Carbohydrate Polymers 86 (2011) 1519–1524

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Hydroxypropyl cellulose from α-cellulose isolated from *Lantana camara* with respect to DS and rheological behavior

Neetu Bhatt[a], P.K. Gupta[a,*], Sanjay Naithani[b]

[a] *Centre for Advanced Studies in Chemistry of Forest Products, Forest Research Institute, P.O. New Forest, Dehra Dun 248006, India*
[b] *Cellulose and Paper Division, Forest Research Institute, P.O. New Forest, Dehra Dun 248006, India*

ARTICLE INFO

Article history:
Received 4 May 2011
Received in revised form 15 June 2011
Accepted 17 June 2011
Available online 24 June 2011

Keywords:
Hydroxypropyl cellulose
Lantana camara
Hydroxypropylation

ABSTRACT

Hydroxypropylation of alpha cellulose isolated from *L. camara* was carried out with propyleneoxide in presence of sodium hydroxide under different reaction conditions. Variables studied were concentrations of sodium hydroxide and propyleneoxide, reaction temperature and time. The degree of substitution (DS) and apparent viscosity (η) were determined. The optimum conditions for preparing hydroxypropyl cellulose (DS 1.42) were 23.18 M/AGU propyleneoxide and 1 M/AGU sodium hydroxide at 70 °C for 3 h. The optimized product exhibited cold-water solubility and a clear solution in aqueous medium suggesting interesting rheological properties. The optimized product was also further evaluated with IR, SEM, TGA/DTA and WAXDs.

1. Introduction

Lantana camara, most abundant in India as one of the most troublesome weeds (Sharma & Sharma, 1989), is quite rich in lignocellulosic material. Several attempts have been made to prepare cellulose derivatives of alpha cellulose isolated from *L. camara* (Bhatt, Gupta, & Naithani, 2007, 2008).

Cellulose is the most abundant natural polymer from renewable sources. It is insoluble in most of organic and inorganic solvents, a major limitation of its application. To overcome this problem and to extend its application, a large number of cellulose derivatives have been investigated. Derivatization of cellulose give up to trisubstituted cellulose, suggesting that three hydroxyl groups are free per glucose unit that is one primary and two secondary groups which play an influential role in the preparation of cellulose derivatives (Hebeish & Guthrie, 1981).

Etherification of cellulose is one of the most important routes of cellulose derivatization. Patents disclosing the preparation of cellulose ethers date back to the early 1900s (Lilienfeld, 1912, 1916). The important cellulose ether is the HPC and methods for its manufacture have been reported in the literature (Obara, 2004; Tanno & Obara, 2003).

Water-soluble HPC is obtained by treating cellulose with propyleneoxide in dispersing medium like isopropyl alcohol. Commercial HPC, generally has an average degree of substitution ≤12% was soluble in water, samples with substitution degree ≥12% were soluble in ethanol. Hydroxypropyl cellulose is a water soluble thixotropic substance which finds application as thickeners, binders, stabilizers, emulsifiers, drilling, etc.

Water-soluble HPC was prepared by etherification of alpha cellulose from *L. camara* in a heterogeneous medium. Conditions were optimized, viz., reaction time, temperature, concentration of propyleneoxide and concentration of aqueous NaOH with respect to DS and the optimized product was examined for solubility in aqueous medium and the rheological studies were carried out.

2. Experimental

2.1. Materials

L. camara used in the study was collected from the field of Forest Research Institute, Dehra Dun, India campus. All the chemicals used were of analytical grade.

2.2. Isolation of alpha cellulose

Alpha cellulose was isolated from *L. camara* by already optimized method (Varshney et al., 2006).

