Carbohydrate Polymers 104 (2014) 87–93

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Graft copolymers of natural fibers for green composites

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ARTICLE INFO

Article history:
Received 30 November 2013
Received in revised form
31 December 2013
Accepted 5 January 2014
Available online 10 January 2014

Keywords:
Natural cellulose
Graft copolymers
SEM
FTIR
TGA
Physico-chemical characteristics

ABSTRACT

In the present study, free radical induced graft-copolymerization of natural cellulosic polymers (*Grewia optiva*) has been carried out to develop the novel materials meant for green composites and many other applications. During the graft copolymer synthesis diverse reaction parameters that significantly affect the percentage of grafting were optimized. The structural, thermal and physico-chemical changes in the natural cellulosic polymers based graft copolymers have been ascertained with scanning electron micrography, Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA) and swelling studies. The swelling studies of the grafted cellulosic polymers have been carried out in different solvents to assess the possible applicability of these natural polymers. Green composites were also prepared using raw/grafted cellulosic polymers. It has been found that grafted polymers (*Grewia optiva*) based green composites gives better tensile properties than the parent natural cellulosic polymers based composites.

1. Introduction

Synthetic polymers are one of the most wonderful materials developed by human being during the last century that have innovated the research in various fields due to their better performance and ever increasing demand (Azaman, Sapuan, Sulaiman, Zainudin, & Khalina, 2013; Bachtiar, Sapuan, Khalina, Zainudin, & Dahlan, 2012; Chalivendra, Shukla, Bose, & Parameswaran, 2003). A lot of research efforts have been made to further explore their applications in everyday life and have resulted in numerous kinds of materials (Crowley & Chalivendra, 2008; Dhakal, Zhang, Bennett, & Reis, 2012; Kamel, 2012; Mansor, Sapuan, Zainudin, Nuraini, & Hambali, 2013; Sahari, Sapuan, Zainudin & Maleque, 2013; Singh, Srivastava, & Mall, 2013). However, instead of the advantages offered by the synthetic polymers, at present there is great demand for natural polymers based materials as the synthetic polymers based materials are commonly prepared using petroleum–based chemicals which are non-degradable as well as non-desirable from the environmental point of view (Basta & El-Saied, 2008; Maclure, Chalivendra, & Ramotowski, 2009; Ishak et al., 2013; Suresh, Srivastava, & Mishra, 2011; Wanasekara, Chalivendra, & Calvert, 2011). Compared to the synthetic polymers, natural polymers offer various new materials with eco-efficiency and eco-friendly advantages such as promising biodegradability, non-toxicity etc. (Azaman, Sapuan, Sulaiman, Zainudin, & Abdan, 2013; Bajpai, Singh, & Madaan, 2012; Basta, El-Saied, & Lotfy, 2013). Indeed natural polymers based materials have been used by human civilization since hundreds of years for miscellaneous applications (Basta, El-Saied, El-Hadi, & El-Dewiny, 2013; Bharti, Mishra, & Sen, 2013). Green materials from natural polymers can form the basis for a new class of environmental friendly materials (Dhakal, Zhang, Guthrie, & Bennett, 2013; Sabo, Basta, & Winandy, 2013; Yusriah, Sapuan, Zainudin, & Mariatti, 2012; Wu, 2012).

However, the biggest obstacle in the practical applications of natural cellulosic polymers is their sensitivity towards weathering conditions such as swelling in water and poor resistance to chemicals (El-Saied, Basta, Hassanen, Korte, & Helal, 2012; Dhakal, Zhang, & Bennett, 2012; Dhakal, Zhang, Reis, Surip, & Bennett, 2012; Khoathane, Sadiku, & Wambua, 2012; Pinto, Chalivendra, Kim, & Lewis, 2013a,b). To overcome the shortcoming of the natural bio-polymers, graft copolymerization is one of the frequently used techniques for transforming the properties of these polymers without changing its inherent properties (Mishra, Rani, & Sen, 2012; Nazi, Malek, & Kotek, 2012; Rani, Sen, Mishra, & Jha, 2012; Rani, Mishra, & Sen, 2013). This technique involves the chemical induction of copolymerization using bio-polymers as the polymeric backbone (Rani, Mishra, Sen, & Jha, 2012; Thakur & Singha, 2011a,b; Thakur, Singha, & Thakur, 2012a–d). In case of natural cellulosic fibers; graft copolymerization imparts physical, thermal and

