CERIC-INDUCED GRAFTING OF ACRYLONITRILE ONTO ALPHA CELLULOSE ISOLATED FROM *Lantana camara*

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Ceric-induced grafting of acrylonitrile onto alpha cellulose isolated from stems of *Lantana camara* was carried out with acrylonitrile as monomer, and ceric ammonium nitrate as initiator. The optimized conditions were the following: monomer, initiator and nitric acid concentration, and reaction time and temperature. The optimized grafted product was evaluated by IR, SEM, TGA/DTA and WAXDs.

Keywords: grafting, alpha cellulose, *Lantana camara*

INTRODUCTION

Forest-based lignocellulosic raw materials have been commercially utilized for the preparation of highly purified cellulose, commonly known as 'alpha cellulose' or 'dissolving cellulose'. A large number of plant species are identified as sources of cellulosic raw materials for pulp and paper making, even if only few studies have been devoted to their utilization for alpha cellulose preparation.[1-4]

The use of ceric ions to initiate graft copolymerization of vinyl monomers on various cellulosic materials (wood pulp, cotton, rayon and paper) has gained considerable importance. Since the ceric ion is a powerful oxidizing agent, it has a high efficiency on both grafting and oxidation of cellulose.[5] It is possible that, by grafting of monomers onto cellulose, different properties – including water sorbency, elasticity, ion-exchange capabilities, thermal resistance and resistance to microbiological attack – could be obtained.[6] Grafting of hydrophobic monomers, such as acrylonitrile[7-9] and methyl methacrylate,[9-11] resulted in a decrease in water sorbency. However, the water retention values of cellulose could be increased by first grafting with acrylonitrile or methyl methacrylate, and then by hydrolyzation of the grafted product.[12,13] Most of the grafting methods involve creation of free radicals on the cellulose molecule, by means of redox systems.[7,14-17]

Lantana camara (the Verbenaceae family), a fast-growing weed with encroached large areas worldwide, is rich in lignocellulosic material. In response to the above discussion, chemical means were provided for isolating alpha cellulose from the stems of *L. camara* under optimized conditions,[18] and an attempt has been made for ceric-induced grafting of acrylonitrile onto alpha cellulosic materials. The present study reports the synthesis of acrylonitrile-grafted cellulose with alpha cellulose extracted from the stems of *L. camara*, through ceric ion-induced redox polymerization. While attempting to optimize the conditions of grafting, the influence of various parameters – such as reaction time, temperature, monomer, initiator and nitric acid concentrations – were also studied, and the product characteristics were evaluated.

EXPERIMENTAL

Materials

The *Lantana camara* used in the study was collected from the field of the institute's campus. All chemicals used were of analytical grade.

Isolation of alpha cellulose

Alpha cellulose was isolated from the stems of *L. camara* by an already optimized method.[18]

Grafting copolymerization of alpha cellulose

The grafting reaction was carried out under nitrogen atmosphere, in a 250 mL, 3-necked flask equipped with a stirrer, a gas inlet system, and a reflux condenser immersed in a constant-temperature water bath. In a typical reaction, a freshly prepared 100 mL solution of ceric ammonium nitrate (CAN) (0.1-0.4 M/AGU) in nitric acid (0.1-0.4 N) was dissolved in a definite amount of alpha cellulose isolated from the stems of *L. camara* (1 g), constantly stirring and bubbling a slow stream of nitrogen at the desired temperature (20-50 °C). Acrylonitrile (AN) monomer (5-25 M/AGU) was added after half an hour, on maintaining a continuous supply of nitrogen throughout the whole reaction duration. In all assays, the total reaction volume was kept constant. The grafting reaction was carried out for varying periods of time (1-4 h). The zero time of the reaction occurred at the time of monomer addition. After completion of the reaction, the mixture was washed with water, then with pure methanol. The crude copolymer thus obtained was dried until constant weight was reached under vacuum at 40 °C. The dried product was extracted with dimethylformamide, under continuous stirring for 24 h, to remove the homopolymer (polyacrylonitrile). The grafted *Lantana* cellulose was again dried to a constant weight under vacuum at 40 °C.

