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Graft copolymers from cellulose: Synthesis, characterization and evaluation

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ABSTRACT

Cellulose, a linear polysaccharide polymer with numerous glucose monosaccharide units is of enormous interest because of its applications in biosorption, biomedical, packaging, biofiltration and biocomposites. In this study, cellulose-graft-poly(butyl acrylate) copolymers were synthesized under microwave conditions. Effects of microwave radiation doses and different reaction parameters were optimized to get the optimum percentage of grafting. The dependence of optimum conditions for better physico-chemical properties of the cellulosic polymers was also determined. Fourier transform infrared spectroscopy (FT-IR) analysis was used to authenticate the chemical reaction taking place between cellulosic polymers and monomer. The thermogravimetric behavior of the raw and grafted cellulosic polymers was characterized by thermogravimetric analysis (TGA). The surface structure of the raw and grafted cellulosic polymers was analyzed through scanning electron microscopy (SEM). The graft copolymers have been found to be more moisture resistant and also showed better chemical and thermal resistance.

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1. Introduction

The economy of depleting petroleum resources coupled with increasing environmental have ignited the interest in the use of renewable cellulosic polymers from different resources for making new materials (Nazi, Malek, & Kotek, 2012; Qiu, Ren, & Hu, 2012). Natural cellulosic polymers such as lignocellulosic natural fibers offer well-known advantages as compared to the traditional synthetic materials which include eco-friendliness, toxicologically harmless, biodegradability, carbon dioxide (CO_2) neutral, easy availability, enhanced energy recovery, non corrosive nature and usually lower cost (Singha & Thakur, 2010a). These cellulosic natural polymers are also characterized by a huge degree of variability and diversity in their properties depending upon the place of their origin (Thakur & Singha, 2011a). During the last few years a great deal of interest has been dedicated to the natural cellulosic polymers based materials as the unique properties exhibited by natural polymers are never offered by non cellulosic polymers. Naturally derived cellulosic polymers are usually eco-friendly, and therefore materials prepared using these polymers such as composites reinforced with natural fibers should also be eco-friendly (Liu, Wu, & Zhang, 2009; Singha & Thakur, 2010a). Polymer composite materials containing cellulosic polymers exhibit enhanced properties and are less expensive than the starting polymer in overall material costs (Singha & Thakur, 2010b; Thakur & Singha, 2011b). Novel green materials based upon natural cellulosic polymers have been the subject of intense international research since last two decades and a number of practical applications are now emerging in various fields, including packaging, biomedical, bioenergy, bioplastics, and in aerospace industry(Akar, Altinisik, & Seki, 2012; Alila, Ferraria, do Rego, & Boufi, 2009; Bao, Ma, & Sun, 2012). Commercial interest in manufacturing different products using cellulosic polymers is driven by the derivation of these polymers from environmental friendly renewable sources as well as by their specific properties including biodegradability (Cheema, El-Shafei, & Hauser, 2013; Wu, 2012). However the natural cellulosic polymers are inferior to harsh environmental conditions due to hydrophilic natural of the cellulose and need to be modified for superior applications (Thakur, Singha, & Thakur, 2012a).

Among various natural cellulosic polymers, only few studies have been reported on the *cellulosic pine needles* based materials (Singha & Thakur, 2009; Thakur & Singha, 2011a). These needles are obtained from *Pinus* which is one of the most popular trees in almost all around the globe and is a rich source of cellulose in the form of *pine needles*. These needles are automatically shed off by the trees during whole year especially in summer and are one of the major reasons for destruction of different kinds of flora and fauna. In order to increase the physico-chemical properties of

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these needles for different potential applications we are working in the modification of the properties of these cellulosic polymers by graft copolymerization. Various modification techniques have been reported to improve the physico-chemical properties of natural polymers (Eissa, Khosravi, & Cimecioglu, 2012; Zhong, Chai, & Fu, 2012), and among these graft copolymerization have received much more attention during the last few decades (Abdel-Halim, 2012a; Mwaikambo & Ansell, 2002; Sand, Yadav, & Behari, 2010). It is one of the most facile methods to incorporate desired functional groups on to natural polymers depending upon the targeted application (Abdel-Halim, 2012b; Abdel-Halim & Al-Deyab, 2012; Oza, Meena, & Siddhanta, 2012; Unlu, Oztekin, & Atici, 2012). Surface modification of cellulosic polymers by graft copolymerization of vinyl monomer increases their functional properties, thus making them suitable for a number of applications (Ofomaja, Ngema, & Naidoo, 2012; Teli & Sheikh, 2012; Thakur, Singha, & Thakur, 2012b, 2012c). Our most recent work has explored the possibility of modifying the surface properties of a number of cellulosic polymers and their possible use as potential reinforcement in green composites (Thakur et al., 2012b). As a continuation, the present work describes an investigation of the effect of microwave radiation on the graft copolymerization of butyl acrylate onto *cellulosic pine needles*.