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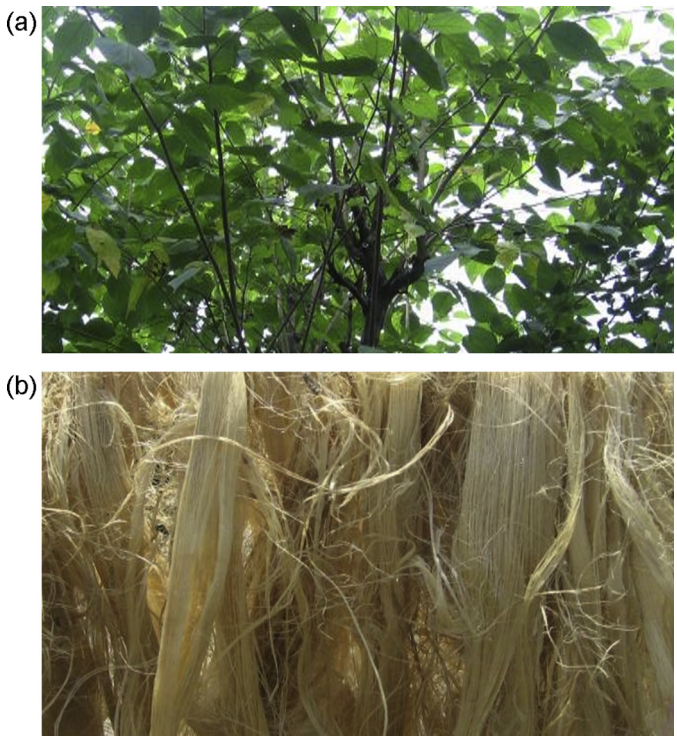
0144-8617/$ – see front matter © 2014 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2014.01.016



Scheme 1. Photographic images of (a) *Grewia optiva* plant (b) fibers derived from *Grewia optiva* plant.

chemical resistance to the fibers depending upon the monomer used for graft copolymerization (Thakur, Thakur, & Gupta, 2013a–f). A number of natural polymers have been modified for their use in different applications such as in metal ion-sorption, drug delivery, water purification studies and as reinforcement in green composites (Khoathane, Vorster, & Sadiku, 2008; Unlu, Oztekin, & Atici, 2012; Teli & Sheikh, 2012).

In the present communication, we report our studies on the graft copolymerization onto natural cellulosic fibers (*Grewia optiva*) using vinyl monomers for green composites applications. Different reaction parameters such as initiator, concentration of monomer, reaction time, temperature and solvent were evaluated, to get the optimum percentage of grafting. The natural cellulosic fibers based graft copolymers were characterized by different characterization techniques. The existing literature has revealed scanty information on the graft copolymerization of vinyl monomers onto surface modified natural cellulosic polymers (*Grewia optiva fibers*) and their application as reinforcement for green composites applications (Thakur et al., 2012a,c,d; Thakur et al., 2013a,e). *Grewia optiva* has been known as a multipurpose tree species in Himalayan region (Thakur et al., 2012a,c,d; Thakur et al., 2013a,e). It is a small to medium-sized deciduous tree that grows to 9–12 m in height with smooth, pale silvery–brown branches (Singha & Thakur, 2012). The bark of this plant has been generally found to be dark brown, thick and roughish. Scheme 1(a, b) shows the photographic images of the *Grewia optiva* plant and its fibers after extraction (Singha & Thakur, 2012). The fibers in this plant are located in the bast. It is used for a number of applications starting from fodder, fiber, nutritional, medicinal material etc., (Thakur et al., 2012a,c,d; Thakur et al., 2013a,e). Cellulosic fibers obtained from the *Grewia optiva* plant generally contain cellulose, hemicellulose and lignin in the ranges of (58–75%; 10–12%; 7–12%) respectively (Singha & Thakur, 2012). Recently we have reported some of our studies on graft copolymerization of *Grewia optiva fibers* using different techniques as well as on the preparation of green composites (Thakur et al., 2012a,c,d; Thakur et al., 2013a,e). This study is one step forward in the direction of altering the surface properties of these natural cellulosic polymers (*Grewia optiva fibers*) for potential green composites.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), sodium hydroxide (NaOH), acetone, potassium persulphate (KPS), phenol, and formaldehyde solution were used for the graft copolymerization of the *Grewia optiva fibers* and preparation of green composites. Cellulosic *Grewia optiva fibers* collected from local resources of Himalayan region were soaked in a detergent solution for one hour, followed by extensive washing with tap water until free from any detergent. After this, these fibers were mercerized as per standard method reported earlier to facilitate graft copolymerization (Thakur et al., 2012a; Thakur et al., 2013a,e). Both, the raw and grafted *Grewia optiva fibers* were converted into particle form of dimension 300 μ to be used as reinforcement in the composites.