2.3. Hydroxypropylation of alpha cellulose

Synthesis of hydroxypropyl cellulose was carried out in two steps, alkalization and etherification of alpha cellulose under heterogeneous conditions. Alkalization was carried out at 30 °C for 01 h

---

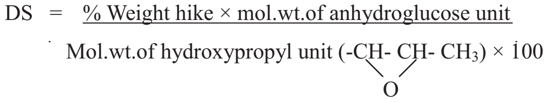
* Corresponding author. Tel.: +91 9358126046/1352224207; fax: +91 662 2154459.
E-mail address: guptapk@icfre.org (P.K. Gupta).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.06.054

and NaOH 0.5–2 M/AGU was added to a vigorously stirred slurry of α-cellulose (2 g) in 40 ml iso-propanol. The excess of alkali was squeezed out from the alkaline mixture. The alkaline alpha cellulose is then stirred with 11.59–46.36 M/AGU of propylene oxide for 2–4 h at 50–90 °C. Further the reaction mixture was cooled and washed with isopropanol followed by acetone and dried at 45 °C in oven. *Yield*: 105–144%

2.4. Analysis and measurement—determination of degree of substitution (DS)

The degree of substitution (DS) of hydroxypropylation cellulose was calculated by the following formula (Chauhan, Bhatt, Kumar, & Lal, 2002).



$$DS = \frac{\%\ \text{Weight hike} \times \text{mol.wt.of anhydroglucose unit}}{\text{Mol.wt.of hydroxypropyl unit } (\text{-CH- CH- CH}_3) \times 100}$$

2.5. Determination of apparent viscosity (η)

The apparent viscosity (η) of products (5.0% solution in water) was determined at the shear rate of 3.4 s^{-1} using a Brookfield Digital Viscometer model 'RVTD', Stoughton, USA. Apparent viscosity of the optimized product was also determined at different shear rates ranging from 3.4 to 34 s^{-1}. All measurements were made at temperature 25 ± 1 °C.

2.6. IR spectra

Infrared (IR) spectra of hydroxypropyl cellulose and extracted cellulose were recorded on a JOSCO FT-IR 5300 spectrophotometer, Tokyo, Japan, using KBr disk pallets from 4000 to 400 cm^{-1} with resolution of 2 cm^{-1} with a five times scan per sample.

2.7. Scanning electron microscope

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

2.8. Thermal studies (TGA/DTA)

Thermogravimetric analyses of the samples were carried out using Perkin Elmer (Pyris Diamond), Massachusetts, USA, in nitrogen with rate 10 °C/min.

2.9. Wide angle X-ray diffractions (WAXDs)

WAXDs of solid samples were recorded using a Bruker AXS D8 Advance X-ray powder diffractometer, Wisconsin, USA, with a Cu KÜ target.

3. Results and discussion

Hydroxypropyl cellulose was prepared by reacting alkali cellulose with propylene oxide at elevated temperatures and pressures. As indicated in the following equations, the alkali-catalyzed hydropropyl ether formation is accompanied by reaction of water molecule with propylene oxide molecule. The propylene oxide can be substituted on cellulose by ether linkage at the three reactive hydroxyls present on each anhydroglucose monomer unit of cellulose chain. The secondary hydroxyl available in a side chain is available for further reaction with the oxide, which results in the formation of side chains containing more than one mole of combined propylene oxide.

Hydroxypropylation of α-cellulose isolated from *L. camara* was optimized by varying the process parameters such as reaction time, temperature, concentration of propyleneoxide and concentration of aqueous NaOH with respect to DS and η (Table 1). Each of the parameters was varied one by one keeping the remaining parameters constant in the reaction. Degree of substitution (DS) and η was determined and its dependence on each of the variables was investigated.

Main reaction

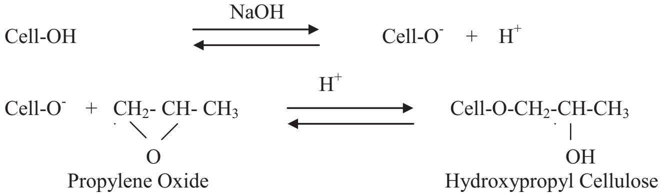


Table 1
Reaction parameters used in hydroxypropylation onto *Lantana* cellulose.

