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Optimization of reaction conditions for grafting of α-cellulose isolated from *Lantana camara* with acrylamide

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ABSTRACT

Lantana camara, a noxious weed is a serious threat to the ecosystems and demands concerted efforts for its management. Though a number of approaches have been adopted for effective management of *L. camara*, however each approach has inbuilt limitation and satisfactory approach is yet to be seen. Utilisation of abundantly available cellulosic biomass derived from *Lantana* could be a practical proposition for the management of the weed. Therefore, chemical analysis of the raw material was done to isolate α-cellulose followed by its characterization. Graft copolymerization of acrylamide onto α-cellulose was studied with ceric ammonium nitrate as a redox initiator in an aqueous medium. The reaction conditions were optimized by varying concentration of ceric ammonium nitrate, nitric acid, acrylamide, time and temperature. The products were characterized by IR, SEM and thermal analysis. Grafting of acrylamide chains onto the α-cellulose enhances its thermal stability. A reaction mechanism is also proposed.

1. Introduction

Biopolymers, being renewable raw materials, are gaining considerable importance because of the limited existing quantities of fossil supplies and the recent environment-conservative regulations. Cellulose is one of the most abundant and readily available polysaccharide produced in large volumes by plants and an excellent starting material for the production of a variety of useful products (Kumar, 2010). Vast array of derivatives derived from cellulose are currently available and utilized for a variety of industrial applications. Cellulose derivatives have gained acceptance for pharmaceutical, cosmetics, food, and packaging uses, and enjoy generally recognized as safe (GRAS) status. They are also used as flocculants, wetting agents, thickeners, binders, absorbents, and personal care products.

However, pure cellulose cannot be isolated from all plants due to its strong linkage with a number of associated compounds viz. lignin, hemicellulose, tannin, etc. as well as percent variability, thereby isolation being practical only for a few raw materials. Interestingly, cellulose may be obtained from the abundantly available weeds which are causing threat to biological diversity around the globe due to their (exotic species) invasion. Weeds, owing to inherent properties of efficient nutrient uptake and use, easily invade through forestry and agricultural plantations with adverse effects on the ecosystem. *Lantana camara* is one such weed which has spread to all parts of the world including India. In forestry, it tends to over-run young plantations and prevents access to older plantations. It has spoiled the natural vegetation and has colonized in natural areas. A number of approaches have been adopted for effective management of *L. camara.* Since each approach has inbuilt limitation, e.g. high cost, impracticability, environmental safety, temporary relief, etc., satisfactory approach is yet to be seen (Love, Suresh, & Babu, 2009). Utilisation of *Lantana* can be an effective method for managing the weed (Fan & Marston, 2009). Utilisation based management of *Lantana* may lead to interesting products viz. α-Cellulose and its derivatives, handmade paper, natural dyes, proteins, etc. for industrial applications. The utilisation approach will also enable to get rid of its negative social and environmental impacts and promote economic upliftment of rural economy in areas inhabited by the plant through value added applications (Ghisalberti, 2000). Keeping the above in view, α-cellulose was isolated from *L. camara* followed by grafting of acrylamide on to α-cellulose so as to develop a commercially viable product.

The modification of α-cellulose isolated from *L. camara* can be done in several ways viz. by substitution of hydroxyl groups whereby the cellulose molecules are altered by introduction of side groups usually by etherification or esterification. The aim of the substitution reactions is to increase the solubility of the derivatised cellulose as well as to introduce the desired functional groups. In other modification, branched cellulose or graft copoly-

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mer of cellulose is produced in which synthetic polymer are grafted onto cellulose so as to synthesize materials with best properties of both. Grafting of the cellulose provides a potential route for significantly altering the physical and chemical properties of cellulose backbone because by choosing suitable monomers, one can impart additional properties without affecting the basic properties of cellulose. Grafting of cellulose has great potential for tailoring properties for specific end uses. Most graft copolymers are formed by radical polymerization. A considerable number of free radical grafting methods have been tried to effect grafting onto cellulose backbone.

Among chemical methods, redox-initiated grafting is advantageous because in the presence of redox systems, grafting can be carried out under milder conditions with minimum side reactions. The grafting of acrylamide onto natural polymers like α-cellulose, guar gum, *Cassia tora* gum, starch, chitosan, etc. with different redox systems has been reported. Nada, Alkady, and Fekry (2008) studied the grafting of cellulose with acrylamide using ceric ammonium nitrate followed by metal ion sorption of the grafted products. In another study, grafting of acrylamide onto cellulose derived from Egyptian cotton linters was studied using ceric ammonium nitrate (Mostafa, Nada, Elmasry, & Mahdi, 2007). Tripathy also synthesized polyacrylamide grafted carboxymethyl cellulose in aqueous system using ceric ammonium nitrate (Tripathy, 2007). In another report, Gupta and Khandekar (2006) studied graft copolymerization of acrylamide onto cellulose in presence of ceric ammonium nitrate as initiator. Literature reported that the dielectric properties of cotton cellulose increased on grafting with acrylamide in presence of ceric ion initiator (Youssef, Hanna, Ibrahem, & Foad, 1991).