Analysis and measurement

Percentage grafting (%G) and percentage grafting efficiency (%GE) were calculated from the increase in weight of *Lantana* cellulose after grafting, in the following manner:[19]

% G = (Weight of grafted polymer/ initial weight of backbone) x 100

% GE = (weight of grafted polymer/weight of grafted polymer + weight of homopolymer) x 100

Measurement of water sorbency

The water sorbency of parent and grafted cellulose, determined according to the method described by Ali *et al*.,[3] was expressed as the water retention value (WRV), in grams of water per gram of oven-dry sample weight, being calculated as:

WRV (g/g) = (WET - DRY)/DRY

WET= Weight of sample after immersion in water

DRY= Dry weight of the sample

IR spectra

The infrared (IR) spectra of grafted and extracted cellulose isolated from the stems of *L. camara* were recorded on a JOSCO FT-IR 5300 spectrophotometer, using KBr disk pallets from 4000-400 cm^{-1}, at a resolution of 2 cm^{-1}, with five scans per sample.

Scanning electron microscopy

SEM images were recorded on a Leo instrument 435 VP model. The samples were coated with a thin film of gold, to make the surface conductive, to prevent surface change and to protect the surface material from thermal damage by the electron beam.

Thermal studies (TGA/DTA)

Thermogravimetric analyses of the samples were carried out with a Perkin Elmer (Pyris Diamond) in nitrogen, at a 10 ºC/min rate.

Wide angle X-ray diffraction (WAXDs)

The WAXDs of the solid samples were recorded on a Bruker AXS D8 Advance X-ray powder diffractometer with a Cu-KÜ target.

RESULTS AND DISCUSSION

Ceric ion-induced grafting of acrylonitrile (AN) onto the alpha cellulose isolated from *Lantana* was carried out and the conditions were optimized. The studied variables were: reaction time, temperature and concentration of nitric acid, concentration of ceric ammonium nitrate (CAN) and concentration of acrylonitrile. The grafted product was evaluated by IR, SEM, TGA/DTA and WAXDs.

Effect of ceric ammonium nitrate concentration

Grafting of AN onto *Lantana* cellulose was carried out at various CAN concentrations, between 0.1-0.4 M/AGU in 100 mL HNO_3 (0.1N) at a temperature of 30 °C, AN concentration of 10 M/AGU and reaction time of 2 h – the results are shown in Figure 1. It is evident from the data that the grafting percentage increases with the increase in initiator concentration, reaching its maximum value – of 238 – at 0.2 M/AGU. Further increase in CAN concentration is accompanied by decreases in the grafting yield. The observed increase in G%, within the CAN concentration range of 0.1-0.2 M/AGU in 100 mL HNO_3 (0.1N), may be due to the fact that, under such conditions, activation along the backbone takes place immediately, followed by graft copolymerization of the monomer onto the backbone. A relatively high concentration of initiator may cause reduction of grafting, due to an increased number of backbone radicals terminated prior to AN addition. Furthermore, homopolymer formation at

higher initiator concentration, which competes with the grafting reaction for the available monomer, could lead to a decrease in grafting yield.

Figure 1 also evidences a decrease in GE% with increasing initiator concentration. The fast dissociation of CAN may account for its higher GE in the initial stages, since the total amount of Ce (IV) would be available for initiation.

In ceric ion-initiated graft copolymerization, the higher the concentration of Ce (IV), the greater will the termination of the growing grafted chain be, resulting in the reduction of both G and GE%. It is therefore reasonable to expect a similar termination with the increase in initiator concentration, which leads to a steady decrease in grafting efficiency.[13,19]

