.	4.32	4.26	1.01	4.32	2.46	0.58

^a [CAN]: 1.82×10^{-2} mol L⁻¹; [AAc]: 3.50×10^{-1} mol L⁻¹; Time: 120 min; Temp: 45°C. ^b [CAN]: 2.73×10^{-2} mol L⁻¹; [AAc]: 2.33×10^{-1} mol L⁻¹; Time: 15 min; Power:110W.

However, P_g decreased with a further increase in the nitric acid concentration beyond the optimum value (2.88×10^{-1} mol/L), probably due to the termination of growing grafted chains, which had been accelerated because of formation of considerable amounts of $[Ce^{4+}]$ and $[CeOH]^{3+}$. Increased concentration of nitric acid may also result in hydrolysis (Scheme 2) of the fiber (Nevell 1986).

Effect of Monomer Concentration

Percentage of grafting and percent efficiency for graft copolymerization of AAc onto *Grewia Optiva* fiber in air and under MWR was studied as a function of monomer concentration, and the results are shown in Table 5. It can be obtained from the table that P_g increased with an increase in AAc concentration, giving a maximum P_g of 7.86% at [AAc] = 3.50×10^{-1} mol/L in air and 5.24% at [AAc] = 2.91×10^{-1} mol/L under MWR.



Scheme 2. Hydrolysis of the cellulosic fiber due to increased HNO_3 concentration (Nevell 1986)

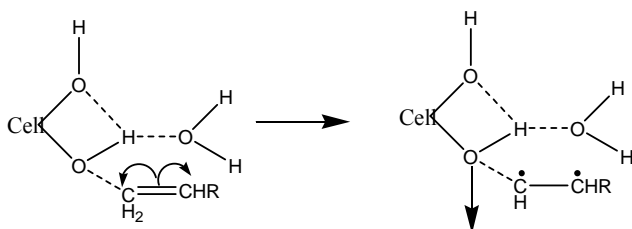
An increase in P_g with an increase in monomer concentration may be explained by the fact that initially more and more free radicals reach onto the polymeric backbone, resulting in an increase in P_g . However, a decrease in P_g beyond the optimum value is probably due to preferential homopolymerization over graft copolymerization.

Table 6. Optimization of Monomer Concentration

Sr. No	<i>Grewia optiva</i> -g-poly(AAc) in Air ^a			<i>Grewia optiva</i> -g-poly(AAc) Under the Influence of MWR ^b		
	[AAc] x 10 ⁻¹ Mol/L	Percent Grafting (P_g)	Percent Efficiency (P_e)	[AAc] x 10 ⁻¹ Mol/L	Percent Grafting (P_g)	Percent Efficiency (P_e)
1.	2.33	4.16	1.34	1.75	2.28	0.88
2.	2.91	4.52	1.69	2.33	2.76	1.11
3.	3.50	7.86	1.55	2.91	5.24	1.24
4.	4.08	5.26	0.89	3.50	4.06	0.8
5.	4.66	4.50	0.66	4.08	2.56	0.43

^a [CAN]: $1.82 \times 10^{-2} \text{ mol L}^{-1}$; [HNO_3]: $2.88 \times 10^{-2} \text{ mol L}^{-1}$; Time: 120 min; Temp: 45°C. ^b [CAN]: $2.73 \times 10^{-2} \text{ mol L}^{-1}$; [HNO_3]: $2.88 \times 10^{-2} \text{ mol L}^{-1}$; Time: 15 min; Power: 110W.

Increased AAc concentration gives rise to a 3- component complex (Scheme 3) comprising substrate, monomer, and water, which subsequently rearrange themselves to give the requisite free radical site with liberation of hydrogen (Kaur et al. 2010). The liberated hydrogen initiates homopolymerization, leading to a decrease in grafting.



Scheme 3. A three-component complex leads to increased homopolymerization (Kaur et al. 2010).

Low graft yield in the case of grafting under the influence of microwave radiation is because of high speed oscillation of chain carrier free radicals, which undergo rapid collision between different radical species. These rapid collisions cause the formation of small molecular chain graft copolymers and ultimately low graft yield. However, in the case of grafting in air, the growing free radical chains do not face rapid collision and yield long chain graft copolymers.