2.2. Methods

2.2.1. Graft copolymerization

The graft copolymerization reaction was initiated by immersing the appropriate amount of *Grewia optiva fibers* in a definite amount of distilled water for 24 h. The polymerization reaction was subsequently preceded in a preheated water bath at the desired temperatures by the addition of certain amounts of initiator (KPS) and monomer (MMA). Different reaction parameters e.g. time, amount of solvent, temperature, initiator and monomer concentration were optimized by varying one parameter while keeping other constant to get the maximum percentage of grafting (Fig. 1).

The true percentage grafting (P_g) was calculated as per procedure reported earlier (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). When the grafting time was over, the homo-polymer formed during graft copolymerization was removed by extraction with acetone in a Soxhlet extraction apparatus for 50 h. The graft copolymers free from homopolymer were then allowed to dry in an air oven at 60 °C, until constant weight.

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

where W is the weight of raw *Grewia optiva fibers*W_g is the weight of grafted *Grewia optiva fibers*

2.2.2. Swelling and chemical resistance studies

Swelling, moisture absorbance and chemical resistance studies of grafted and raw *Grewia optiva fibers* were carried out as per methods reported somewhere else (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). The moisture absorbance behaviour of the raw and grafted cellulosic *Grewia optiva fibers* was studied using humidity chamber from Data Physics Instruments GmbH Germany. For swelling studies, requisite amounts of raw and grafted *Grewia optiva fibers* were immersed in different solvents such as water, methanol, dimethyl formamide; and isobutyl alcohol for 24 h. The percent swelling was calculated from the increase in initial weight in the following manner:

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

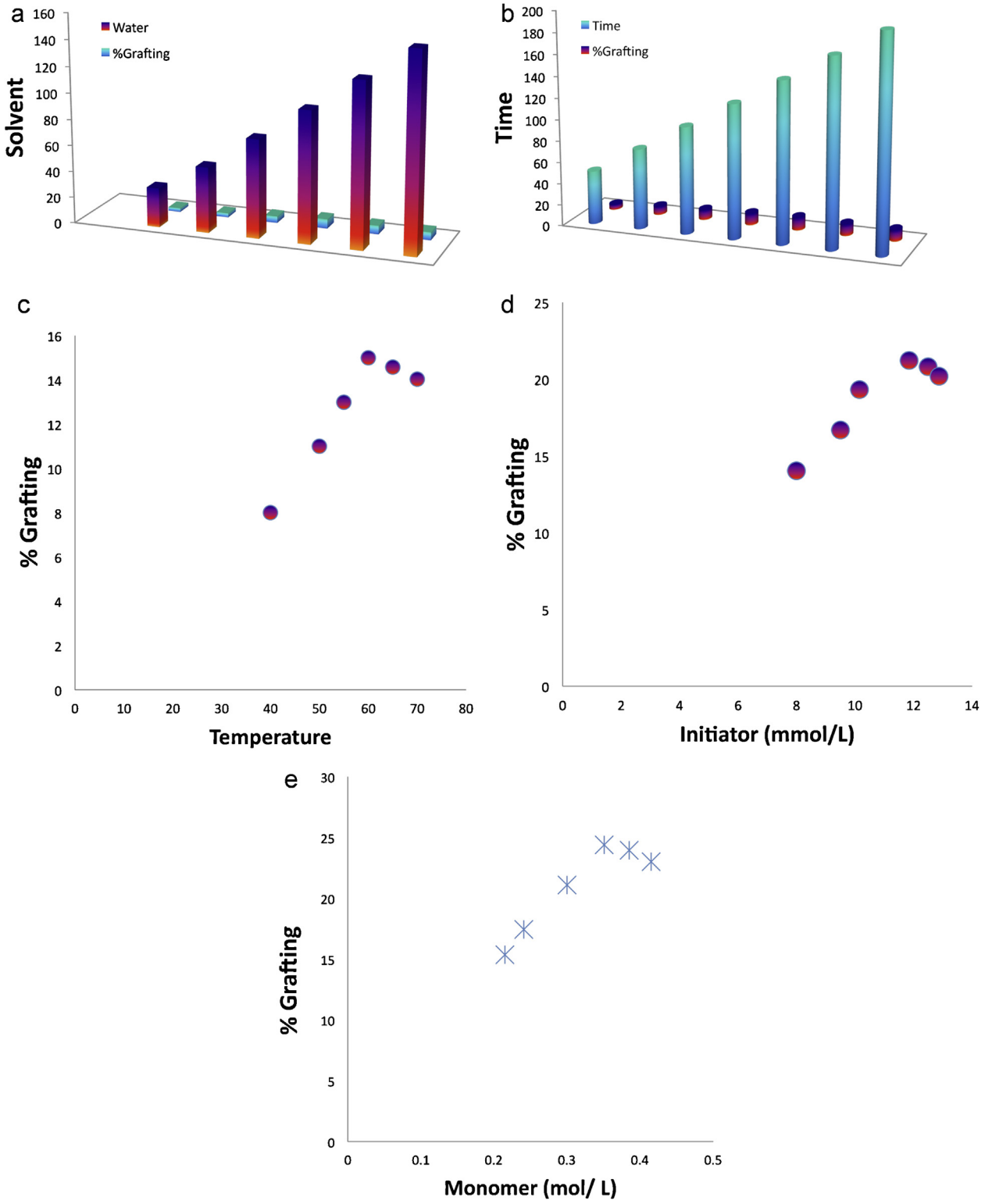


Fig. 1. (a) Optimization of solvent amount for graft copolymerization onto *cellulosic fibers*. (b) Optimization of reaction time for graft copolymerization onto *cellulosic fibers*. (c) Optimization of reaction temperature for graft copolymerization onto *cellulosic fibers*. (d) Optimization of initiator amount for graft copolymerization onto *cellulosic fibers*. (e) Optimization of monomer concentration for graft copolymerization onto *cellulosic fibers*.

The chemical resistance behavior of the raw and grafted *Grewia optiva fibers* was studied towards acid and base in terms of percentage weight loss in the following manner:

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

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

2.2.3. Preparation of green composites

Both grafted and ungrafted *Grewia optiva fibers* of dimension 300 μ were mixed thoroughly with *phenol-formaldehyde* resin using mechanical stirrer with suitable loading (5%) in terms of weight. Then above mixture of fibers/polymers were poured into specially made molds and composite sheets of size 150 × 150 × 5.0 mm were prepared by compression molding

technique (Thakur et al., 2012a). Tensile properties of the green composites were tested in accordance with ASTM D 3039, method.

2.2.4. Characterization of graft copolymerized cellulosic fibers

A PerkinElmer RXI spectrophotometer ranging from 400 to 4000 $cm^{-10}$was used to confirm the synthesis of graft copolymers *Grewia optiva*-g-poly-(MMA). The surface morphology of ungrafted and grafted *Grewia optiva fibers* was investigated using scanning electron microscopy machine. Thermogravimetry (TG) for the raw and grafted *Grewia optiva fibers* samples along with their composites was performed using a thermal analyzer (PerkinElmer) at a heating rate of 10 °C/min.