2. Experimental

2.1. Materials

Cellulosic pine needles were collected from local resources of Himalayan region. Reagent grade chemicals namely, butyl acrylate (BA), ferrous ammonium sulphate (FAS), potassium per sulphate (KPS), sodium hydroxide (NaOH) and tetrahydrofuran were kindly supplied by Qualigens Chemicals Ltd. Company. Purification of *cellulosic pine needles*, grafting reactions, and separation of homopolymer from the grafted *cellulosic pine needles* were carried out according to the standard procedure reported in literature (Singha & Thakur, 2009; Thakur, Singha, & Misra, 2011). The chemicals used were purified where necessary.

2.2. Graft copolymerization onto cellulosic pine needles

Prior to graft copolymerization synthesis, chemical modification of the *cellulosic pine needles* was done through mercerization of these cellulosic needles as per standard method reported in our earlier studies (Singha & Thakur, 2009; Thakur et al., 2012a). Graft copolymerization synthesis was carried out by immersing *mercerized cellulosic pine needles* in a specific amount of distilled water for 24 h followed by addition of known amount of initiator (FAS–KPS) with continuing stirring for 5–10 min in order to create sufficient free radical sites on the surface of the cellulosic fibers. Then to start the copolymerization, monomer (BA) was added into the reaction flask containing the mercerized cellulosic biofibers in the microwave oven. The reaction mixture was stirred at selected doses for different time intervals to optimize different conditions of solvent, time, initiator and monomer concentration for maximum percentage of grafting (Kamel, 2012; Mishra, Rani, & Sen, 2012; Thakur & Singha, 2011b). After the completion of the reaction, the sample was filtered, washed with distilled water several times and then air-dried. The dried *cellulosic pine needles* were extracted with tetrahydrofuran in a Soxhlet extraction apparatus for 50 h to remove the homo-polymer formed during graft copolymerization. After extraction, the samples were washed with distilled water to remove impurities. The graft copolymers freed from homopolymer was then dried in a hot air oven to a constant weight.

2.3. Determination of percentage of grafting

The percentage grafting (P_g) was calculated as per the standard method in the following manner (Thakur et al., 2012a):

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

where W is the weight of raw cellulosic polymer, W_g is the weight of grafted cellulosic polymer.Characterization of poly(BA)-g-*cellulosic pine needles*

2.3.1. Infra red spectroscopy (IR)

The changes in the chemical structure of the *cellulosic pine needles* as a result of graft copolymerisation synthesis with BA monomer was characterized using Fourier transform infra red spectroscopy (FTIR) with the help of KBr pellets on Perkin Elmer RXI Spectrophotometer in order to confirm the synthesis of graft copolymers *cellulosic pine needles*-g-poly-(BA). The spectrum was recorded in the range of 400–4000 cm^{-1}.

2.3.2. Scanning electron microscopy (SEM)

The surface morphology of raw and grafted *cellulosic pine needles* was observed by using scanning electron microscopy machine (LEO 435 VP). All the samples were gold coated before observation.

2.3.3. Thermal analysis

Thermo gravimetric analyses (TGA) of the raw and grafted *cellulosic pine needles* were carried out in nitrogen atmosphere on a thermal analyzer (Perkin Elmer) at a heating rate of 10 °C/min. The sample weights of raw and grafted *cellulosic pine needles* for TGA studies were 10 mg each.

2.4. Physico-chemical characterization of raw and grafted cellulosic pine needles

2.4.1. Swelling behavior

Swelling studies of the raw and grafted *cellulosic pine needles* were carried out as per standard method in different solvents such as dimethyl formamide, water, methanol and isobutyl alcohol. The percent swelling was calculated from the increase in initial weight in the following manner (Thakur et al., 2012a):

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

2.4.2. Moisture absorbance behavior

The study of the moisture absorbance behavior of the raw and grafted *cellulosic pine needles* was made in a humidity chamber. Known weights of dry grafted and raw *cellulosic pine needles* were placed in the humidity chamber for particular time interval under different humidity levels ranging from 20% to 90%. Final weights of the samples exposed to different humidity levels were then noted. The percent moisture absorbance ($\%M_{abs}$) was calculated from the increase in initial weight in the following manner (Thakur et al., 2012a):

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

where W_f is the weight of grafted *cellulosic pine needles*; W_i is the weight of raw *cellulosic pine needles*.Chemical resistance behavior