Effect of acrylonitrile concentration

The results reported in Figure 2 show that, at a temperature of 30 °C and CAN concentration of 0.2 M/AGU in 100 mL (0.1N) HNO_3 for 2 h, when monomer concentration was varied from 5 to 25 M/AGU, an increase in G% occurred, reaching a maximum at 15 M/AGU and showing a decreasing trend with further increase in monomer concentration. An enhancement of G and GE% with increasing monomer concentration to an optimum value could be explained by the higher availability of the grafting sites to the monomer. However, the decreasing trend of G and GE% beyond optimum monomer concentration may have been due to the competition between homopolymerization and graft copolymerization, when the former prevailed over the latter at higher AN concentration.[3,19]
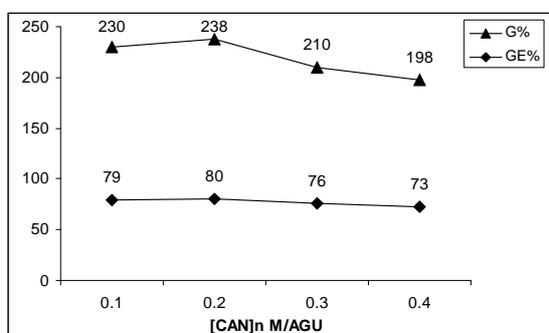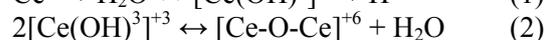
Effect of nitric acid concentration

Figure 3 shows the dependence of percentage grafting and of percent grafting efficiency on nitric acid concentration, at a temperature of 30 °C, CAN concentration of 0.2 M/AGU, AN concentration of 15 M/AGU, for 2 h. The concentration of nitric acid was varied between 0.1-0.5 N. A critical concentration of nitric acid (0.2N), which permits the maximum percent grafting, may be also observed. Beyond this concentration, percent grafting decreases. The observed low grafting, *i.e.* of 246, for 0.1N concentration of HNO_3, can be explained as follows:

In an aqueous medium, Ce (IV) is believed to combine with water in the following manner:

$$Ce^{+4} + H_2O \leftrightarrow [Ce(OH)^3]^{+3} + H^+ \qquad (1)$$
$$2[Ce(OH)^3]^{+3} \leftrightarrow [Ce-O-Ce]^{+6} + H_2O \qquad (2)$$

In the absence of the acid, Ce^{+4} primarily exists as $[Ce]^{+4}$, $[Ce(OH)^3]^{+3}$ and $[Ce-O-Ce]^{+6}$. Due to its large size, $[Ce-O-Ce]^{+6}$ is incapable of entering the complex formation with *Lantana* cellulose. Thus, with the increase in acid concentration, equilibria (1) and (2) shift towards the formation of more $[Ce(OH)^3]^{+3}$ and Ce^{+4}, at the expense of $[Ce-O-Ce]^{+6}$, Ceric $[Ce]^{+4}$ and $[Ce(OH)^3]^{+3}$ which, being smaller in size, are more effective in forming complexes with *Lantana* cellulose molecules than with $[Ce-O-Ce]^{+6}$, a higher percentage of grafting thus resulting. A decrease in the grafting percentage beyond 0.2N HNO_3 could be attributed to the termination of the growing grafted chains, due to the presence of a higher concentration of this species:[9]

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

Figure 1: Effect of ceric ammonium nitrate concentration on G and GE%
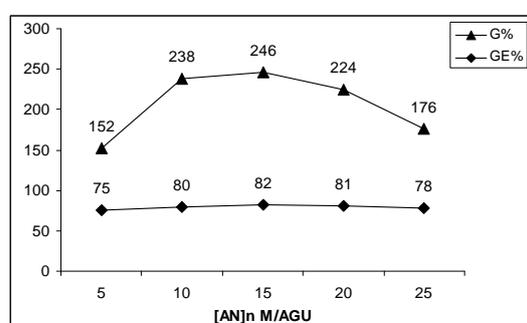
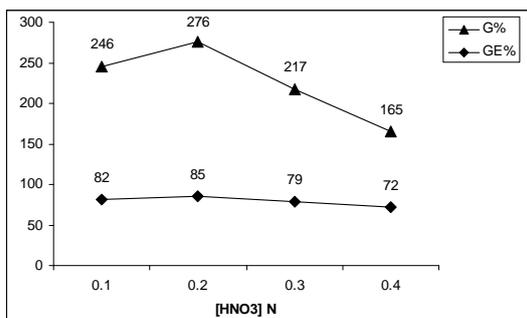Figure 2: Effect of acrylonitrile concentration on G and GE%