3. Results and discussion

The mechanism for vinyl monomers graft copolymerization onto cellulosic fibers using KPS as initiator has been recently reported (Thakur et al., 2012a,b,c; Thakur, Thakur & Gupta, 2013a–d). The effect of different parameters on percentage grafting has been depicted in Fig. 1. The effect of amount of water as the solvent on the percent grafting is represented in Fig. 1a. The results clearly reveal the increase in the percent grafting with increasing the solvent amount until 100 ml and then slightly decreases and levels off. This behaviour can be attributed to the various hydrogen abstraction reactions as well as due to decreased $SO_4^{-\bullet *}$ and $OH^{\bullet}$ free radical concentration (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). The effect of the reaction time on the percentage grafting onto *Grewia optiva fibers* is shown in Fig. 1b. The highest grafting percentage onto *Grewia optiva fibers* was 12.17% when the reaction period was 150 min. From the results, it is observed that the percentage of grafting increases with the increase of the reaction period from 75 to 150 min and then levels off. This behavior is attributed to the increase of the extent of initiation and propagation of the graft copolymerization with time and is in agreement with the observation reported earlier in the study of graft copolymerization of vinyl monomer onto cellulosic fibers (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). The decrease in percentage grafting beyond optimum reaction time is primarily attributed to the predominance of homopolymerization over graft copolymerization as well as due to disintegration of poly (MMA) chains grafted onto *Grewia optiva* back-bone. The graft copolymerization of MMA onto *Grewia optiva fibers* was carried out from 40 to 70 °C and the results are shown in Fig. 1c. It is obvious from the results that the % grafting was increased with increasing of reaction temperature from 30 to 60 °C and further increasing of reaction temperature led to a decrease in grafting which may be due to supplementary homopolymerization at high temperature and disintegration of graft copolymers and is reasonable for a free radical polymerization (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). Fig. 1d illustrates the effect of initiator (KPS) concentration on the percent grafting onto *Grewia optiva fibers*. It may be observed form the Fig. 1d that, the percentage of grafting increases with the initial increase in the concentration of the monomer, which could be the result of the increase in rate of grafting at optimum concentration of initiator and after optimum concentration, the grafting percentage decreases, which may result from the decay of the macroradicals by their reaction with the initiator and/or the increase of grafting rate at low initiator concentration (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). Fig. 1e represents the effect of monomer concentration on the percent grafting onto *Grewia optiva fibers*. These results clearly disclose the increase in the percentage grafting onto *Grewia optiva fibers* with increasing the monomer concentration while keeping other parameters constant. It was observed that, the degree of grafting increased as the monomer amount was increased in the grafting reaction, and may be a consequence of the increased grafting rate and gel effect and decreases at higher concentration of monomer as the primary radicals starts attacking the monomer instead of reacting with the *Grewia optiva* cellulose, thereby; initiating homopolymerization reaction and thus lowering the percentage grafting beyond optimum monomer concentration (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d).

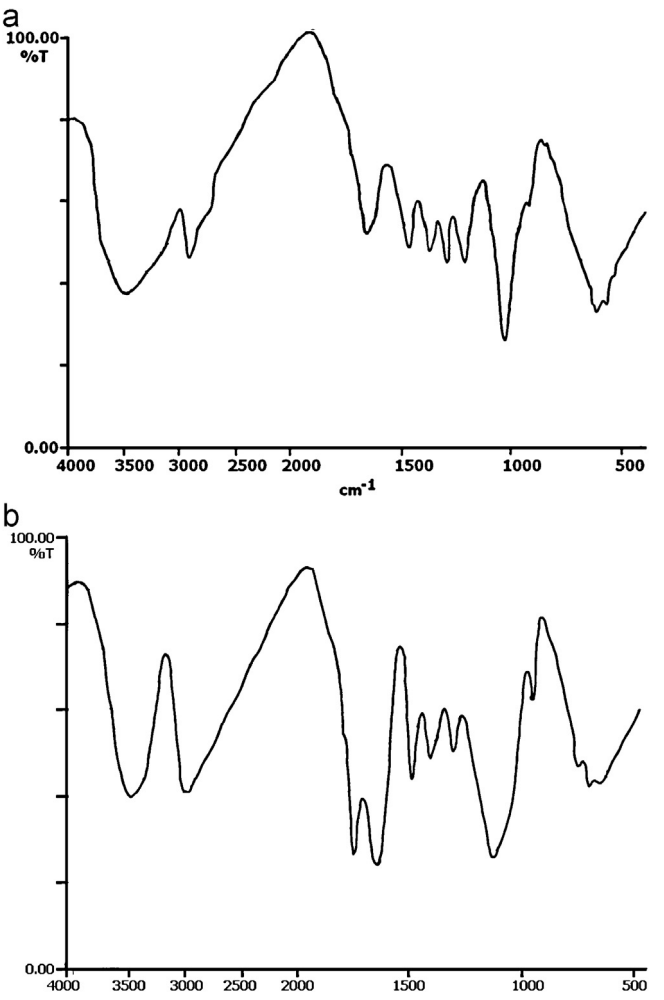


Fig. 2. (a) FTIR spectrum of raw *Grewia optiva fibers*. (b) FTIR spectrum of grafted *Grewia optiva fibers*.