The chemical resistance behavior of the raw and grafted *cellulosic pine needles* was studied in acid and base environments. Acid and base resistance was found out by placing a known weight (T_w) of *cellulosic pine needles* in 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 *cellulosic*

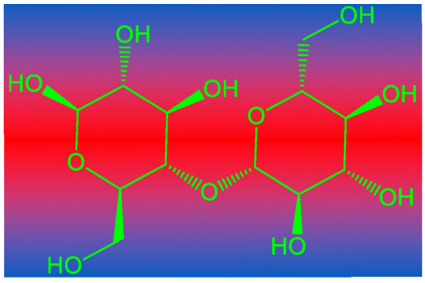
pine needles toward acid and base in terms of percentage weight loss was studied as in the following manner:

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

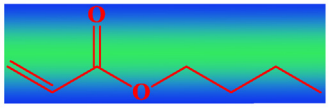
where T_w is the total weight and W_{aci} is the weight after certain interval.Results and discussion

2.5. Mechanism

Natural *cellulosic pine needles* consist of linear glucan chains with repeating $(1 \rightarrow 4)$ β-glucopyranose units. The presence of the reactive hydroxyl groups on each unit of cellulose *pine needles* makes it susceptible to get modified through free radical graft copolymerization (Scheme 1a). In *cellulosic pine needles* containing cellulose as the prime constituents; C_2, C_3 and C_6 —OH groups and C—H sites are the active centers for grafting of BA chains (Scheme 1b) onto cellulosic backbone. During the graft copolymerization synthesis, under microwave conditions, the radical formation for the initiation reaction can occur either on the cellulosic backbone or on the monomer to be grafted (Kamel, 2012; Mishra et al., 2012; Thakur & Singha, 2011b). Along with copolymerization synthesis, homopolymerization and various other side reactions also take place. KPS is known to take part in a redox reaction with Fe^{2+} through the



(a) Structure of *Cellobiose (Repeating unit of the Pine needles cellulose polymer)*



(b) Structure of *Butyl acrylate monomer*

Scheme 1. (a) Structure of Cellobiose (repeating unit of the Pine needles cellulose polymer). (b) Structure of *Butyl acrylate monomer*.

Initiation Reaction

$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \rightarrow 2SO_4^{-\bullet}$ (1)

$2SO_4^{-\bullet} + H_2O \rightarrow HSO_4^{-} + {}^{\bullet}OH$ (2)

$\text{Cell-OH} + SO_4^{-\bullet} \rightarrow \text{Cell-O}^{\bullet} + HSO_4^{-}$ (3)

$\text{Cell-OH} + {}^{\bullet}OH \rightarrow \text{Cell-O}^{\bullet} + H_2O$ (4)

$M + {}^{\bullet}OH \rightarrow {}^{\bullet}\text{M-OH}$ (5)

$M + SO_4^{-\bullet} \rightarrow {}^{\bullet}\text{M-}SO_4^{-}$ (6)

Propagation Reaction

$\text{Cell-OH} + {}^{\bullet}\text{M-OH} \rightarrow \text{Cell-O-M}^{\bullet} + H_2O$ (7)

$\text{Cell-O-M}^{\bullet} + nM \rightarrow \text{Cell-O-(M)}_n\text{-M}^{\bullet}$ (8)

$\text{Cell-O}^{\bullet} + nM \rightarrow \text{Cell-O-(M)}_{n-1}\text{M}^{\bullet}$ (9)

${}^{\bullet}\text{M-OH} + nM \rightarrow \text{HO-(M)}_n\text{-M}^{\bullet}$ (10)

Termination Reaction

$\text{Cell-O-(M)}_n\text{-M}^{\bullet} + \text{M}^{\bullet}\text{-(M)}_n\text{-O-Cell} \rightarrow \text{Cell-O-(M)}_n\text{-M}_2\text{-(M)}_n\text{-O-Cell}$ (Graft copolymer) (11)

$\text{Cell-O-(M)}_{n-1}\text{-M}^{\bullet} + \text{M}^{\bullet}\text{-(M)}_{n-1}\text{-O-Cell} \rightarrow \text{Cell-O-(M)}_{n-1}\text{-M}_2\text{-(M)}_{n-1}\text{-O-Cell}$ (Graft copolymer) (12)

$\text{Cell-O-(M)}_n\text{-M}^{\bullet} + {}^{\bullet}OH \rightarrow \text{Cell-O-(M)}_{n+1}\text{-OH}$ (13)

$\text{HO-(M)}_n\text{-M}^{\bullet} + {}^{\bullet}\text{M-(M)}_n\text{-OH} \rightarrow \text{HO-(M)}_n\text{-M}_2\text{-(M)}_n\text{-OH}$ (Homopolymer) (14)

$M^{\bullet}$ =Monomer free radical Cell-$O^{\bullet}$ =Pine needle Cellulose free radical

Scheme 2. Mechanism for graft copolymerization of butyl acrylate onto *cellulosic pine needles*.