In our laboratory, seed gums (*C. tora*/*Cyamopsis tetragonoloba*/Tamarind Kernel Powder) were modified via carboxymethylation (Goyal, Kumar, & Sharma, 2007; Sharma, Kumar, Soni, & Sharma, 2003), carbamoylethylation (Sharma, Kumar, & Soni, 2003a, 2004), cyanoethylation (Goyal, Kumar, & Sharma, 2008a; Sharma, Kumar, & Soni, 2003b) and grafting (Goyal, Kumar, & Sharma, 2008b, 2009; Sharma, Kumar, & Soni, 2002, 2003c, 2003d). A number of derivatives of α-cellulose derived from *L. camara* has been synthesized including sulphate (Bhatt, Gupta, & Naithani, 2008), cyanoethyl (Bhatt, Gupta, & Naithani, 2007) and carboxymethyl (Varshney et al., 2006) derivatives. In addition, *Lantana* has been utilized for preparation of fibreboards (Negi, Prabhakar, Wazir, & Chawla, 1987), isolation of proteins, etc. (Chatterjee & Sanwal, 1999). Vats utilized lignocellulosic substrate derived from *Lantana* for cultivation of *Pleurotus sajor caju* (Vats, Sood, Gulati, & Sharma, 1994). Kuhad also made an attempt to prepare bioethanol from *L. camara* (Kuhad, Gupta, Khasa, & Singh, 2010). In addition to above, natural dye with good wash and color fastness onto fiber has been isolated from *L. camara* (Dayal, Dobhal, Kumar, Onial, & Rawat, 2006; Rawat & Jahan, 2003). However, no work has been directed towards grafting of vinyl monomers onto α-cellulose isolated from *L. camara*. With a view that grafted cellulose may find better applications in comparison to native α-cellulose, the work of graft copolymerization of acrylamide onto α-cellulose was investigated in the presence of ceric ammonium nitrate (CAN) as redox initiator and the reaction conditions for graft copolymerization were optimized.

2. Experimental

2.1. Materials

L. camara used in the present study was collected from FRI campus. CAN, dimethylformamide and methanol were of laboratory grade (S.D. Fine-Chem. Ltd., Mumbai, India), nitric acid (AR grade, Ranbaxy Laboratories Ltd., India). The infrared spectrum (IR) of grafted sample was measured in KBr pellets using a Shimadzu FTIR-8400S spectrophotometer in the range 4000–650 cm^{-1}

Table 1a
Proximate chemical analysis of *Lantana camara*.

S. No	Parameters	Value (%)	Method used
1	Hot water solubility	7.0	APPITA P 4 M-61
2	1% NaOH solubility	18.0	APPITA P 5 M-61
3	Alcohol benzene solubility	4.45	APPITA P 5 M-70
4	Holocellulose	71.34	TAPPI 9 M-54
5	Alpha cellulose	54.91	TAPPI T-203 OM 88
6	Pentosans	13.0	TAPPI T-203 OM 84
7	Klason lignin	26.32	TAPPI T-203 OM 88
8	Ash	1.8	APPITA P 3 M-69

2.2. Methods

2.2.1. Proximate chemical analysis

The moisture content and bulk density of the material was determined and found to be 65.88% and 210.76 kg/m^3 respectively. The raw material was chopped to 1.5–2.0 in. size and air-dried. Chips were reduced to dust and the dust passing through 40 mesh and retained on 60 mesh was taken for the studies. Proximate chemical composition of the plant material was studied using the standard methods to access the quality and solubility of the raw material for further processing and the results of the analysis are presented in Table 1a.

2.2.2. Isolation of α-cellulose

The air dried chips were subjected to following treatments. The conditions at each stage were optimized and 1 kg production of α-cellulose (yield 38.76%; Brightness 81.0% ISO) was carried out under optimized conditions.

2.2.2.1. Water prehydrolysis. The chips were prehydrolysed in autoclave keeping bath ratio 1:4 at 100 °C for 30.0 min. The yield after prehydrolysis was 95.5%.

2.2.2.2. Alkali hydrolysis. Water prehydrolysed chips were treated with 2% NaOH. The bath ratio was maintained 1:4 and heated in autoclave to 120 °C for 60 min. The yield was 85.9%.

2.2.2.3. Pulping. The pulping of alkali hydrolysed chips was carried out with 20% NaOH at 160 °C for 90.0 min. The kappa number of the pulp was 26 and the pulp yield was 48% with 3.8% screen rejects.

2.2.2.4. Bleaching. Bleaching was carried out using hypochlorite (2.0%)/chlorine dioxide (2.0%)/hydrogen peroxide (1.0% bleaching sequence).

2.2.3. Characterization of the cellulose

Cellulose as above was characterized for its DP and composition and the results are presented in Table 1b. DP was determined by CED viscosity method using the following formula:

$$\mathrm{DP}^{0.905} = 0.75(n)$$

where n is the intrinsic viscosity.

Table 1b
Characterization of the cellulose isolated from *Lantana camara*.

S. No	Characterization of cellulose	Value	Method used
1	α-Cellulose	94.8%	TAPPI T-203 OM 88
2	β-Cellulose	2.50%	
3	γ-Cellulose (by difference)	1.42%	
4	Lignin	0.80%	TAPPI T222
5	Ash	0.485	APPITA P3 M-69
6	Viscosity	576 cm^3 g	SCAN 15
7	Av. DP	430	SCAN 15

Table 1c
Fiber morphology of *Lantana camara*.