3.1. Structural characterization of graft copolymerization onto natural polymers

The presence of the MMA onto the *Grewia optiva fibers* was determined by FT-IR spectroscopy, prior to and after graft copolymerization. Fig. 2(a–b) shows comparative spectrums of the raw *and* MMA grafted *Grewia optiva fibers*. Fig. 2(a) shows the parental peak of OH groups in the FTIR spectra at 3100–3500 cm^{-1} which is due to the bonded hydroxyl groups. The other peaks in the region 1350–1470 cm^{-1} and at 1734 cm^{-1} can be assigned to for the C–O ring of lignin and carboxylic groups of pectin and hemicellulose present in the raw cellulosic *Grewia optiva fibers*. Fig. 2(b) on the other hand, shows some new peaks with an additional peak with much higher intensity at 1732 cm^{-1} confirming the presence of the poly (MMA) chains grafting onto *Grewia optiva fibers*. Scanning electron microscopy was used to visualizing the surface of the *Grewia optiva fibers* prior to and after to graft copolymerization synthesis. Fig. 3(a–b) depicts the images of the raw and MMA grafted cellulosic fiber surface. Visual examination of these images shows

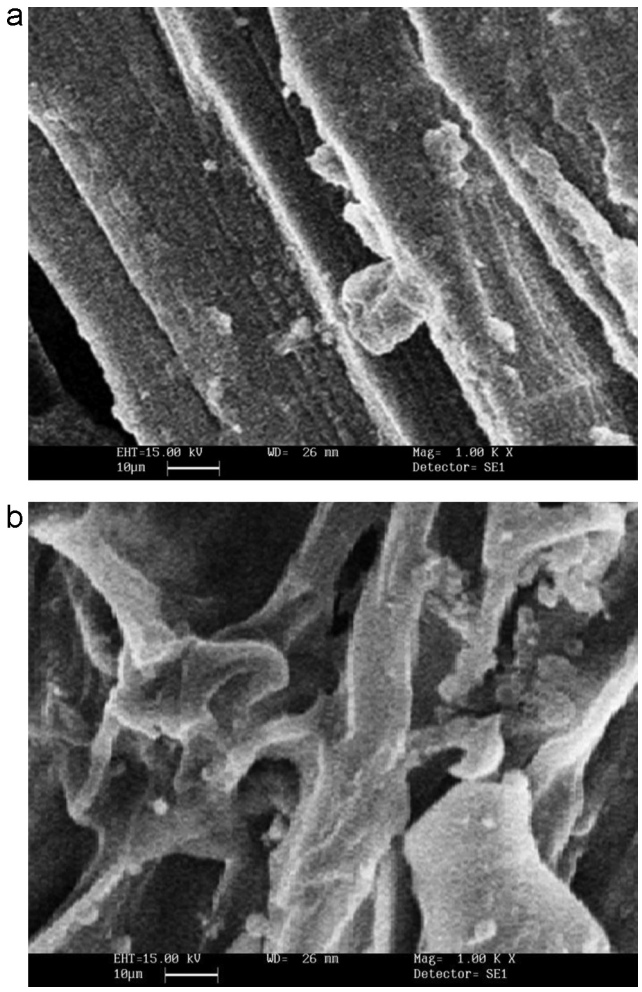


Fig. 3. (a) Scanning electron micrograph of raw *Grewia optiva fibers*. (b) Scanning electron micrograph of grafted *Grewia optiva fibers*.

the incorporation of MMA monomer onto the *Grewia optiva fiber* surface.

3.2. Physico-chemical characterization onto natural polymers

Physico-chemical characterization of the *Grewia optiva fibers* was carried by estimating the gravimetric percent swelling/moisture absorbance using the repeated water swelling method and gravimetric weight loss in chemical resistance studies (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). Fig. 4 shows the swelling behaviour of raw and grafted cellulosic *Grewia optiva* in different solvents. It has been observed that due to different affinity of the raw and grafted fibers towards different solvents, the trend of swelling of grafted *Grewia optiva* was opposite to that of the raw *Grewia optiva fibers*. The swelling behavior of raw cellulosic fibers follows the trend as $H_2O > CH_3OH >$ iso-BuOH > DMF while the surface grafted fibers follow the trend; DMF > $CH_3OH > H_2O >$ iso-BuOH due to incorporation of hydrophobic functional groups onto cellulosic backbone (Thakur et al., 2012a,b,c; Thakur et al., 2013a,b,c,d). Fig. 5 depicts the moisture absorption behaviour of the *Grewia optiva fibers* at different humidity levels under ambient laboratory conditions. The grafted fibers have been found to exhibit more moisture absorbance (M_{abs}) behavior with the increase in percentage grafting due to the attachment of poly (MMA) chains which are strongly adhered onto the *Grewia optiva fibers*. The chemical resistance behavior of the *Grewia optiva fibers* was studied in 1 N HCl acid and 1 N NaOH base by dipping