Exp/number	NaOH			PO			DS	Viscosity 5% (cps)
	Time (h)	Temp. (°C)	Concn. (M/AGU)	Concn. (M/AGU)	Time (h)	Temp. (°C)		
1)a	2	30	0.5	34.17	3	70	0.736	15
b			1				1.368	120
c			1.5				1.005	75
d			2				0.642	5
2)a	2	30	1	11.59	3	70	1.089	75
b				23.18			1.42	150
c				34.17			1.368	120
d				46.36			0.949	50
3)a	2	30	1	23.18	2	70	0.935	50
b					2.5		1.326	90
c					3		1.42	150
d					3.5		1.34	110
e					4		0.614	15
4)a	2	30	1	23.18	3	50	0.823	20
b						60	1.019	75
c						70	1.42	150
d						80	1.22	90
e						90	0.977	50

In all the experiments 2 g *Lantana* cellulose was used.

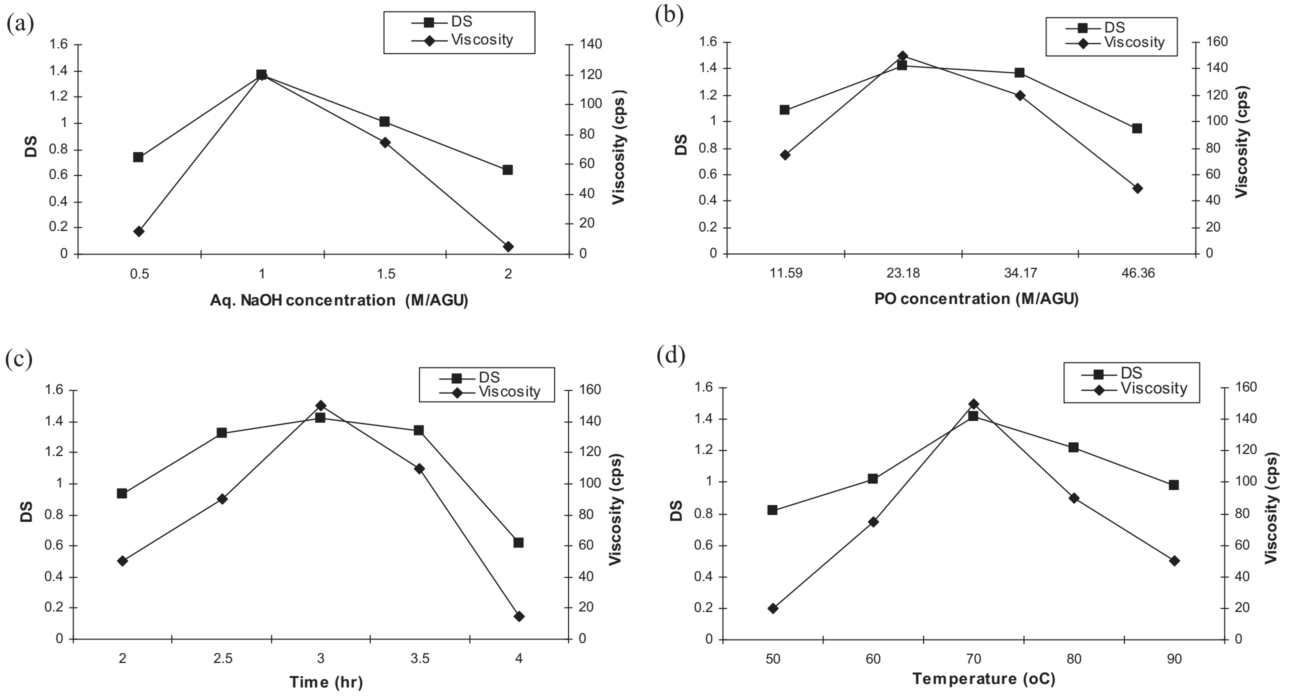
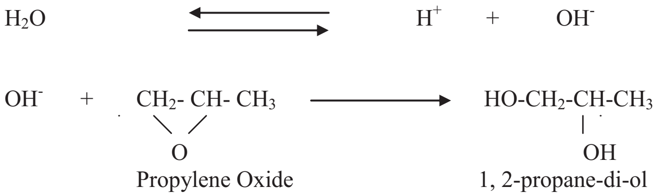


Fig. 1. Effect of (a) NaOH concentration, (b) PO concentration, (c) time and (d) temperature on DS of HPC.