Physical and Chemical Properties

Swelling behavior as a function of percentage of grafting

Percent swelling of the raw and AAc-grafted fiber in doubly distilled water, butanol, dimethyl formamide, and carbon tetrachloride is shown in Fig. 1. The raw fiber possesses hydrophilic –OH groups at C2, C3, and C6 of the glucose unit, and these have a strong affinity with water. Therefore the raw *Grewia optiva* fiber showed maximum swelling with polar solvents like water and n-butanol and the least swelling with the nonpolar solvents like CCl₄. It can also be observed from the figure that percent swelling of *Grewia optiva*-g-poly(AAc) increased with an increase in percent grafting and was found to be 19.23% higher than raw fiber in distilled water at the 7.86% graft level.

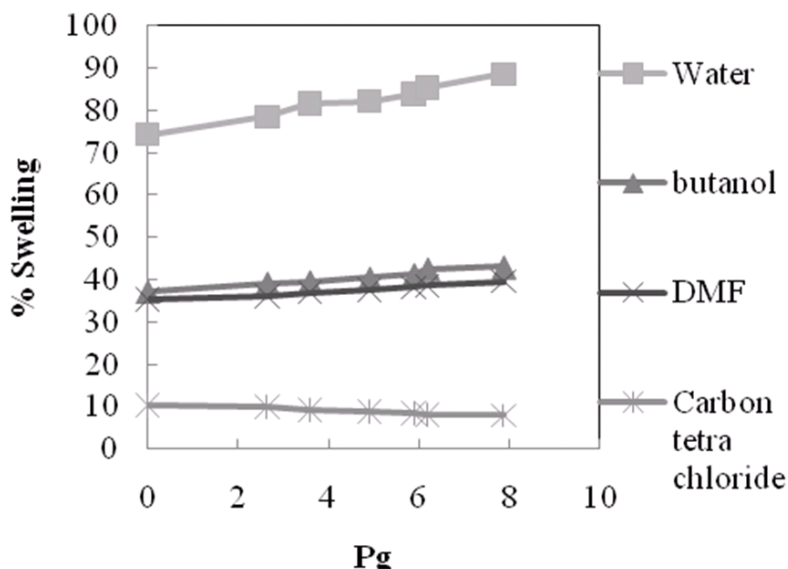


Figure 1. Effect of P_g on swelling behavior against different solvents

The percent swelling in butanol and DMF for 7.86% graft level was also higher, while the percent swelling in carbon tetrachloride was less than that of the raw fiber. The lower percent swelling of the *Grewia optiva*-g-poly(AAc) fiber in carbon tetrachloride was due to less interaction of CCl₄ with carboxyl groups in comparison to the hydroxyl groups of the raw fiber.

Acid and base resistance study

The acid and base resistance of *Grewia optiva*-g-poly(AAc) in air was studied as a function of percent weight loss against the acid/base solution. It can be observed from Figs. 2 and 3 that with an increase in P_g , weight loss of the grafted fiber increased. This

happened because of the formation of the corresponding sodium salts and to some extent also due to the solubility of the polyacrylic acid chain (Giri et al. 1989).