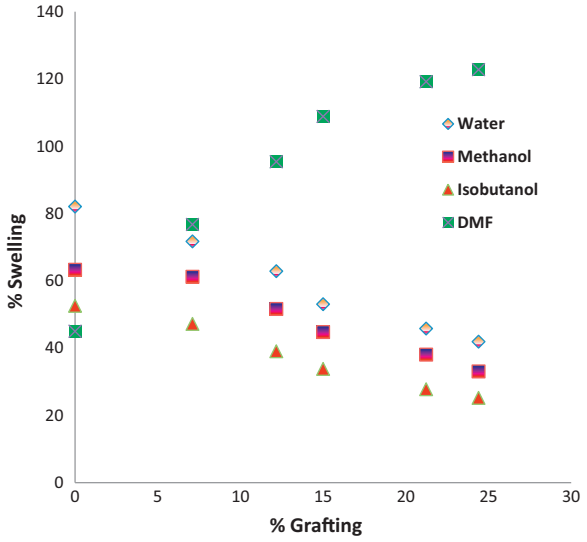


Fig. 4. Swelling behaviour of raw and grafted *Grewia optiva fibers* in different solvents.

the particular samples in the respective chemical reagents for definite time intervals. After proper drying, the samples were then weighed, and the percentage weight loss/gain were determined (Fig. 6a and b). The increased chemical resistance behavior of the grafted fibers is due to blockage of active sites vulnerable to the chemical attack by poly (MMA) on the *Grewia optiva* polymer backbone resulting in more resistance towards the chemicals.

3.3. Mechanical characterization of grafted/ungrafted fibers reinforced composites

For the preparation of green composites, *phenol -formaldehyde* polymer resin was used as the matrix, and synthesized by the condensation of phenol with formaldehyde contains hydroxyl groups as per standard method (Thakur et al., 2012a). Subsequently, green composites were prepared using both the grafted/ungrafted fibers as reinforcement in particle form, and evaluated for their tensile strength properties. It is evident from Fig. 7 that green composites reinforced with natural grafted *Grewia optiva fibers*, showed

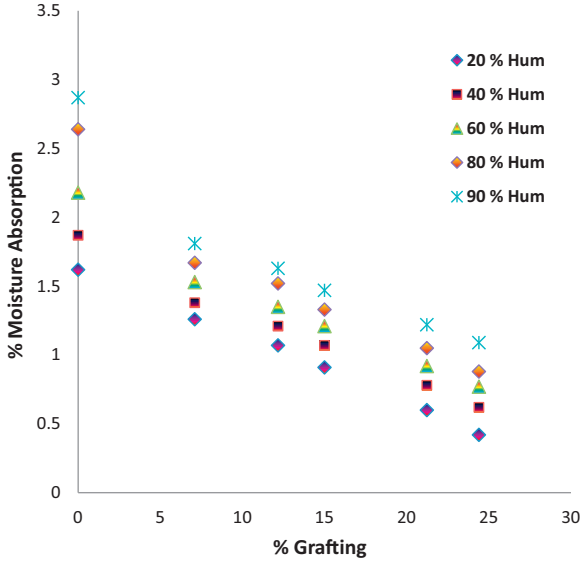


Fig. 5. Moisture absorbance behaviour of raw and grafted *Grewia optiva fibers* at different humidity levels.