Side reaction



3.1. Effect of NaOH concentration

Performing the reaction at 70 °C for 3 h with concentration of PO (34.17 M/AGU), effect of NaOH concentration (0.5–2 M/AGU) on DS and η was investigated and the results are illustrated in Fig. 1(a). It was observed that on increasing the concentration of aqueous NaOH from 0.5 to 1 M/AGU the DS increased from 0.736 to 1.368. This may be explained in light of better and more uniform accessibility of the cellulose chains within the fibre at such a higher concentration. Further increase in the concentration of alkali up to 1.5 M/AGU caused a decrease in DS which could be attributed to the depolymerization of the cellulose (Klemm, Phillip, Heinze, Heinze, & Wagenknetch, 1998). The valve of η was found to be

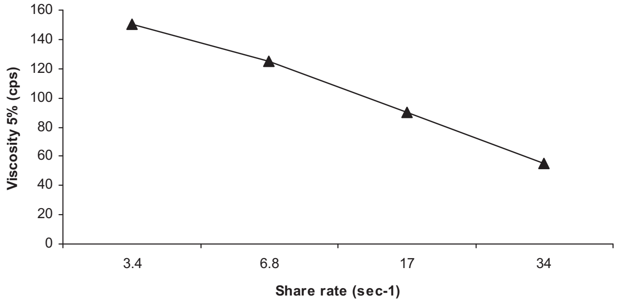


Fig. 2. Effect of shear rates on the apparent viscosity of the aqueous solution (5%) of the optimized HPC.

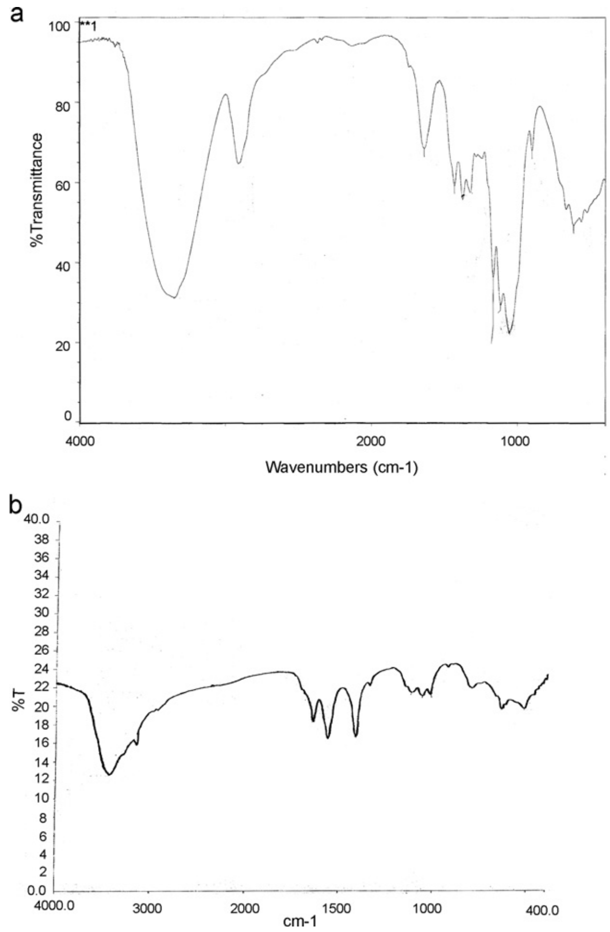


Fig. 3. IR spectra of (a) alpha cellulose isolated from *L. camara* and (b) hydroxypropyle cellulose.