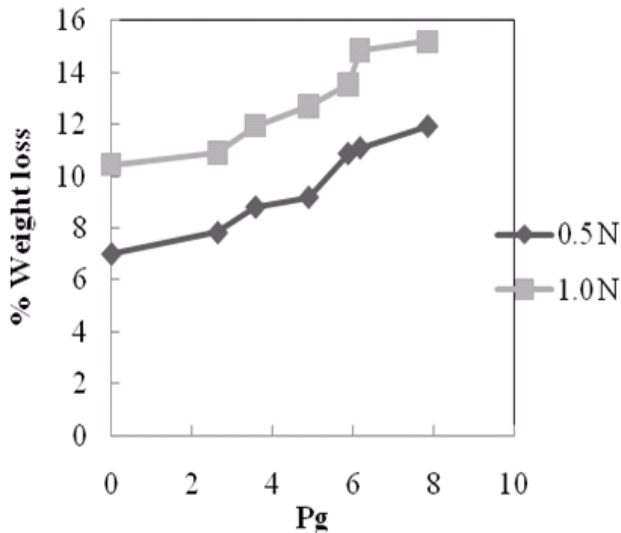


Figure 2. Effect of P_g on resistance to acid

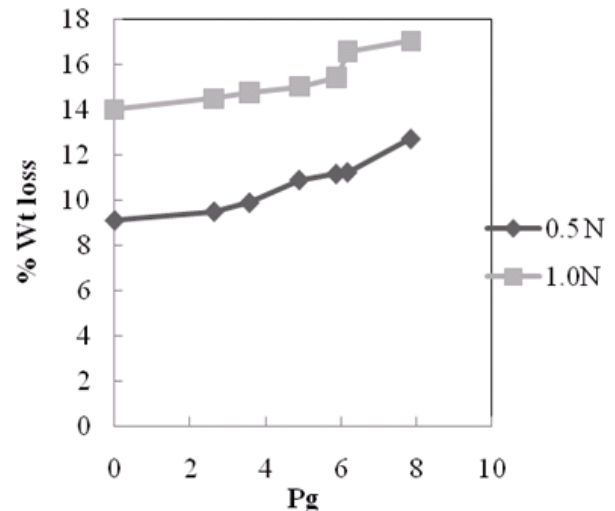


Figure 3. Effect of P_g on resistance to base

Moisture Absorbance

Raw *Grewia optiva* fibers have been found to show 1.91, 2.45, 3.21, and 3.75% moisture absorbance at 20, 40, 60, and 80% humidity levels, respectively (Figure 4).

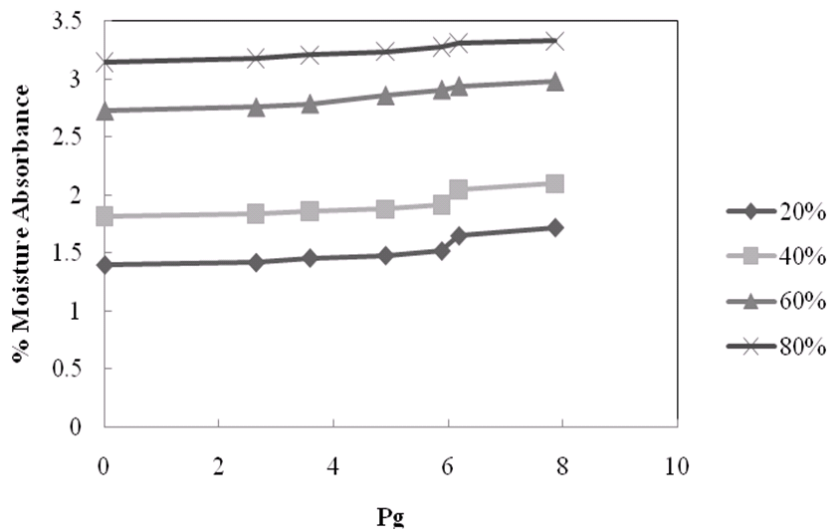


Figure 4. Effect of P_g on moisture absorption behavior

From the figure it is clear that the *Grewia optiva*-g-poly (AAc) in air fiber showed higher moisture absorption, which increased with increases in P_g . This could be due to the fact that with an increase in the graft yield, more carboxyl groups are available for formation of the hydrogen bond with the water molecules.