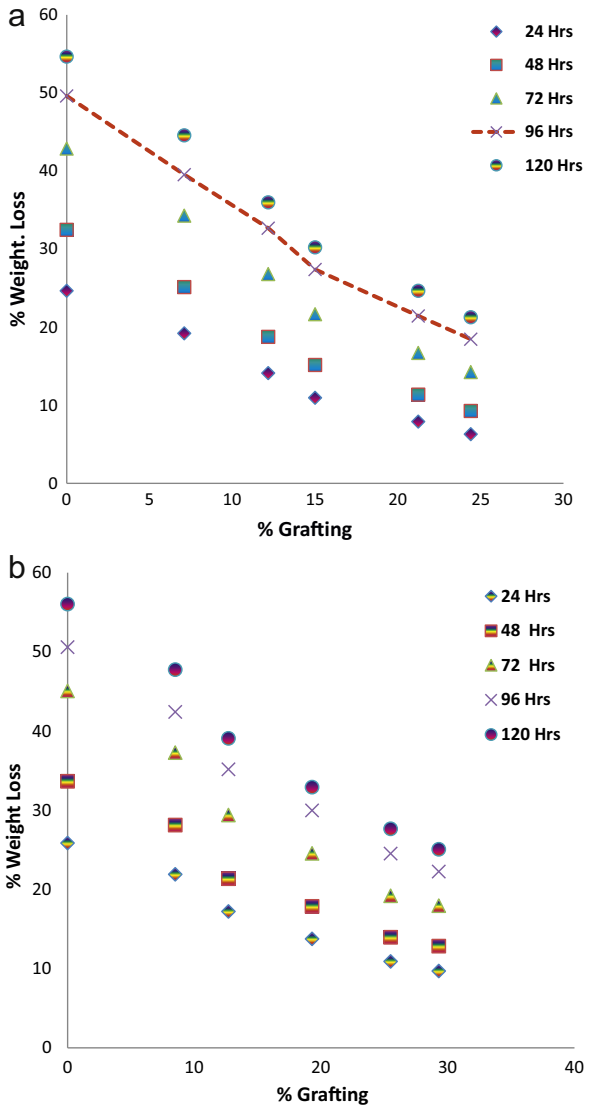


Fig. 6. A: Acid resistance behavior of raw and grafted *Grewia optiva fibers in* 1 N HCl at different time intervals. B: Base resistance behaviour of raw and grafted *Grewia optiva fibers in* 1 N NaOH at different time intervals.

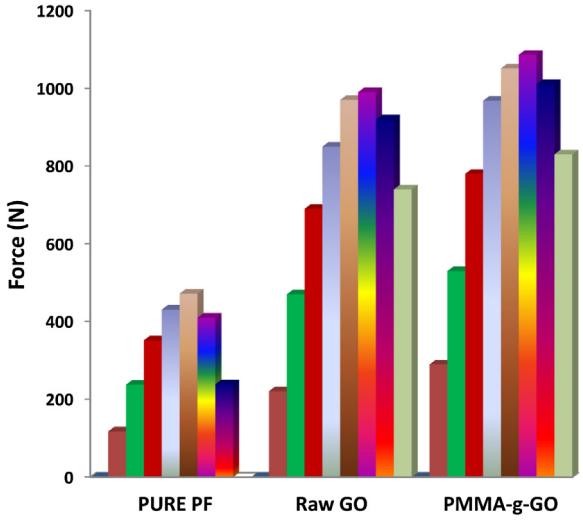


Fig. 7. Tensile strength of raw and grafted *Grewia optiva* particle fibers reinforced composites.

better tensile strength in comparison to parent polymer matrix as well as raw fibers reinforced composites. In polymer composites, to achieve good fiber reinforcement, interfacial strength between the reinforcement and the matrix play a significant role (Thakur et al., 2012a; Mansor et al., 2013; Sahari et al., 2013). The fibers and matrix must interact in a comprehensive manner to be an effective load bearing system. The increase in tensile strength of grafted fiber reinforced composites as compared to raw *Grewia optiva fibers* can be attributed to fact that graft copolymerization, improves the adhesive characteristics of *Grewia optiva* surface by removing natural and artificial impurities, thus producing a rough surface topography that results in enhanced fiber aspect ratio offering a better fiber/matrix interface (Thakur et al., 2012a). Better interaction between the grafted fibers and polymer matrix, thus increases the tensile strength due to enhanced load transfer between matrix and fiber interface.

4. Concluding remarks

Present research work demonstrates that it is possible to perform potassium persulphate initiated grafting of methyl methacrylate onto the cellulosic *Grewia optiva fibers* in aqueous medium. The surface morphology of the cellulosic *Grewia optiva fibers* was examined using SEM and provided clear evidences for surface modifications. The results of the FTIR analysis also confirmed the incorporation of MMA monomer onto the structure of *Grewia optiva fibers*. Furthermore, the green composites prepared using the grafted *Grewia optiva fibers*, show enhanced tensile strength properties demonstrating the potential industrial applications of these fibers.

Acknowledgement

Authors wish to thanks their parental institutes for providing the necessary facilities to accomplish the present research work.

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