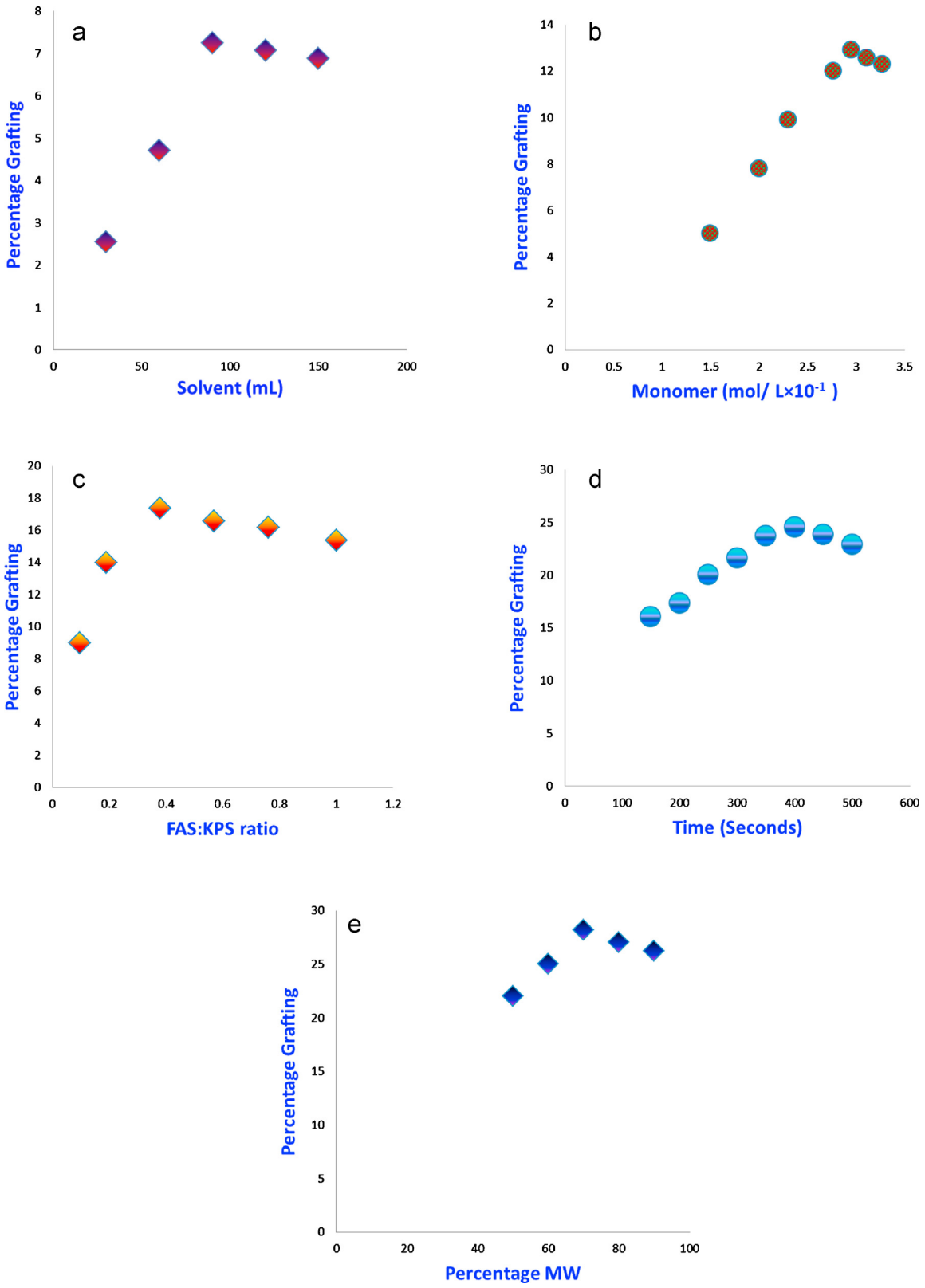


Fig. 1. (a) Optimization of solvent amount for graft copolymerization of butyl acrylate onto *cellulosic pine needles*. (b) Optimization of monomer for graft copolymerization of butyl acrylate onto *cellulosic pine needles*. (c) Optimization of initiator ratio for graft copolymerization of butyl acrylate onto *cellulosic pine needles*. (d) Optimization of reaction time for graft copolymerization of butyl acrylate onto *cellulosic pine needles*. (e) Optimization of microwave power for graft copolymerization of butyl acrylate onto *cellulosic pine needles*.

reaction shown in (Scheme 2). In the presence of BA 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 pine needles* backbone with the creation of a free radical on to the monomer, that is, a chain is initiated. Subsequent addition of BA monomer molecules to the initiated chain propagates grafting onto the cellulosic backbone (Thakur et al., 2012a).