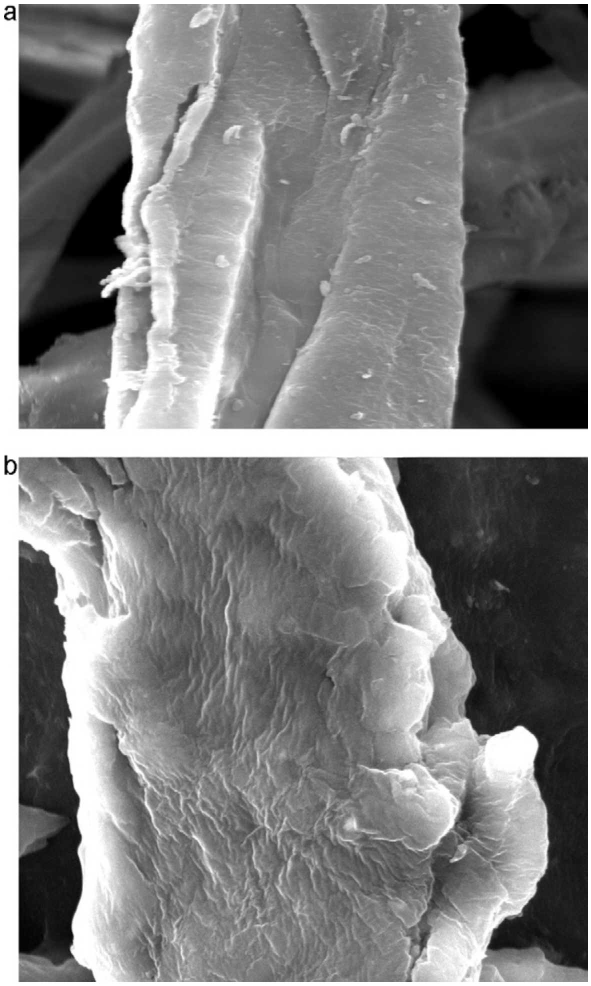


Fig. 4. SEM of (a) alpha cellulose isolated from *L. camara* and (b) hydroxypropyle cellulose (3000×).

120 cps at 1 M/AGU and on further increase resulted, decline in the value of η from 75 to 5 cps. These results suggest that, during hydroxypropylation, with further increase in the concentration of NaOH, a significant degradation of cellulose molecule occur causing a decline in the molar mass and consequently a drop in the viscosity.

3.2. *Effect of propylene oxide (PO) concentration*

Using NaOH concentration 1 M/AGU, hydroxypropylation time of 3 h and temperature 70 °C, the effect of PO concentration on DS and η was examined by varying PO concentration from 11.59 to 46.36 M/AGU. The results are plotted in Fig. 1(b). It was observed that DS increased from 1.089 to 1.420 on increasing PO concentration up to 23.18 M/AGU. With increase in concentration of PO, value of η also changed in a parallel fashion from 75 to 150 cps and then decreases by 50 cps with further increase in PO concentration. This could be associated with greater availability of PO molecules in the vicinity of cellulose at increase PO concentration. Above this concentration the side reaction between the PO and water molecules become more significant reducing thereby the input of PO.

3.3. *Effect of time of hydroxypropylation*

Effect of duration on DS and η was investigated by performing hydroxypropylation at different length of time (2–4 h) using NaOH concentration 1 M/AGU, PO concentration 23.18 M/AGU and temperature 70 °C. The effect is illustrated in Fig. 1(c). On increasing the hydroxypropylation time from 2 to 3 h, DS was found to increase from 0.935 to 1.420. However, with further increase in the time, DS fall down to 0.614. The increment in DS on increasing the duration of hydroxypropylation up to 3 h is due to the direct consequence of the favourable effect of time to induce better contact between the PO and the low rate of hydroxypropylation. Significant decrease in DS on prolonging the hydroxypropylation time may probably be due to the deactivating effect of the additional methyl group (Klemm et al., 1998). The valve of η increases from 50 to 150 cps on increasing time from 2 to 3 h and further increase results, decline in the value of η from 110 to 15 cps.