FTIR analysis

IR spectra of raw and AAc graft copolymerized lignocellulosic fibers were recorded with KBr pellets on a PERKIN ELMER RXI Spectrophotometer (Fig. 5). The FT-IR spectrum of raw *Grewia optiva* fiber showed broad peaks at 615.71 cm^{-1} (due to out of plane -OH bending), 896.31 cm^{-1} (due to β -glycosidic linkage), and 1247.68 cm^{-1} (due to -C-O-C- and -C=O stretching in xylan side substituent and lignin aromatic C=O stretching). Milder peaks occurred at 1377.2 to 1431.31 cm^{-1} (due to -CH , -CH_2 , and -CH_3 bending), 1638.82 cm^{-1} (due to H-O-H bending of absorbed water and for lignin C-H deformation), 1729.9 cm^{-1} (due to carbonyl group of pectins), 2131.29 cm^{-1} (due to O-H stretching of absorbed moisture), 2335.5 cm^{-1} (due to C-H stretching in polysaccharide chains), and 2923.49 cm^{-1} (for C-H stretching vibration of aliphatic methylene group). Finally, there was an intense broad peak ranging from 3024 to 3691 cm^{-1} (due to the hydrogen bonded -OH vibration of the cellulose structure fiber). The AAc-grafted *Grewia optiva* fibers, on the other hand, showed additional characteristic absorption bands at 1733 cm^{-1} and 1576 cm^{-1} due to carbonyl stretching of pendant carboxylic acid groups and unsaturated groups, respectively.