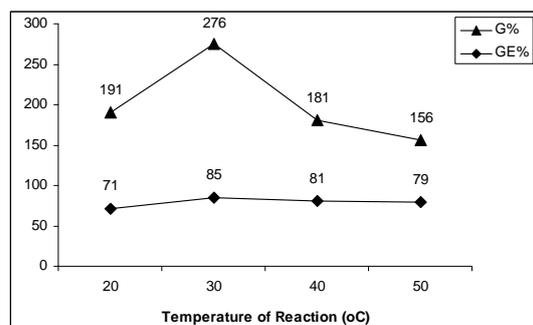Figure 3: Effect of nitric acid concentration on G and GE%
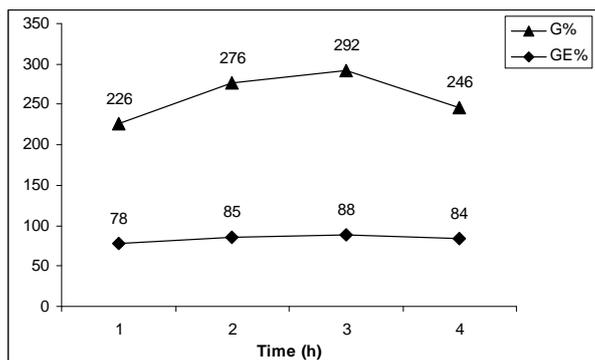

Figure 4: Effect of temperature on G and GE%

Figure 5: Effect of reaction time on G and GE%

Thus, the nitric acid plays a definite role in grafting of acrylonitrile onto *Lantana* cellulose.

Effect of temperature

Grafting reactions were carried out at different temperatures, between 20-50 °C, at CAN concentration of 0.2 M/AGU in 100 mL (0.1N) HNO₃, AN concentration of 15 M/AGU for 2 h. The influence of temperature on grafting is shown in Figure 4, which illustrates that both G and GE% increase with the rise of temperature from 20 to 30 °C, but decrease with further increase of temperature. The maximum G% (276) was obtained at 30 °C. The increase in temperature seems to cause a higher rate of initiator dissociation, as well as diffusion and mobility of the monomer from the aqueous phase to the backbone, a considerable improvement in grafting yield thus resulting. With further increase of temperature, graft copolymerization occurs with poor selectivity, while the various hydrogen abstraction and chain transfer reactions might be accelerated, leading to the decrease of G as well as of GE%.

The decrease in GE% with rising temperature may be attributed to an increased solubility of the monomer in the aqueous phase at a higher temperature, and

also to the acceleration of the termination process, which led to the formation of more homopolymer. Similar results have been reported in literature.[3,19]

Effect of reaction time

Figure 5 shows the G and GE% of AN onto *Lantana* cellulose at different reaction periods, at 30 °C, CAN concentration of 0.2 M/AGU in 100 mL (0.1N) HNO₃, AN concentration of 15 M/AGU. Although percent grafting exhibits progressive improvement with the increase in reaction time, maximum G% occurred at 3 h. Such an effect of time on grafting can be explained as follows: it is obvious that the higher the contact time of the monomer molecules with the *Lantana* cellulose macro radicals sites, the higher will grafting be, while decrement of *Lantana* cellulose after a certain time can only be attributed to the depletion of initiator and monomer concentration with the progress of the reaction. Further on, with the increase in the reaction time, mutual annihilation of growing grafted chain occurs, leading to a decrease in G and GE%.[3,19]

Characterization

The IR spectra of true grafted polyacrylonitrile cellulose (Fig. 6(b)) showed a characteristic band at 2245 cm⁻¹, specific to

the nitrile group, C≡N, which is absent in alpha cellulose (Fig. 6(a)), thereby indicating formation of PAN grafted cellulose.