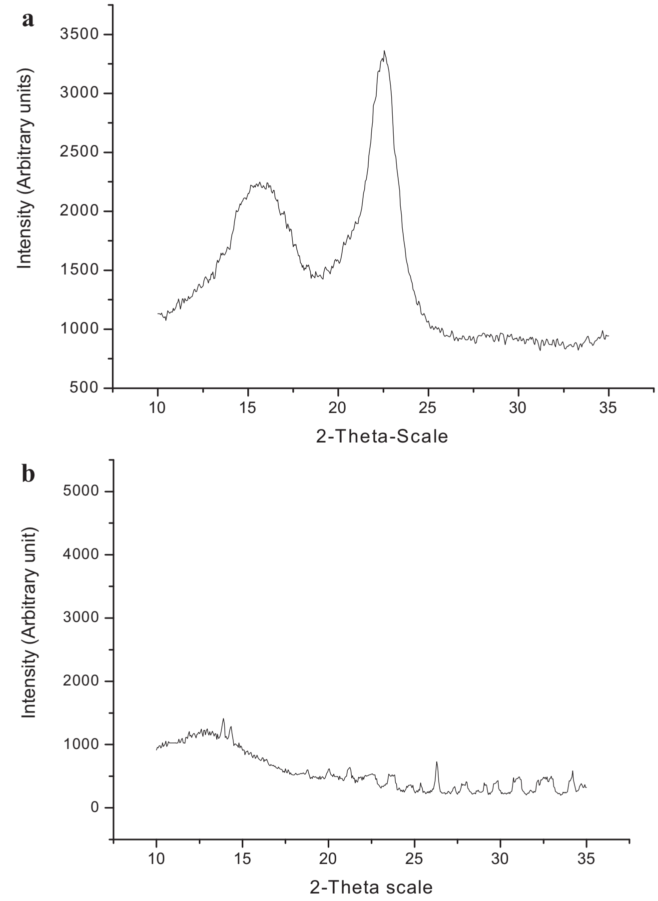


Fig. 5. WAXD of (a) alpha cellulose isolated from *L. camara* and (b) hydroxypropyle cellulose.

3.4. *Effect of temperature*

With NaOH concentration 1 M/AGU, hydroxypropylation time of 3 h and PO concentration 23.18 M/AGU, the effect of temperature on DS was studied by varying the temperature from 50 °C to 90 °C. As shown in Fig. 1(d), an increase in DS from 0.823 to 1.420 was observed with the increase in temperature from 50 °C to 70 °C followed by a fall in DS at 80 °C also with increase in temperature, value of η also changed in a parallel fashion from 20 to 150 cps and then decreases by 50 cps with further increase in PO concentration. The increase in DS up to 70 °C could be linked with the advantageous effect of temperature on main reaction due to lower reaction rate. Lowering of DS beyond 80 °C could be attributed to the homopolymerization of PO.