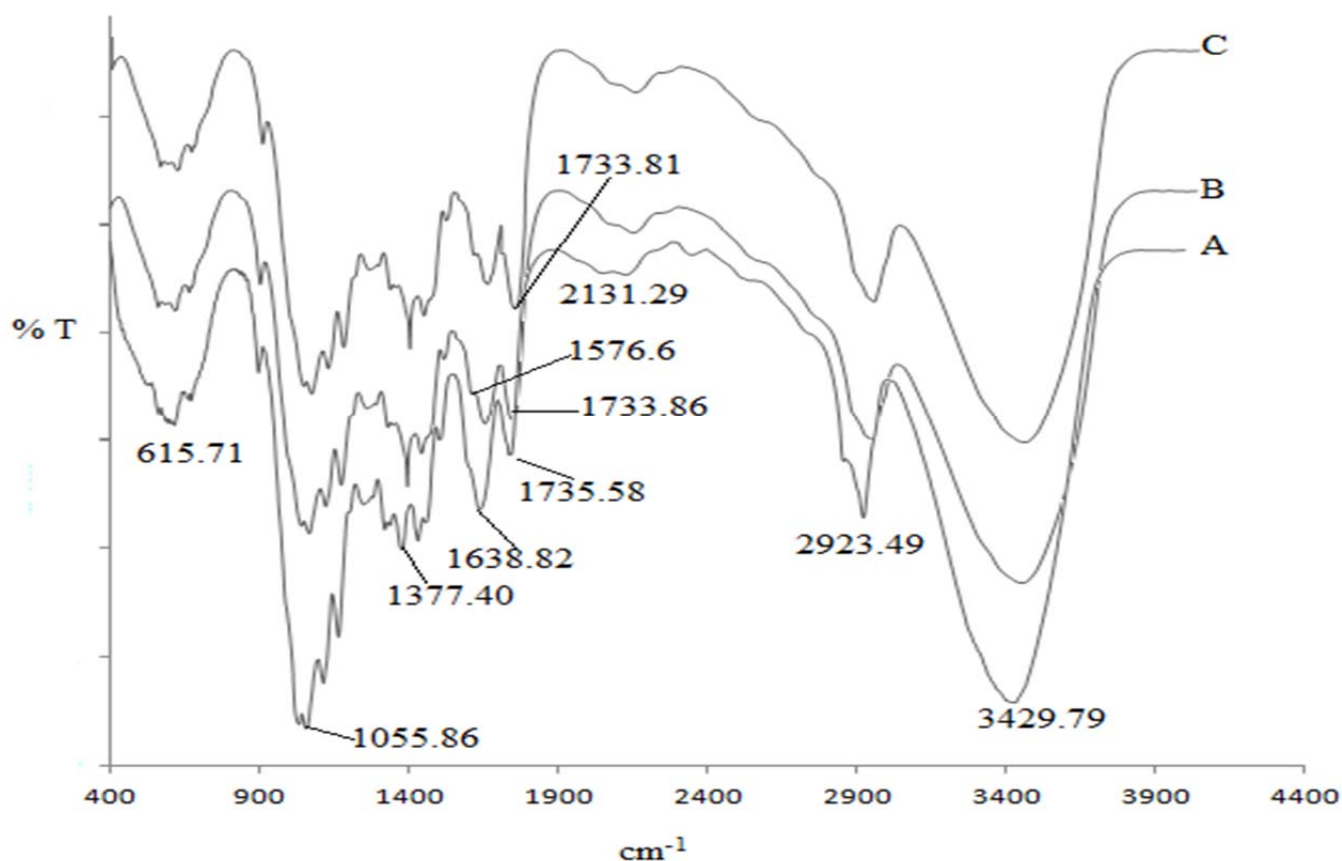


Figure 5. FTIR spectrum of (A) raw (B) *Grewia optiva*-g-poly(AAc) Under the Influence of MWR and (C) *Grewia optiva*-g-poly(AAc) in Air fiber

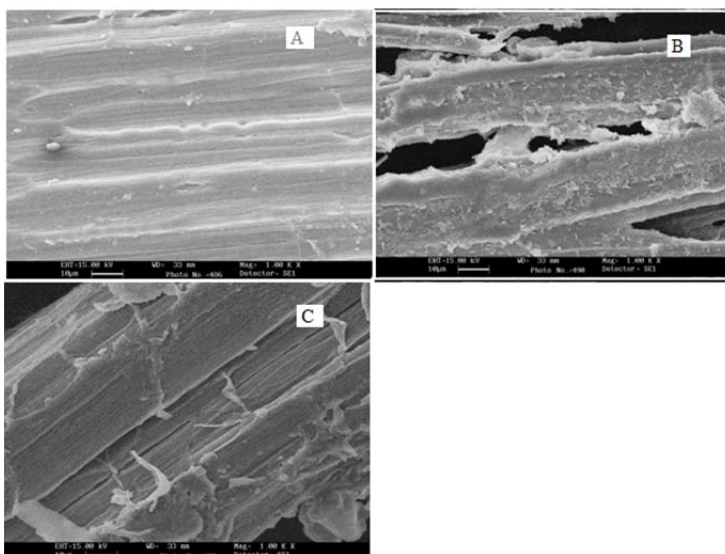


Figure 6. Surface morphology of (A) raw, (B) *Grewia optiva*-g-poly(AAc) in air, and (C) *Grewia optiva*-g-poly(AAc) under MWR

Morphological studies

Surface topology of raw and surface-modified *Grewia optiva* fibers was studied with scanning electron microscopy on a LEO 435 VP electron microscope, and the results are shown in Fig. 6. In order to conduct the SEM imaging, all the samples were gold-plated to promote conductivity. All the images were taken at a resolution of 1000x. The comparison of the scanning electron micrographs of the raw, *Grewia optiva*-g-poly(AAc) in air, and *Grewia optiva*-g-poly(AAc) under MWR showed that the morphology of the fiber changes upon grafting, indicating that a considerable amount of poly(AAc) had been grafted onto *Grewia optiva* fiber surface.

Thermal stability

Thermogravimetric analysis of raw *Grewia Optiva* fiber, *Grewia optiva*-g-poly(AAc) in air, and *Grewia optiva*-g-poly(AAc) in MWR was carried out in a nitrogen atmosphere at a heating rate of 15 °C/min. on a Mettler Toledo auto-sampler. The decomposition of samples was studied as a function of percent weight residue with increase in temperature (Fig. 7). In the case of cellulosic fibers, cellulose decomposed in three stages. The first stage of weight loss between 60 and 120 °C occurred due to volatilization of water molecules chemically adsorbed onto the fiber surface, while the second stage of weight loss was due to reactions such as depolymerization, dehydration, and glucosan formation. Dehydration usually took place between 150 and 250 °C, followed by cleavage of C-H, C-C, and C-O bonds (Chauhan et al. 1999). The third stage of weight loss at about 460 °C may be due to further decomposition of the product of stage II, leading to formation of tar through levoglucosan.

For raw *Grewia Optiva* fiber, the initial decomposition temperature (IDT) was found to be 262.5 °C (3.26% weight loss), and the final decomposition temperature (FDT) was 394.32 °C (66.93% weight loss).