2.6. Optimization of different reaction parameters for grafting onto cellulosic pine needles

The various reaction parameters that have been optimized to get the maximum graft yield are monomer concentration, initiator, reaction temperature, reaction time, solvent etc. Fig. 1a–e shows different values of percentage grafting during optimization of the reaction parameters. The optimum conditions for maximum percentage of grafting (28.18%) as depicted in figure one was: solvent – 90 mL; monomer – (2.95×10^{-1} mol/L), time – 400 s; FAS:KPS – 1:0.390 mmol/L and microwave power = 70%.

2.6.1. Effect of amounts of water as solvent

To study the effect of amount of water during grafting of BA, graft copolymerization has been carried out as a function of amount of water and the results are presented in Fig. 1a. It has been observed that percentage of grafting of BA shows an initial jump in percentage of grafting with increasing amount of water, from 50 mL to 150 mL giving maximum grafting in 90 mL and then decreases sharply on further increase in the amount of water and becomes almost constant (Thakur et al., 2012a).

2.6.2. Effect of monomer concentration

The effect of the addition of BA amount on the grafting parameters is shown in Fig. 1a. It is quite clear that the graft yield increases with the initial increase in monomer concentration reaches the optimum value and then slightly decreases with further increase in the monomer concentration (Fig. 1b). The above behavior may be explained on the basis that initially more and more radicals reach onto the backbone, resulting in the increase in grafting. However, with further increase in the monomer concentration, homopolymerization dominates over graft copolymerization, leading to decreased graft yield. Enhancement in the grafting percentage can be explained by the higher availability of the BA monomer molecules around the *cellulosic pine needles* macroradicals which is a perquisite for graft initiation and propagation. As we know that fiber macroradicals are relatively immobile, and so for grafting to occur, the monomer molecule needs to be in close proximity to those fibers macroradicals. So the enhancement in the grafting percentage can be attributed to the formation of long chains (Thakur et al., 2012a).

2.6.3. Effect of initiator

The variation on the grafting parameters with FAS:KPS initiator concentration is shown in the Fig. 1c. The results demonstrate increase in grafting with increase in the initiator concentration. The optimum molar ratio for the maximum graft yield was found to be 1:0.390. It has been observed that with further increase in molar ratio, grafting was found to decrease. This is probably due to formation of more Fe^{3+} ions at higher molar ratio, which results in the termination of growing chains (Thakur et al., 2012a). These results of increase in enhancements in the degree of grafting signify the necessity of certain amount of initiator as the initiator produces fiber macroradicals which are capable of initiating grating.

2.6.4. Effect of reaction time

The optimum reaction time of the graft copolymerization synthesis reaction has been found to be 400 s (Fig. 1d). With the initial

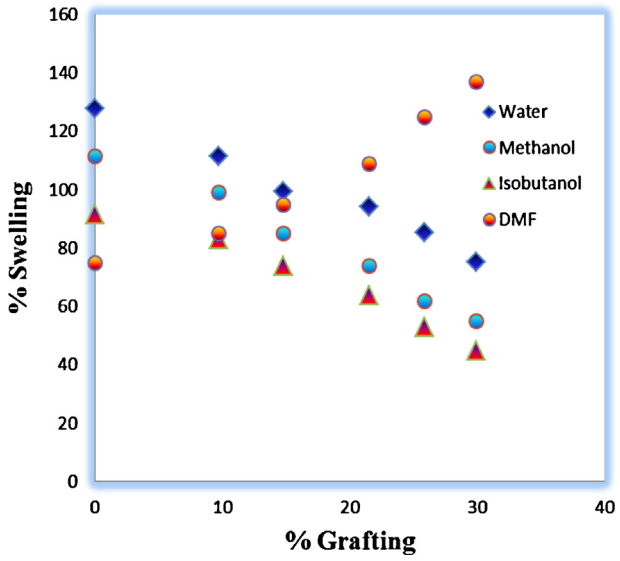


Fig. 2. Swelling behavior of raw and grafted *cellulosic pine needles* in different solvents.

increase in time grafting increases, reaches an optimum value at 400 s, and decreases with further increase in reaction time. This variation of percent graft yield with time can be explained on the basis that as the reaction time increases, more and more radicals move onto the backbone, resulting in the increased graft yield. After reaching the optimal value with further increase in reaction time, most of the active sites on the backbone are occupied by the radicals and the formation of the homopolymer dominates the graft copolymerization.