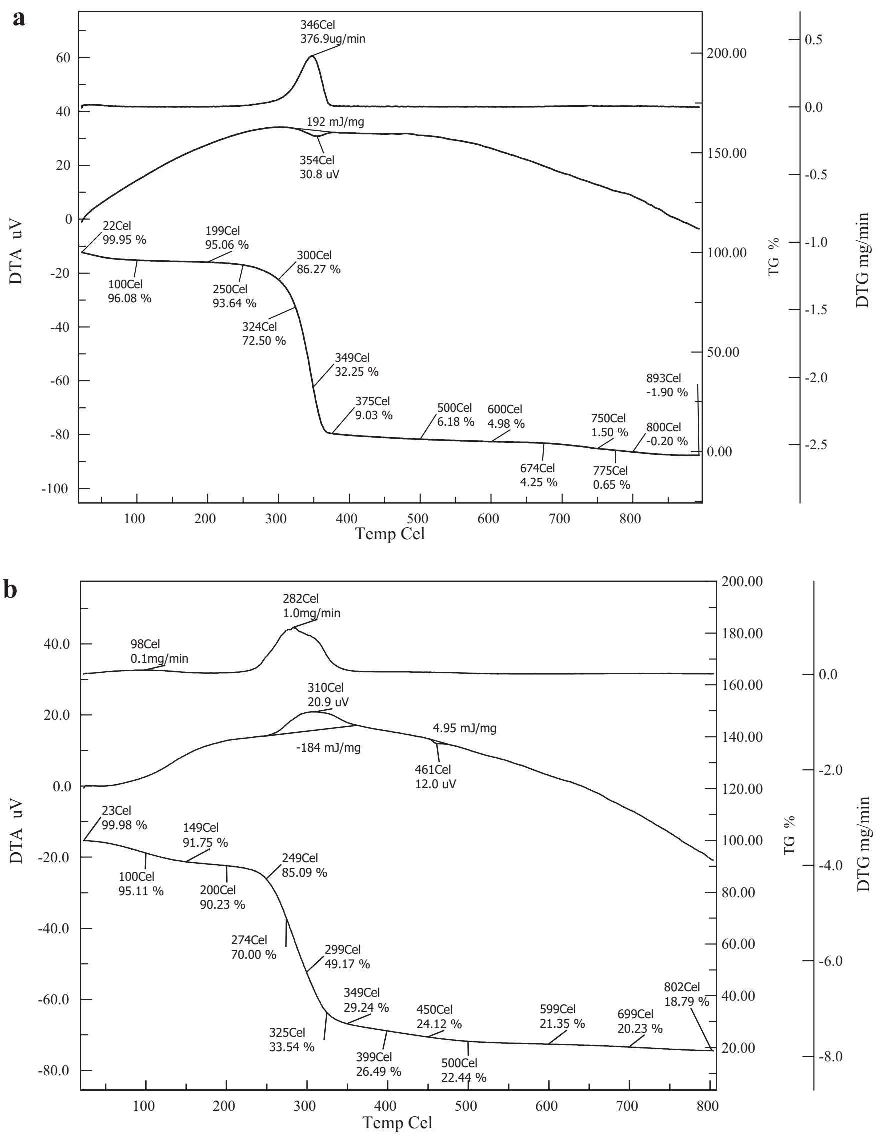


Fig. 6. TGA/DTA of (a) alpha cellulose isolated from *L. camara* and (b) hydroxypropyle cellulose.

3.5. *Rheological characterization*

Consideration of the end uses for HPC makes it immediately apparent that the rheological properties of the HPC solution are of prime importance. Rheological properties of the optimized HPC were, therefore, studied in which apparent viscosity (η) of its 5% aqueous solution was determined and influence of different shear rates on the apparent viscosity was also examined. The values of η of this solution as a function of shear rates are given in Fig. 2. It is evident that η is a decreasing function of the shear rate. Thus, the solution of the optimized product exhibits non-Newtonian pseudo plastic behavior.

3.6. *IR characterization*

The IR spectra of hydroxypropyl cellulose (Fig. 3(b)) displays two prominent bands at 3398 and 1060 cm^{-1} and a shoulder at 2974 cm^{-1} which are assigned to –OH stretching, $-CH_2-O-CH_2$ stretching and –CH stretching of the methyl group characteristics for the hydroxypropyl group, but absent in alpha cellulose (Fig. 3(a)) thereby indicating the formation of hydroxypropyl cellulose.

3.7. *Scanning electron microscopy*

Fig. 4a and b shows the scanning electron micrographs of pure alpha cellulose and hydroxypropyl cellulose fibre, respectively. The surface topology of raw alpha cellulose was found to be even, while the modified alpha cellulose revealed that the fibre surface had deposit of hydroxypropyl molecules and the evenness of the fibre surface was not present.

3.8. *Wide angle X-ray diffraction (WAXD)*

As shown by the WAXD studies, the degree of crystallinity of extracted cellulose (Fig. 5(a)) is 53%. On hydroxypropylation

(Fig. 5(b)) this was further reduced to 21% due to less intermolecular chain interactions. Such decrease in crystallinity was desirable in the direction of maximum homogenization of linear chain of hydroxypropyl cellulose for network formation and the surface-active nature of hydroxypropyl cellulose should have further contribution to facilitate uniform network formation (Chauhan, Lal, & Mahajan, 2004).