S. No	Parameters	Value
1	Fiber length (μm)	
	Min.	684
	Max.	1134.2
	Avg.	912
2	Fiber diameter (μm)	22
3	Lumen diameter (μm)	16
4	Wall thickness (μm)	3.06
5	Runkel ratio	0.43
6	Length/width ratio (*L*/*D*)	0.68
7	Shape factor	0.37

2.2.4. *Anatomy and fiber morphology*

The morphology of fibers plays a very important role on the structural properties of the product. The development of the properties is influenced by the fiber length, fiber diameter, lumen diameter, wall thickness, runkel ratio, length/width ratio (*L*/*D*) whereas shape factor determines fiber coarseness. The anatomical studies are reported in Table 1c.

2.2.5. *Graft copolymerization*

The grafting reaction was carried out under nitrogen atmosphere in a 500 ml, four-necked flask equipped with a reflux condenser, a stirrer, dropping funnel and a gas inlet system immersed in a constant temperature water bath. In a typical reaction, α-cellulose (0.25 mol; 4 g) was dispersed in a definite volume of water (90 ml) with constant stirring and bubbling of a slow stream of nitrogen for 30 min at the desired temperature (20–50 °C). After 30 min, a freshly prepared 10 ml solution of CAN (0.075×10^{-2} to 0.175×10^{-2} mol, 0.411–0.959 g) in nitric acid (0.1–0.3 N) was added and stirred for 10 min. Nitrogen gas was continuously purged through the reaction mixture and AM (0.049–0.25 mol, 6–10 ml) was added. In all the reactions, total volume of the reaction was kept constant (100 ml). The grafting reaction was carried out for varying time intervals (4–6 h). The zero time of the reaction was at the time of monomer addition. After completion of the reaction, the reaction mixture was immediately poured into methanol in the ratio of 1:5 of material to liquor for precipitation. The precipitated product was recovered by centrifugation and washed with pure methanol (2 × 50 ml). The crude copolymer thus obtained was dried till constant weight under vacuum (7.6 mm Hg) for 24 h at 40 °C. The dried product was extracted with dimethylformamide:acetic acid mixture (1:1) for 48 h and washed with methanol to remove the homopolymer (polyacrylamide). The grafted cellulose (cell-g-AM) was dried to a constant weight under vacuum (7.6 mm Hg) for 24 h at 40 °C. The percentage grafting (%G) and percentage grafting efficiency (%GE) were determined from the increase in the weight of cellulose after grafting in the following manner:

$$\%\text{G} = \frac{\text{final cellulose weight} - \text{initial cellulose weight}}{\text{initial cellulose weight}} \times 100$$

$$\%\text{GE} = \frac{\text{final cellulose weight} - \text{initial cellulose weight}}{\text{total polymer weight after reaction} - \text{weight of homopolymer}} \times 100$$

2.2.6. *IR analysis*

The Fourier Transform Infrared Spectrum (FTIR) of grafted cellulose was measured in KBr pellets using a Shimadzu FTIR-8400S spectrophotometer in the range 4000–650 cm^{-1}.

2.2.7. *Scanning Electron Microscopy (SEM) studies*

SEM images at 500 magnifications were obtained for α-cellulose and α-cellulose-g-AM using Zeiss EVO 40 EP Scanning Electron Microscope (Cambridge, England). The sample was laid on the aluminum stub using double sided conducting adhesive tape and was sputter coated with gold.

3. Results and discussion

Ceric ammonium nitrate (CAN) has been used extensively as the redox initiator for effecting grafting of a variety of vinyl monomers onto biopolymers viz. guar gum (Deshmukh & Singh, 1987; Sharma et al., 2003c; Trivedi, Kalia, Patel, & Trivedi, 2005), cellulose (Gurdag, Yasar, & Gurkaynak, 1997) and chitin (Ren & Tokura, 1994). Kubota and Ogiwara (1969) studied the effect of lignin contained in cellulose on the vinyl graft polymerization of lignin containing substrates using the Ce(IV) ion technique. The samples containing highest lignin content contain the lowest graft yield. It is because of the fact that Ce(IV) ions reacted at a faster rate with lignin than with cellulose, but the active sites on the lignin appeared to participate in termination reactions, thus leading to lower grafting (Kubota & Ogiwara, 1969). Ce(IV) enters into complex formation with cellulose, and on disproportionation the complex generates free radicals on the backbone cellulose polymer where grafting of the appropriate vinyl monomer can occur. The formation of free radicals in Ce(IV)-treated cellulose has been confirmed by electron spin resonance (Arthur, Baugh, & Hinojosa, 1966). The mechanism by which Ce(IV) interacts with cellulose to form free radical involves the formation of a coordination complex between the Ce(IV) and the hydroxyl group of cellulose. The Ce(IV)-cellulose complex then disproportionates forming a free radical on the cellulose chain and Ce(III) (Arthur et al., 1966; McCormick & Park, 1981).