2.6.5. Effect of microwave power on grafting

The graft copolymerization of BA monomer onto the *cellulosic pine needles* was carried out at different microwave powers (Fig. 1e). Grafting was found to increase with increase in microwave power up to 70%, and further increase in microwave power resulted in decreased grafting. This behavior could be explained by an increase in the grafting percentage as power is increased, thus generating more macro radicals. Furthermore at optimum power there might

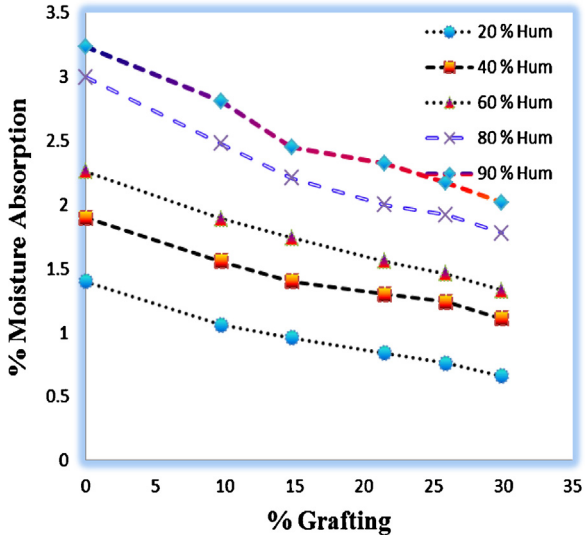


Fig. 3. Moisture absorbance behavior of raw and grafted *cellulosic pine needles* at different humidity levels.

be better decomposition of the redox system giving rise to more free radicals and enhancement in the mobility of the monomer molecule and their collision with the cellulosic *Pine needle* macro-radicals (Kamel, 2012; Mishra et al., 2012; Thakur & Singha, 2011b). 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%.

2.7. Analysis of physico-chemical properties of grafted cellulosic pine needles

2.7.1. Swelling behavior of raw and grafted cellulosic pine needles

Raw and poly BA grafted *cellulosic pine needles* have been found to exhibit different swelling behavior in different solvents (Fig. 2). The swelling behavior of raw *cellulosic pine needles* in different solvents follows the trend as $H_2O > CH_3OH >$ iso-BuOH > DMF. This behavior can be attributed to the fact that the raw *cellulosic pine needles* possesses hydrophilic —OH groups at C_2, C_3 and C_6 of the glucose unit and these have greater affinity with water. In case of grafted fibers, 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 BA chains which cause change in the sorption of the different solvents.

2.7.2. Moisture absorbance behavior of raw and grafted cellulosic pine needles

The moisture absorbance behavior at different humidity levels as a function of P_g has been depicted (Fig. 3). The raw *cellulosic pine needles* show more M_{abs} as compared to grafted fibers and this behavior of grafted fibers may be due to attachment of poly BA chains grafted onto the *cellulosic pine needles* which shows lesser affinity toward water.

2.7.3. Chemical resistance behavior of raw and grafted cellulosic pine needles

The chemical resistance of the raw and the grafted *cellulosic pine needles* has been studied in terms of percent weight loss in 1 N HCl and 1 N NaOH respectively. It has been observed that resistance toward chemicals increase with the increase in %grafting (Fig. 4a and b). This may be due to blockage of active sites vulnerable to the chemical attack by poly(BA) on the polymeric backbone resulting in more resistance toward the chemicals.

2.8. Analysis and characterization of raw and grafted cellulosic pine needles

2.8.1. Characterization by FT-IR spectroscopy

The FT-IR spectrums of raw and grafted *cellulosic pine needles* were recorded with help of *KBr* pellets on the spectrophotometer