Scanning electron microscopy

Figures 7(a) and (b) show the scanning electron micrographs of pure alpha cellulose and PAN grafted alpha cellulose fibres, respectively. The surface topology of raw alpha cellulose was found to be even, while the grafted alpha cellulose revealed that the fibre surface had a deposit of grafted polymer, no evenness of the fibre surface being observed.[20,21]

Wide angle X-ray diffraction (WAXD)

As shown by WAXD studies, the degree of crystallinity of the extracted cellulose (Fig. 8(a)) is 53%. On grafting (Fig. 7(b)), this was further reduced to 25%, as due to fewer interpolymer chain interactions.

Thermal degradation behaviour

The DTA curves for parent cellulose and optimized grafted cellulose samples are shown in Figures 8(a) and (b), respectively. In the case of cellulose, only one endothermic peak is observed while, for grafted cellulose, three endothermic peaks are present at 346 °C in cellulose and at 277, 349 and 420 °C, in the grafted one, resulting from the decomposition occurring in cellulose and grafted cellulose.

In grafted cellulose, the first endothermic peak is due to semi-melting, while the second and third peaks are due to a continuous decomposition of the molecule.

The TGA curve for parent cellulose shows that, after an initial loss of moisture at 100 °C, loss in cellulose weight occurred, attributed to the actual pyrolysis by a minor decomposition reaction at about 250 and 324 °C, and to a major decomposition at 349 and 375 °C. The TGA curve for grafted cellulose reveals that decomposition occurred in three stages, while the latter one – in two stages, after moisture loss was discounted. The crosslinked grafted cellulose lost 5.92 wt%, mostly due to moisture, from 27 to 266 °C, in the first stage of decomposition. The actual decomposition occurred between 266-400 °C, with a sharp weight loss (of 37.72%), over this temperature range most of this weight loss being attributed to the loss of acrylonitrile groups.
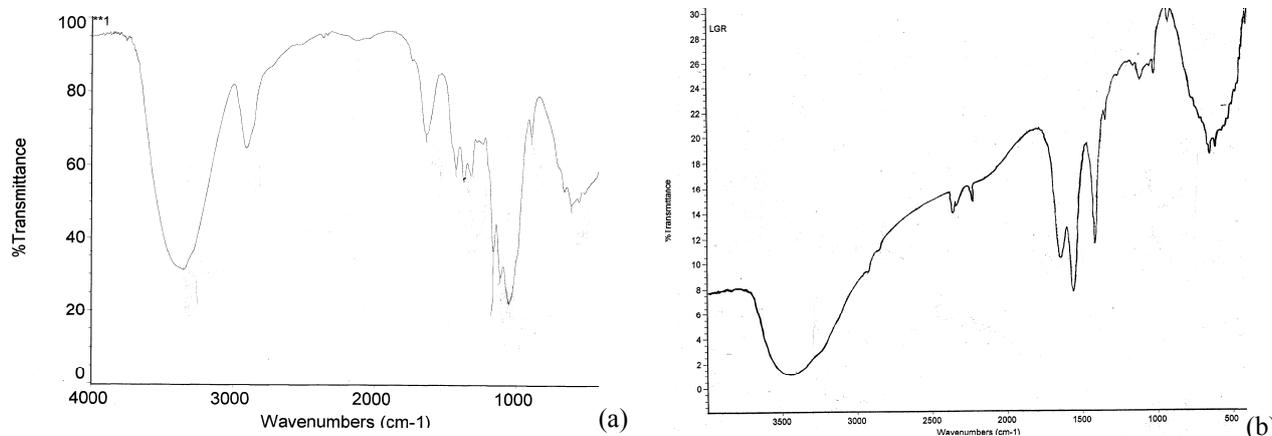