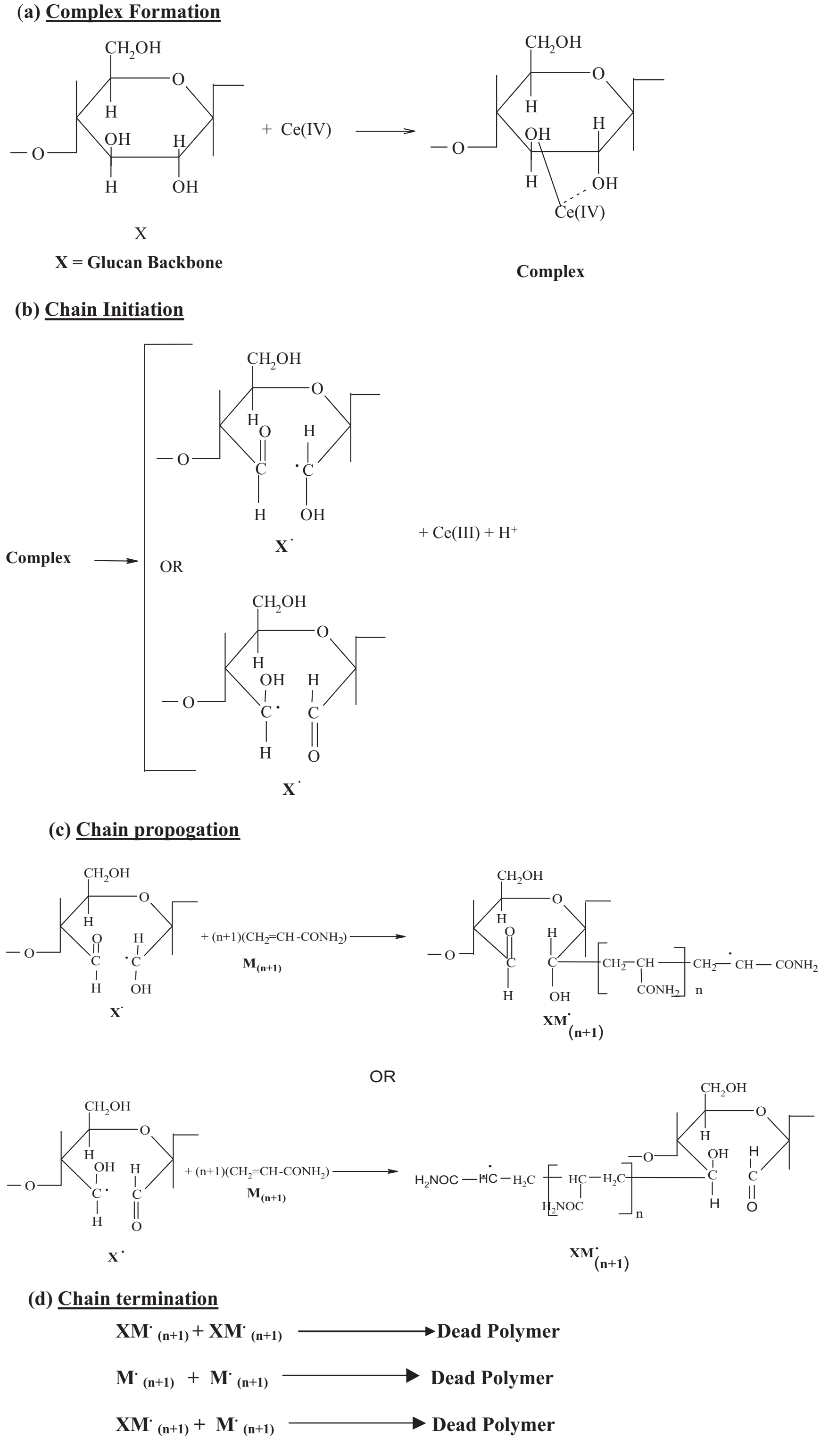
Evidence for complex formation has been obtained by kinetic and spectrophotometric methods for the oxidation of various alcohols and substrates containing alcohol groups by Ce(IV) ions in perchloric and nitric acids (Duke & Bremer, 1951; Duke & Forist, 1949; McCormick & Park, 1981). The postulated mechanism has been supported by the model compound studies of Ce(IV) oxidation of monohydric alcohols and 1,2-glycols and suggest that the C_2–C_3 glycol and the C_6 hydroxyl of an anhydro-D-glucose unit may be preferred sites for free-radical generation (Hintz & Johnson, 1967; Mino, Kaizerman, & Rasmussen, 1959; Pottenger & Johnson, 1970).

The relative rates of oxidation of the C_6 hydroxyl and the C_2–C_3 glycol were examined. Model compounds such as cyclohexanemethanol and tetrahydropyran-2-methanol were used for the C_6 hydroxyl, and *trans*-1,2-cyclohexanediol for C_2–C_3 glycol. The results indicate that diol group oxidized about six times faster than the C_6 hydroxyl. Thus Ce(IV) oxidation will occur mainly at the C_2–C_3 glycol unit and to some extent at the C_6 primary hydroxyl (Hintz & Johnson, 1967).

The equilibrium constants for complex formation show that the presence of adjacent hydroxyl groups in the organic substrate causes a substantial increase in the stability of the complex compared to compounds with only one hydroxyl. Thus, the equilibrium constants for *cis*- and *trans*-1,2-cyclohexanediols are considerably larger than for the monohydric alcohols. The greater stability of the complexes with the 1,2 glycols indicate that these compounds form a chelate complex with Ce(IV) (Hintz & Johnson, 1967).

Furthermore, the equilibrium constants for the *cis*- and *trans*-1,2-cyclohexanediols are consistent with chelate complex formation. In the stable conformations of these compounds, the separation of the hydroxyl groups is about the same, and a relatively large Ce(IV) ion can easily bridge this distance. The formation of a five-membered chelate ring fused to the cyclohexane ring results in a relatively rigid system with the *trans* isomer, whereas the complex with the *cis* isomer is relatively flexible because conformation interconversion can occur as readily in the complex as in the uncomplexed diol. The greater flexibility of the complex with the *cis* isomer thus contributes to its somewhat greater stability (Hintz & Johnson, 1967).