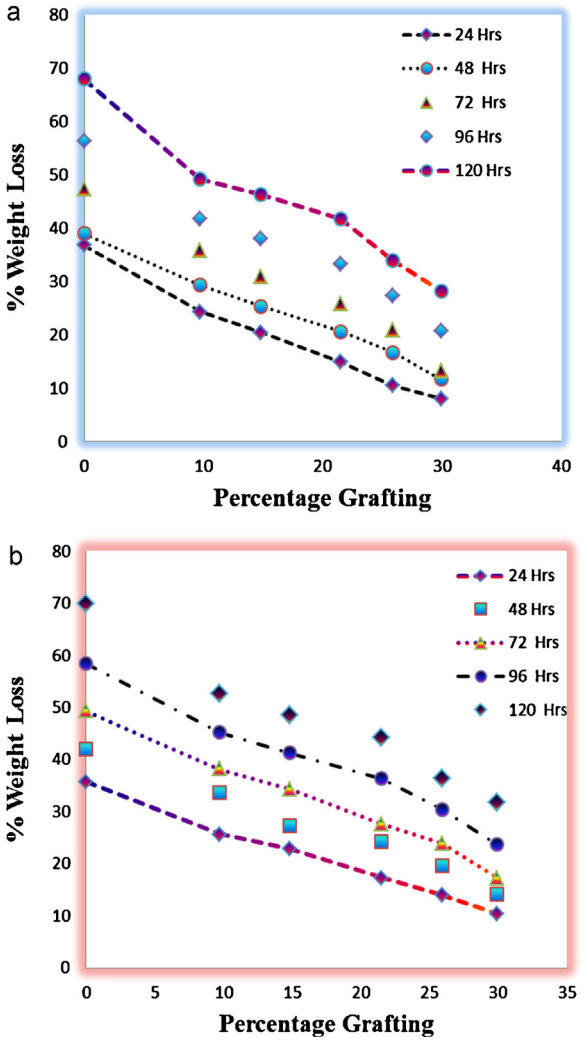


Fig. 4. (a) Acid resistance behavior of raw and MMA grafted *cellulosic pine needles* in 1 N HCl at different time intervals. (b) Base resistance behavior of raw and grafted *cellulosic pine needles* in 1 N NaOH at different time intervals.

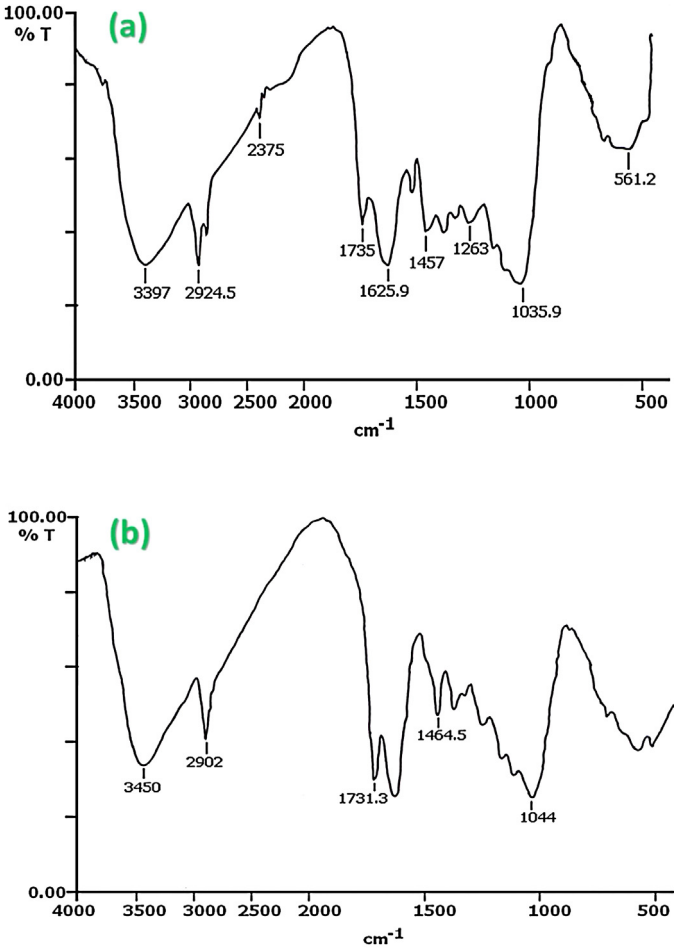


Fig. 5. (a) FTIR spectrum of raw *cellulosic pine needles*. (b) FTIR spectrums of grafted *cellulosic pine needles*.

Table 1
Thermo-gravimetric analysis (TGA) of raw and grafted *cellulosic pine needles*.

Sr. No.	Sample	IDT (°C)	% wt. loss	FDT (°C)	% wt. loss	Final residue (%)
1	*Cellulosic pine needles*	214	20.57	503	81	19
2	Grafted *cellulosic pine needles*	221	22.25	511	77	33

(Fig. 5a and b). In Fig. 5a the a broad peak at 3397 cm^{-1} is due to bonded OH groups and the bands located in the region 1240–1270 cm^{-1} and at 1737 cm^{-1} can be assigned to for the C—O ring of lignin and carboxylic groups of pectin and hemicellulose present in the plain *cellulosic pine needles*. Weaker peaks also occurred at 1372–1457 cm^{-1} due to C—H, —CH_2 and CH_3 bending. The BA grafted *cellulosic pine needles* (Fig. 5b) on the other hand showed additional characteristics absorption band at 1731.3 cm^{-1} along with the reduction in the intensity of the some of the basic peaks of cellulose confirming the successful grafting of poly(BA) into *cellulosic pine needles*.