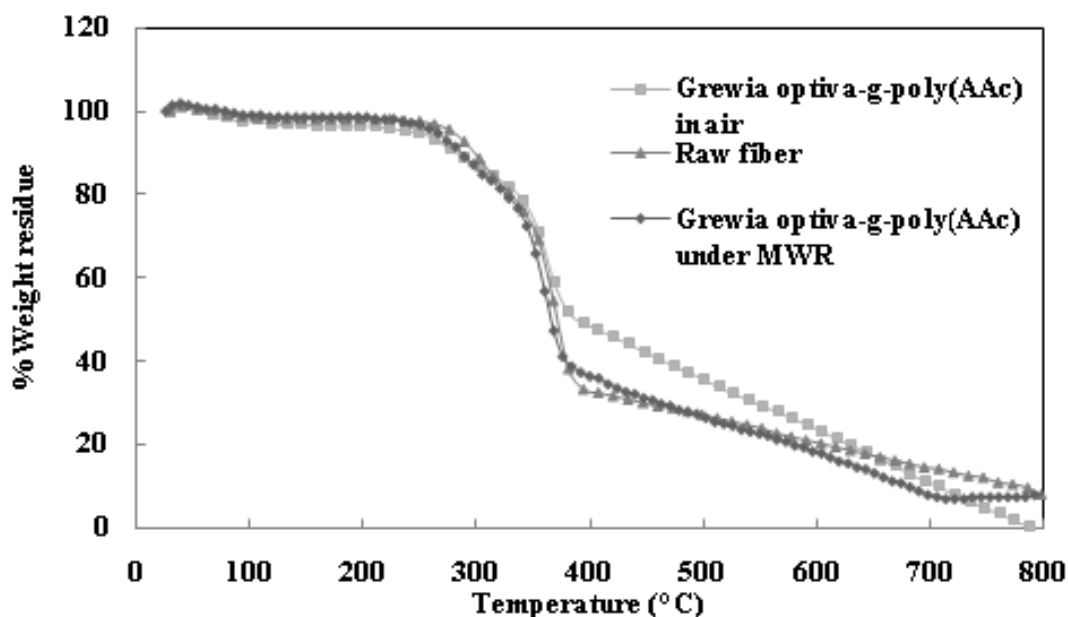


Figure 7. Thermogravimetric analysis of raw, *Grewia optiva*-g-poly(AAc) in air, and *Grewia optiva*-g-poly(AAc) under MWR fibers

In the case of *Grewia optiva*-g-poly(AAc) in air, IDT and FDT were found to be 250.09 °C (4.98% weight loss) and 407.75 °C (52.23% weight loss), respectively. However in the case of *Grewia optiva*-g-poly(AAc) under MWR, IDT and FDT values were found to be 257.54 °C (4.27% weight loss) and 399.70 °C (63.51% weight loss), respectively. It was observed from the above data that the Aac-grafted fiber showed lower thermal resistance behavior at low temperatures but a higher thermal stability at high temperatures as compared to raw fiber.

A decrease in the thermal stability of grafted fibers at a lower temperature (IDT) occurs because of the decomposition of anhydride (formed due to dehydration of carboxylic acid groups) of poly(AAc) chains to carbon dioxide in the temperature range of 150 to 275 °C, accompanied by an overall decrease in the acrylic acid content (McGaugh and Kottle 1967).

It was also observed that between *Grewia optiva*-g-poly(AAc) in air and *Grewia optiva*-g-poly(AAc) under MWR, the former showed lower IDT and a higher FDT compared to the latter. This may be due to the higher percent grafting in air, which causes a high decomposition of AAc at lower temperatures, compared to low-grafted samples (*Grewia optiva*-g-poly(AAc) under MWR). Also, if decomposition temperature is taken (DT) at 20, 40, and 60% weight loss for all samples as a standard of comparison, it is observed that *Grewia optiva*-g-poly (AAc) fibers in air are thermally more stable than the raw and *Grewia optiva*-g-poly (AAc) fibers under MWR at higher temperatures (Table 7).