In view of the above, it is proposed that in the Ce(IV)-initiated graft copolymerization onto α-cellulose, the oxidation reaction of Ce(IV) with α-cellulose will occur preferably at the C_2–C_3 glycol unit and to a lesser extent at the C_6 primary hydroxyl as a result of one electron transfer process. The Ce(IV) ion initially forms a Ce(IV)–α-cellulose complex. This complex is then reduced to Ce(III) ion with the formation of free radical at either C_2 or C_3 on the backbone as shown in Scheme 1 (Arthur et al., 1966). The free radical then reacts with the vinyl monomer, which is present in the reaction mixture to initiate graft copolymerization. The grafting occurs mainly at C_2–C_3 as discussed above. The grafting was also confirmed by the IR spectrum of the grafted sample, which showed an additional absorption band at 1660 cm^{-1} due



Scheme 1. Grafting mechanism.

to –C=O stretching of the amide group confirming the grafting of acrylamide onto α-cellulose.

3.1. Determination of the optimum reaction conditions

To optimize the conditions for grafting of AM onto α-cellulose isolated from *L. camara*, the concentration of CAN, nitric acid, monomer, time and temperature were varied.

3.1.1. Effect of CAN concentration

The effect of variation in CAN concentration on %G and %GE is shown in Fig. 1(a). CAN concentration was varied from 0.075×10^{-2} to 0.175×10^{-2} mol. It is evident from the data that the %G increases with an increase in the initiator concentration, and reaches a maximum value of 293.2% at 0.15×10^{-2} mol conc. of CAN. Further increase in CAN concentration (0.175×10^{-2} mol) is accompanied by a decrease in the %G (265.45%). The observed increase

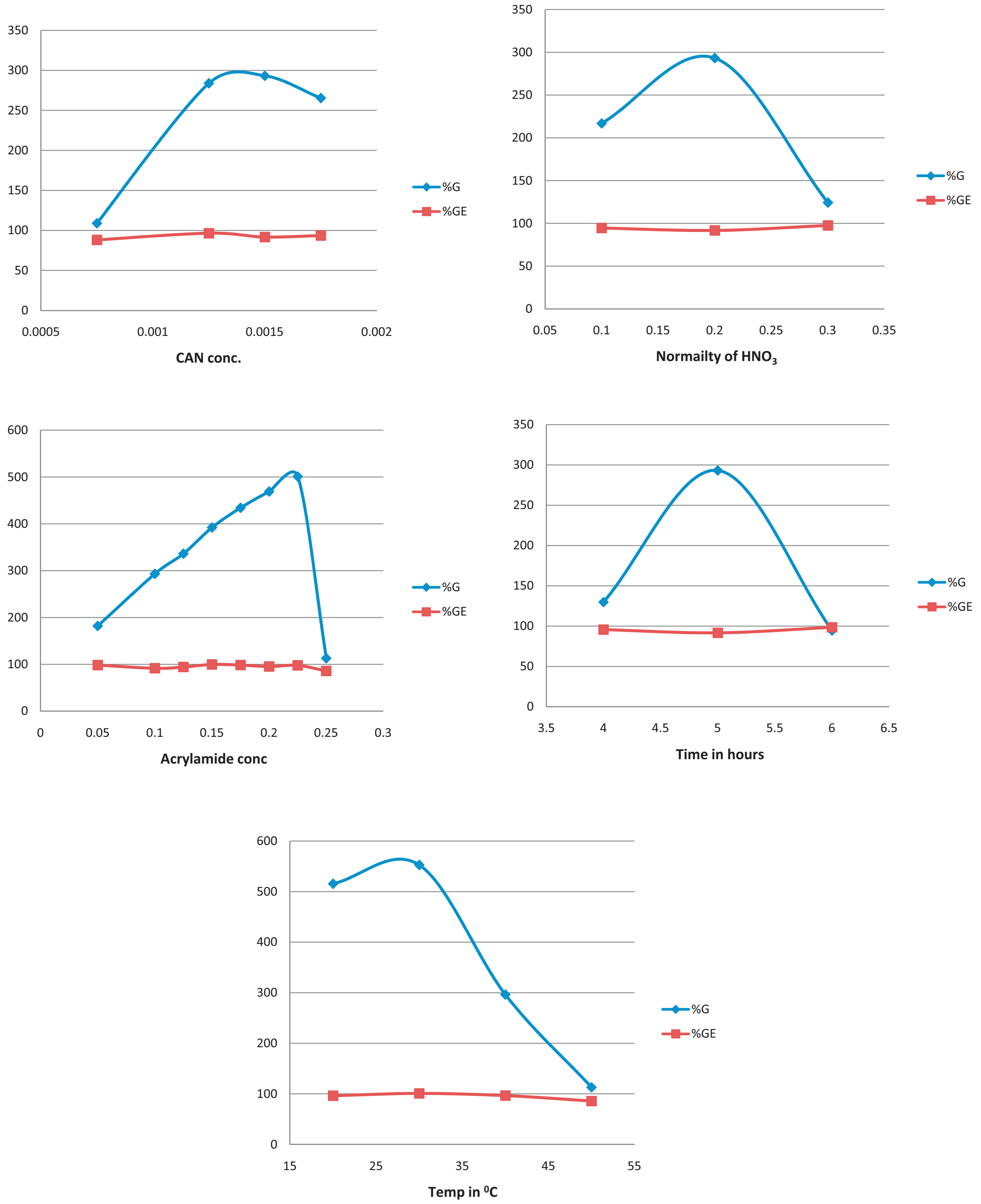


Fig. 1. (a) Effect of CAN conc., (b) effect of HNO_3 normality, (c) effect of acrylamide conc., (d) effect of time, and (d) effect of temp.