2.8.2. Characterization by scanning electron microscopy

Surface topography of the raw and grafted *cellulosic pine needles* was studied using scanning electron microscopy and the results are shown in the Fig. 6a and b. The comparison of the micrographs clearly shows that the surface morphology of the *cellulosic pine needles* changes upon grafting fibers (Fig. 6b) indicating that a considerable amount of poly BA has been grafted onto *cellulosic pine needles* (Thakur & Singha, 2011b).

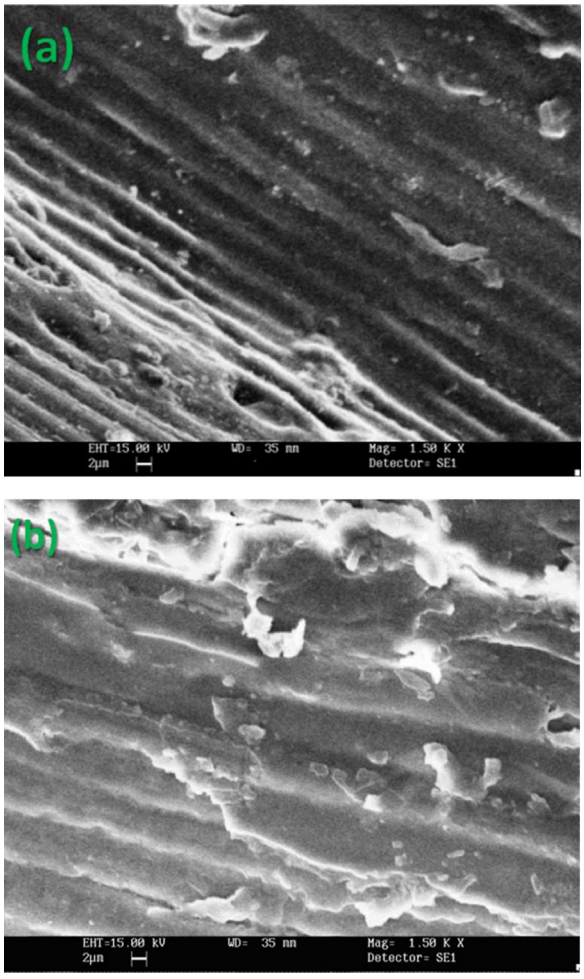


Fig. 6. Scanning electron micrographs of (a and b) raw and grafted *cellulosic pine needles*.

2.8.3. Characterization by thermal analysis

Thermal stability of raw and grafted *cellulosic pine needles* was studied as a function of percent weight residue with increase in temperature. During thermal analysis initially the samples get degraded by dehydration, glycogen formation and depolymerization (Thakur & Singha, 2011b). The thermal degradation behavior of the *cellulosic pine needles* depends upon the chemical composition and structure. In case of raw *cellulosic pine needles*, the initial decomposition (IDT) temperature has been found to be 214 °C with a percent weight loss of 20.57% and the final decomposition temperature (FDT) to be 503 °C with a percent weight loss of 81% (Table 1). However in case of the butyl acrylate grafted *cellulosic pine needles*, the grafted fibers shows enhanced thermal stability with an initial decomposition temperature (IDT) of 221 °C with percentage weight loss of 22.25% and the final decomposition temperature of 511 °C with percentage weight loss of 77% (Table 1). From above discussion it is clear that graft copolymerization affects the properties of *cellulosic pine needles* to a significant extent.

3. Conclusions

The recent trends in developing new green eco-friendly materials from natural resources is driven not only by environmental concern and demand for sources alternative to petroleum, but also to the advancements happening in the field of science and technology. The present research work appraised the possibility of obtaining new functional cellulosic polymers from *cellulosic pine needles* which are considered as waste bio materials. The present research work explores that:

- Graft copolymerization of BA onto *cellulosic pine needles* can be successfully accomplished using microwave radiation in the presence of FAS–KPS as redox initiator system.
- The presences of poly BA chains onto the grafted *cellulosic pine needles* were indicated by FTIR spectroscopy, SEM and thermal studies.
- The grafted *cellulosic pine needles* exhibit promising enhanced thermal and physico-chemical properties, making them potential cellulosic functional polymers for different applications such as in packaging and bioplastics industries.

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