3.9. Thermal degradation behavior

DTA curves for parent cellulose and optimized hydroxypropyl cellulose samples are shown in Fig. 6(a) and (b), respectively. In case of cellulose, only one endothermic peak is observed while for hydroxypropyl cellulose derivative two endothermic peaks are observed at various temperatures. Endothermic peaks occurred at 346 °C in cellulose and at 98 °C and 282 °C in case of hydroxypropyl cellulose. These endothermic peaks are formed due to decomposition which occurred in cellulose and hydroxypropyl cellulose. In hydroxypropyl cellulose these endothermic peaks are due to semi-melting and decomposition of the hydroxypropyl molecule. TGA curve for parent cellulose sample shows that after initial loss of moisture at 100 °C, loss of weight of cellulose occurred. For cellulose, this loss was attributed to the actual pyrolysis by minor decomposition reaction at about 250 °C and 324 °C and major decomposition proceeded at 349 °C and 375 °C. TGA curve for hydroxypropyl cellulose revealed that after the initial loss of moisture at 100 °C, decomposition has taken place due to pyrolysis and volatilization of hydroxypropyl group at various successive temperatures, viz., 200 °C (90.23%), 274 °C (70.00%), 299 °C (49.17%), 349 °C (29.24%), 599 °C (21.35%) and with 18.79% of the residue was left showing that this left amount of the product is stable at 800 °C. Decomposition temperature of hydroxypropyl cellulose derivative as compared to crude cellulose can be attributed to swelling of cellulose chains due to decrease in its crystallinity on hydroxypropylation.

4. Conclusion

From alpha cellulose isolated from *L. camara* water-soluble HPC ether was prepared by propylation of alpha cellulose using propyleneoxide in a heterogeneous medium. Conditions were optimized, viz., reaction time, temperature, concentration of propyleneoxide and concentration of aqueous NaOH with respect to DS was prepared. Using optimized set of conditions, viz., 1 M/AGU NaOH per 2 g of alpha cellulose, reaction time 3 h, temperature 70 °C and concentration of propyleneoxide 23.18 M/AGU, HPC ether of DS 1.420 was obtained. The optimized product exhibited cold-water solubility and gave clear solution in aqueous medium. The apparent viscosity (η) of optimized product in aqueous medium at 5.0% solution concentration was 150 cps at the shear rate 3.4 s^{-1} and temperature 25 ± 1 °C. The HPC prepared from alpha cellulose from *L. camara* may be utilized as thickener in pharmaceuticals industry.

References

Bhatt, N., Gupta, P. K., & Naithani, S. (2007). *Cellulose Chemistry and Technology*, *41*(7–8), 371–378.

Bhatt, N., Gupta, P. K., & Naithani, S. (2008). *Journal of Applied Polymer Science*, *108*, 2895–2901.

Chauhan, G. S., Lal, H., & Mahajan, S. (2004). *Journal of Applied Polymer Science*, *91*, 479–488.

Chauhan, G. S., Bhatt, S. S., Kumar, S., & Lal, H. (2002). *Journal of Polymer Materials*, *19*, 403–412.

Hebeish, A., & Guthrie, J. T. (1981). *The chemistry and technology of cellulose copolymers*. Berlin: Springer-Verlag.

Klemm, D., Phillip, B., Heinze, T., Heinze, U., & Wagenknetch, W. (1998). *Comprehensive cellulose chemistry* Weinheim: Wiley-VCH., p. 207.

Lilienfeld, L. (1912). *British Patent* 12,854.

Lilienfeld, L. (1916). *US Patent* 1,188,376.

Obara, S. (2004). *US Patent* 6,680,069.

Sharma, O. P., & Sharma, P. D. (1989). *Journal of Scientific and Industrial Research*, *48*, 471–478.

Tanno, F. & Obara, S. (2003). *US Patent* 6,559,134.

Varshney, V. K., Gupta, P. K., Naithani, S., Khullar, R., Bhatt, A., & Soni, P. L. (2006). *Carbohydrate Polymers*, *63*, 40–45.