in %G, with the CAN concentration ranging from 0.075×10^{-2} to 0.150×10^{-2} mol, may be due to the fact that in this concentration range, the increase in concentration of Ce(IV) ion results in an increase in the total number of Ce(IV)–cellulose complex which decompose to give more active sites. Thus, this activation along the backbone is immediately followed by graft copolymerization of monomer onto the backbone. At relatively higher concentration of the initiator (0.175×10^{-2}), the number of backbone radicals increases. This will enhance the possibility of termination of the backbone radicals before grafting takes place. Furthermore, homopolymer formation at higher initiator concentration competes with the grafting reaction for available monomer thereby leading to a decrease in %G.

Fig. 1(a) also shows a decrease in %GE with increase in the CAN concentration. The fast dissociation of CAN may account for higher %GE in the initial stages, since the total amount of Ce(IV) would be available for initiation. The higher the concentration of Ce(IV), the greater will be the termination of growing grafted chains resulting in reduction of %G as well as %GE (Sharma et al., 2002, 2003c; Goyal et al., 2008b).

3.1.2. *Effect of nitric acid concentration*

The concentration of nitric acid was varied from 0.1 N to 0.3 N, keeping fixed the concentrations of all other reagents, time and temperature. The effect of acid concentration on %G and %GE is shown in Fig. 1(b). It is observed that there exists an optimum concentration of nitric acid, which affords maximum percent grafting (293.2%). This corresponds to 0.2 N in present case.

The role of nitric acid for grafting of AM onto α-cellulose is explained by the fact that ceric ion in water is believed to react in the following manner:

$$Ce^{4+} + H_2O \leftrightarrow [Ce(OH)_3]^{3+} + H^+ \qquad (1)$$

$$2[Ce(OH)_3]^{3+} \leftrightarrow [Ce\text{–}O\text{–}Ce]^{6+} + H_2O \qquad (2)$$

Thus ceric ion exists as $[Ce]^{4+}$, $[Ce\,(OH)_3]^{3+}$ and $[Ce\text{–}O\text{–}Ce]^{6+}$ in aqueous solution. The concentration of these species is found to vary with the concentration of nitric acid. The %G increases with increase in acid concentration up to 0.2 N. This is attributed to the increase in the concentrations of $[Ce(OH)_3]^{3+}$and $[Ce]^{4+}$ at the expense of $[Ce\text{–}O\text{–}Ce]^{6+}$. Ceric ion $[Ce]^{4+}$ and $[Ce\,(OH)_3]^{3+}$, being smaller in size, are more effective in their ability to form complexes with cellulose than $[Ce\text{–}O\text{–}Ce]^{6+}$. With further increase in acid concentration beyond 0.2 N, it was observed that %G decreases. This is explained by the fact that as $[H^+]$ increases, the equilibrium, Eqs. (1) and (2) shift towards the formation of more and more $[Ce]^{4+}$ and $[Ce(OH)_3]^{3+}$. These species, at higher concentration of acid, affect the grafting adversely. Instead of propagating the polymeric chain, these species at higher concentration affect the termination steps, thus lowering the %G. Moreover, ceric ion has been reported to be involved in oxidative termination of growing monomeric chain as shown in Eq. (3) (Sharma et al., 2002, 2003c; Goyal et al., 2008b)

$$Ce^{4+} + M_n^{\bullet} \rightarrow Ce^{3+} + M_n + H^+ \qquad (3)$$

Thus, nitric acid plays a definite role in promoting grafting of poly(acrylamide) onto cellulose.

3.1.3. *Effect of monomer concentration*

The effect of monomer concentration on the grafting yields is represented in Fig. 1(c). It is observed from the results that with increase in monomer concentration, %G increases and reaches the maximum value 501.1% at 0.225 mol. A further increase in monomer concentration leads to decrease in %G and %GE. The enhancement of grafting by increasing the monomer concentration could be ascribed to the greater availability of grafting sites on cellulose macroradicals to monomer molecules. However at higher monomer concentration, i.e. beyond 0.225 mol there is a decrease in %G and %GE. This decrease can be attributed to the higher affinity of AM monomer for its homopolymer (polyacrylamide) over the cellulose macroradicals. Thus, most of the monomer is preferentially used up in the formation of homopolymer on increasing the acrylamide concentration, which is evident from the rise in viscosity of the reaction medium at higher concentration (Sharma et al., 2002, 2003c; Goyal et al., 2008b).

3.1.4. *Effect of reaction time*

The effect of polymerization time on %G and %GE is shown in Fig. 1(d). It can be seen from Fig. I(d) that the percent grafting exhibits progressive improvement with the increase in reaction time and showed maximum %G (293.2%) at 4 h. This effect of time on grafting can be explained by the fact that more the contact time of monomer molecules with the cellulose macroradical sites, the higher will be the grafting, but the decrement in %G and %GE occurs beyond 4 h which can be rationalized on account of depletion of monomer and initiator concentration with the progress of the reaction. Further with an increase in the reaction time, mutual annihilation of growing grafted chains also occurs and leads to a decrease in %G (Sharma et al., 2002, 2003c; Goyal et al., 2008b).