Table 7. Thermogravimetric Analysis of the Raw and *Grewia optiva*-g-poly(AAc) Fibers

Sr. No	Sample Designation	IDT (°C)	FDT (°C)	DT (°C) at 20% Wt Loss	DT (°C) at 40% Wt Loss	DT (°C) at 60% Wt Loss	Residual Weight (%) at 600 °C
1	Raw <i>Grewia optiva</i> Fiber	262.65	394.32	328.40	362.86	381.06	20
2	<i>Grewia optiva</i> -g-poly(AAc) in Air	250.09	407.75	341.96	368.31	461.34	23.38
3	<i>Grewia optiva</i> -g-poly(AAc) Under MWR	257.54	397.7	328.33	359.83	383.69	18.34

Crystallinity study

X-ray diffraction studies were performed on an X-ray diffractometer (Bruker D8 Advance) using Cu K α (1.5418 Å) radiation, a Ni-Filter, and a scintillation counter as a detector at 40KV and 40 mA on rotation from 10° to 60° at a 2 θ scale. X-ray diffraction studies of the raw and graft copolymers are shown in Table 8. Since cellulosic fibers generally contain both crystalline and amorphous regions, X-ray diffraction patterns of such materials will show both regions in the form of sharp peaks and diffused patterns.

Table 8. Percentage Crystallinity (% Cr) and Crystallinity Index (C.I.) of Raw and *Grewia Optiva*-g-poly(AAc) Fiber

Sr.No	Sample	At 2 θ Scale		% Crystallinity	C.I
		I_{22}	I_{15}		
1	Raw fiber	1350	805	62.65	0.40340
2	<i>Grewia optiva</i> -g-poly(AAc) in Air	769	511	60.07	0.33550
3	<i>Grewia optiva</i> -g-poly(AAc) Under MWR	814	504	61.76	0.38083

It is evident from Table 8 that *Grewia optiva* fiber, *Grewia optiva*-g-poly(AAc) in air, and *Grewia optiva*-g-poly(AAc) under MWR showed 62.65, 60.07, and 61.76% crystallinity, respectively. The crystallinity index of raw fiber, *Grewia optiva*-g-poly(AAc) in air, and *Grewia optiva*-g-poly(AAc) under MWR was observed to be 0.4039, 0.3355, and 0.38083 respectively. Crystallinity index (C.I.) gives a quantitative measure of the orientation of cellulose crystals in the fibers with respect to the fiber axis. The cause of the decrease in C.I. of *Grewia optiva*-g-poly(AAc) could be the disorienta-

tion of cellulose crystals when poly-(AAc) chains are incorporated in the fiber. Further graft copolymers prepared under microwave radiation showed fewer changes in the crystalline lattice structure compared to graft copolymers prepared in air because the optimum reaction time for graft copolymerization under MWR was very low. However, a lower C.I. for graft copolymers prepared in air indicates poor order of cellulose crystals. Although C.I. gives a quantitative measurement of the orientation of cellulose crystals in fibers, X-ray diffraction patterns are visual indicators of cellulose crystals. The diffraction pattern of raw fiber produces narrow and bright patterns that are characteristic of well oriented crystals (Cao and Billows 1999). However, the diffraction pattern of the *Grewia optiva*-g-poly(AAc) in air and *Grewia optiva*-g-poly(AAc) under MWR showed short diffracting arcs that end sharply because of malorientation of the cellulose crystals.

CONCLUSIONS

1. *Grewia optiva* fiber was successfully modified through graft copolymerization of AAc under both conditions considered in the study, i.e. in air and under the influence of MWR. On comparison it was found that graft copolymerization in air resulted in higher graft yield.
2. It is concluded from the evaluation of physical properties that incorporation of poly(AAc) chains on the surface of cellulosic fiber through graft copolymerization increases the affinity of cellulosic fibers with water. Thus these fibers can be used as super water absorbents as well as for the removal of harmful ions such as Pb, As, etc., from water sources.
3. *Grewia optiva*-g-poly(AAc) in air has been found to be slightly less stable at low temperature, but at high temperatures its thermal stability was found to be better than that of raw and *Grewia optiva*-g-poly(AAc) under MWR. Graft copolymerization causes a slight decrease in percent crystallinity of fiber, and this decrease in percent crystallinity was found to be the highest in case of *Grewia optiva*-g-poly(AAc) in air.

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