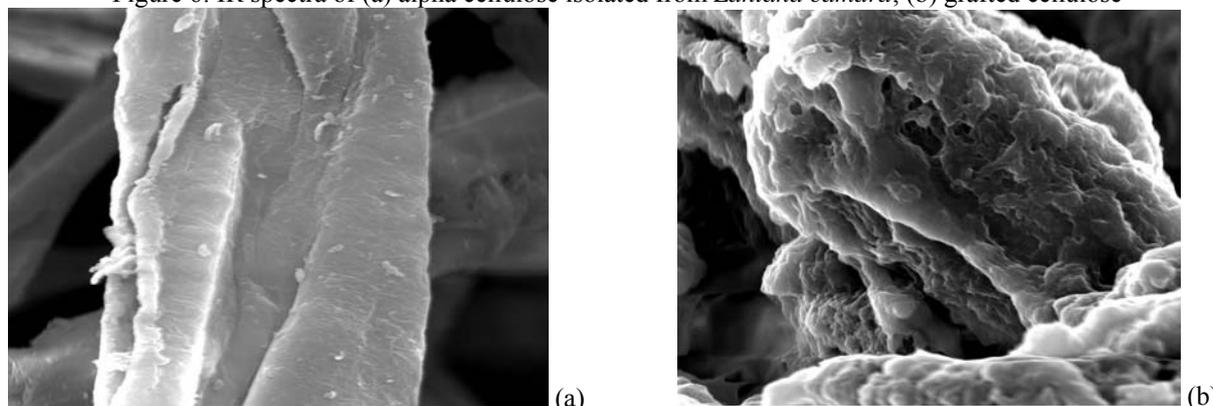Figure 6: IR spectra of (a) alpha cellulose isolated from *Lantana camara*; (b) grafted cellulose