3.1.5. *Effect of temperature*

The grafting copolymerization of AM onto cellulose has been studied at different temperatures (20–50 °C), keeping other variables constant. The effect of temperature on %G and %GE is shown in Fig. 1(e). It is seen from the Fig. 1(e) that the %G as well as %GE, increases with the rise of temperature from 20 to 30 °C, but decreases with further increase in temperature. The maximum %G (552.2) was obtained at 30 °C. The dependence of %G on tempera-

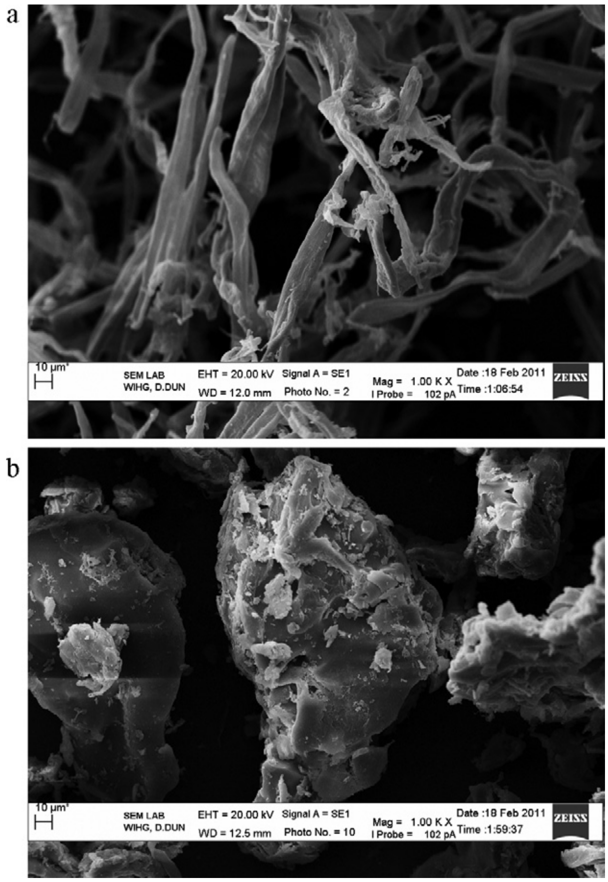


Fig. 2. (a) SEM of α-cellulose and (b) SEM of grafted cellulose.

ture can be ascribed to the enhancement of the rate of diffusion of monomer. Increase in temperature beyond the optimum temperature (30 °C in this case) leads to the graft copolymerization with poor selectivity, and various hydrogen abstraction and chain transfer reactions might be accelerated, leading to the decrease of %G and %GE. It has also been observed by Kulkarni and Mehta (1968) that decay of free radical activity increases rapidly with increasing temperature.

Further at higher temperature, there may also be the acceleration of the termination process, which leads to the formation of

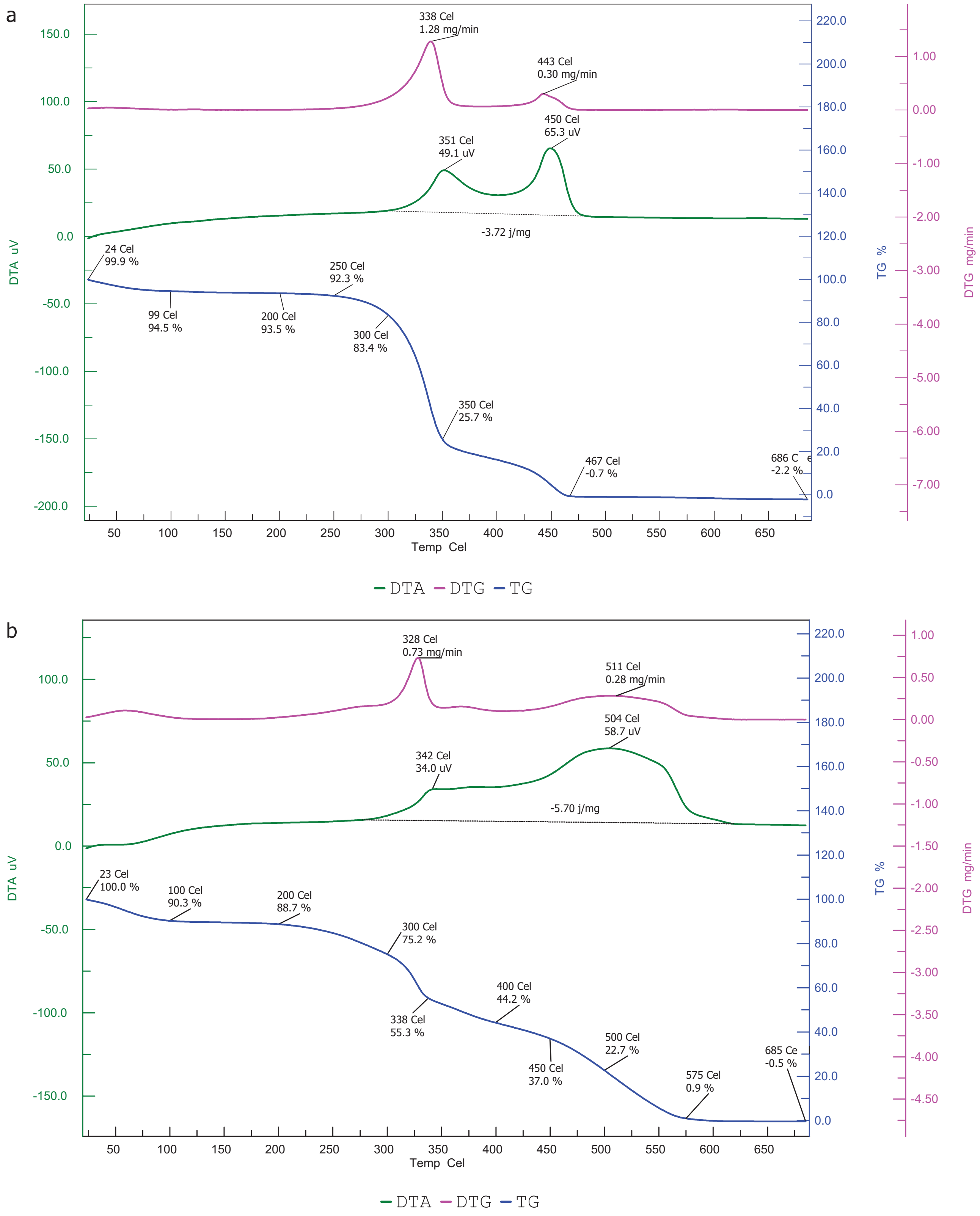


Fig. 3. Thermal stability thermogram and derivatogram of (a) α-cellulose and (b) grafted α-cellulose.

more homopolymer. Similar results have been reported in the literature (Sharma et al., 2002, 2003c; Goyal et al., 2008b).

3.1.6. IR characterization

The IR spectrum of the grafted samples showed an additional sharp absorption band at 1660 cm^{-1} due to –C=O stretching confirming the grafting of acrylamide onto α-cellulose.

3.1.7. Surface morphology

Scanning electron micrograph clearly exhibits the cellulosic fiber nature having chains of glucose moieties. The α-cellulose appears completely fibrous [Fig. 2(a)]. A change in contour of the α-cellulose on grafting and the thick polymeric coating of acrylamide on their surface along with grafting of acrylamide such that all the gap between cellulosic chains have been closed indicate the effect of grafting [Fig. 2(b)]. It can be seen that individual chains of α-cellulose have joined through these surface coatings during grafting process.

3.1.8. Thermal characterization

Understanding the behavior of α-cellulose-g-AM under the influence of thermal load is important to study its properties for different applications. DTG and TGA were used to study the thermal properties of native cellulose and its grafted derivative.

The thermal stability of α-cellulose and α-cellulose-g-AM can be compared on the basis of the onset temperature of decomposition, % weight loss for the different stages of decomposition and the % weight residue at maximum temperature of decomposition. Fig. 3(a and b) shows the primary thermogram (TG) and derivatogram (DTG) for α-cellulose and α-cellulose-g-AM respectively.

Pure α-cellulose [Fig. 3(a)] shows characteristic three-step thermogram. The Ist stage is from 24 to 250 °C which has initial weight 100% at 24 °C. At 100 °C the weight is 94.5% indicating a weight loss of 5.5%. The initial loss in weight (5.5%), is merely due to evaporation of absorbed moisture. The rapid decomposition occurs in second stage (250–350 °C) resulting with the onset of major weight loss of about 17% at 338 °C (T_0) and 74.3% at $T_{\max} = 350$ °C due to the degradation of TKP. The DTG clearly exhibits the temperature for maximum decomposition for this stage as 338 °C. The final stage of decomposition (350–450 °C) is due to the formation and evaporation of some volatile compounds hence is rather slow and results in about 25% weight loss. The α-cellulose completely decomposed up to 467 °C and the char yield is zero at this temperature.

Fig. 3(b) shows four-stage decomposition pattern between 25 °C and 675 °C. The first stage (25–100 °C) is due to loss of moisture showing about 9.7% weight loss, while 33.4% loss occurs in second stage of decomposition in the temperature range of 200–350 °C due to degradation of grafted copolymer (α-cellulose-g-AM). The DTG clearly exhibits the temperature for maximum decomposition for this stage as 328 °C. The third stage from 350 °C to 500 °C during which there was 32.6% weight loss may contribute to the decomposition of different structure of α-cellulose-g-AM whereas the weight loss from 350 °C to 575 °C is 54.4%. Below 300 °C the copolymer had more weight loss than α-cellulose. However the char yield of 22.7% was obtained at 500 °C and 0.9% at 575 °C. Thus, α-cellulose-g-AM has overall high thermal stability than pure α-cellulose.

4. Conclusions

Utilisation of α-cellulose isolated from *L. camara* can be a practical preposition as chemical feedstock in food, pharmaceuticals, cosmetics, fiber and other industries for management of the weed for economic benefits and biodiversity conservation. Encouraged by the above observations, graft copolymerization of acrylamide onto α-cellulose in aqueous medium was initiated effectively with CAN. The reaction conditions were optimized for grafting of AM onto α-cellulose by varying the concentration of α-cellulose, CAN, AM, HNO_3, polymerization time and reaction temperature. The characterization of the grafted products by means of FT-IR, SEM and thermal analysis furnished evidence of grafting of AM onto α-cellulose. The optimized conditions for grafting obtained are cellulose, 0.25 mol; HNO_3 conc., 0.2 N; CAN conc., 0.150×10^{-2} mol; acrylamide conc., 0.225 mol; reaction time, 5 h; reaction temp, 30 °C; total reaction volume, 100 ml. Under the above conditions maximum %G of 552.2 and % GE of 100.1 was obtained. α-Cellulose-g-AM has overall high thermal stability than pure α-cellulose.

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