Figure 7: SEM of (a) alpha cellulose isolated from *Lantana camara*; (b) grafted cellulose (×3000)
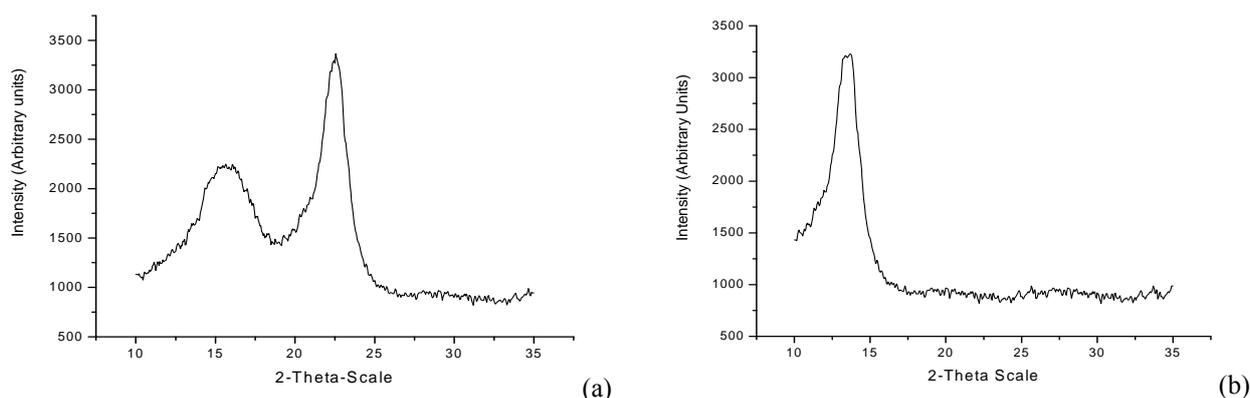
Figure 8: WAXD of (a) alpha cellulose isolated from *Lantana camara*; (b) grafted cellulose
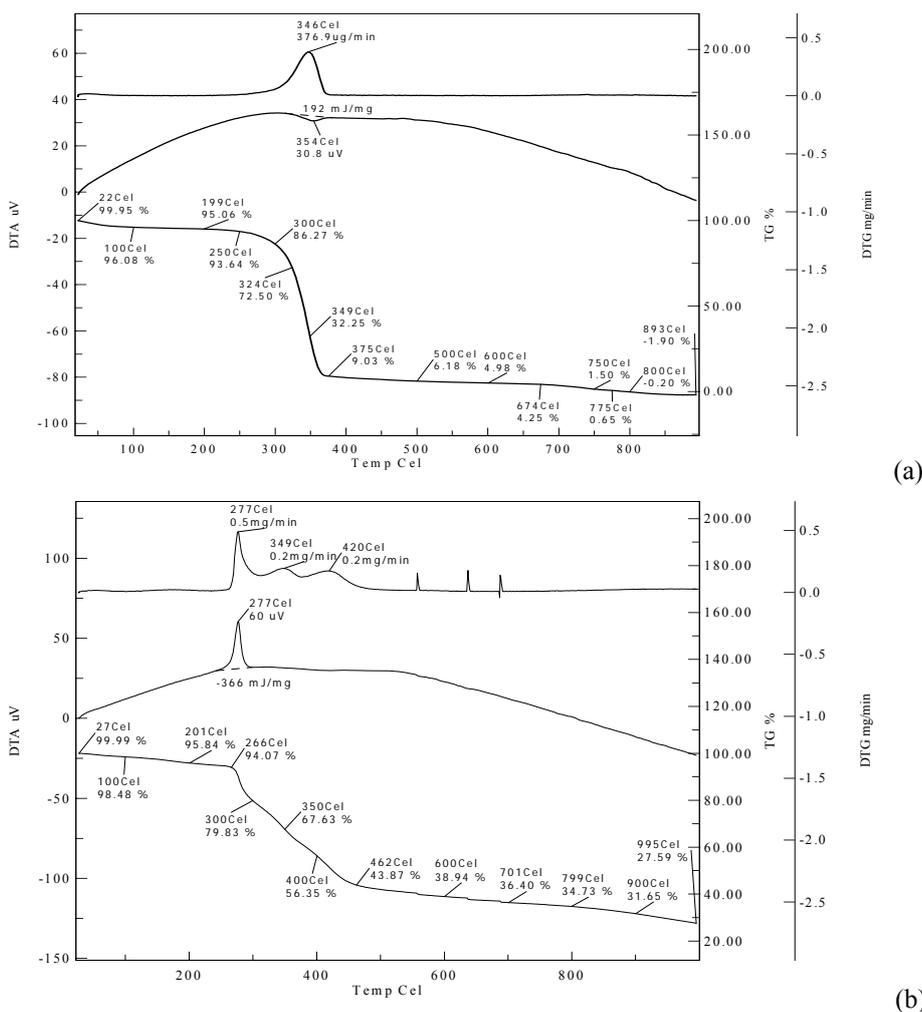

Figure 9: TGA/DTA of (a) alpha cellulose isolated from *Lantana camara*; (b) grafted cellulose

In the following decomposition stage (400-900 °C), 25.70 wt% was lost, due to the volatilization of smaller compounds. Compared to crude cellulose, the decomposition temperature of grafted cellulose can be attributed to swelling of the cellulose chains, as due to a decrease in its crystallinity on grafting.

Water sorbency

The WRV of the ungrafted sample was of 13.45 g/g, while that of the grafted sample was of 5.10 g/g. On grafting, WRV decreases, indicating an increased hydrophobic nature of the fibres upon grafting, which agrees with the report of Ali *et al*.[3]

CONCLUSIONS

The alpha cellulose extracted from *Lantana camara* exhibits characteristic physico-chemical properties of dissolving cellulose. Graft copolymerization of acrylonitrile onto alpha cellulose pulp by ceric ion can be carried out in the presence of nitrogen, under an optimized set of conditions, *viz.*: concentration of CAN – 0.2 M/AGU; concentration of acrylonitrile – 15 M/AGU; concentration of HNO_3 – 0.1N in 100 mL water; grafting time – 3 h, and temperature – 30 °C for grafted cellulose. The water retention value of grafted alpha cellulose pulp was obtained as 5.10 g/g, which is much lower than that obtained with ungrafted alpha cellulose pulp. *L. camara*, therefore, seems to be a potential feedstock for the production of alpha cellulose, which can be subsequently converted into grafted cellulose for several applications.

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