Hydroxypropylation of Cellulose Isolated from Bamboo (*Dendrocalamus strictus*) with Respect to Hydroxypropoxyl Content and Rheological Behavior of the Hydroxypropyl Cellulose

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Received 16 March 2007; accepted 30 November 2008
DOI 10.1002/app.30205
Published online 28 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Bamboo, a lignocellulosic material, is a renewable source of interest as feedstock for production of cellulose derivatives by chemical functionalization. Optimization of hydroxypropylation of cellulosic material (average DP 816), isolated from bamboo (*Dendrocalamus strictus*) was, therefore, performed with respect to maximum percent hydroxylpropoxyl (% HP) contents under varying reaction conditions and studying their effect on the % HP. The optimized reaction conditions were aqueous NaOH concentration 22%, propylene oxide concentration 17.4 mol/AGU, temperature 50°C, duration of hydroxypropylation 4 h to yield hydroxypropyl cellulose of % HP 65.89. The η_{app} of 1 and 2% solutions of the optimized product showed it to be non-Newtonian pseudoplastic. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2450–2455, 2009

Key words: bamboo; hydroxypropyl cellulose; hydroxypropoxyl content; apparent viscosity

INTRODUCTION

Renewable raw materials are gaining considerable importance because of the limited existing quantities of fossil supplies and the recent environment-conservative regulations.[1] In this regard, cellulose-rich biomass acquires enormous significance as chemical feedstock, since it consists of cellulose, hemicellulose, and lignin, which contain many functional groups suitable to chemical derivatization[2] *Eucalyptus* cellulose and *Musanga cecropioides* wood have been modified into carboxymethyl cellulose.[3,4] Graft copolymerization of acrylonitrile and methyl methacrylate onto jute fibers and pineapple leaf fibers has been examined.[5–8] Low quality woods as well as industrial wastes of wood have been used to produce a thermoplastic material through cyanoethylation.[9] Recently, conducted investigations on reactivity of fibers of *Agave lechuguilla* and *Agave fourcroydes* under chemical modification reactions like carboxymethylation, sulfation, acetylation, tritylation, and subsequent carboxymethylation as well as oxidation, and grafting have demonstrated suitability of the agave fibers as a potential feed stock for producing cellulose derivatives for a variety of applications.[10–12] The goal of these modifications is to adjust the properties of macromolecule for different purposes and to increase their consumption.

Bamboo belonging to the grass family *Poaceae* is an abundant renewable natural resource capable of production of maximum biomass per unit area and time as compared with counterpart timber species.[13] Since bamboo stem consists almost entirely of cellulose, hemicellulose (xylans, arabians, polyuronides etc), and lignin,[14] the biomass of bamboo can be used as a feedstock for production of a variety of cellulose derivatives for different broader applications by chemical modification.

Hydroxypropyl cellulose (HPC) is nonionic water-soluble cellulose ether with a remarkable combination of properties. It shows organic solvent solubility, thermo plasticity, and surface activity with the aqueous thickening and stabilizing properties characteristic of other water-soluble cellulose polymers available.[15] HPC is manufactured by reacting alkali cellulose with propylene oxide at elevated temperatures and pressures. As indicated in the following equations, the alkali-catalyzed hydropropyl ether

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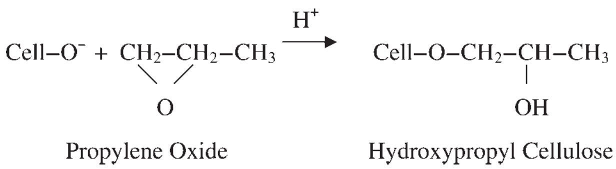
Contract grant sponsors: Indian Council of Forestry Research & Education (ICFRE), Dehra Dun.

formation is accompanied by reaction of water molecules with propylene oxide molecules. The propylene oxide can be substituted on cellulose by ether linkage at the three reactive hydroxyls present on each anhydroglucose monomer unit of cellulose chains. 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. Because of the possible growth of hydroxypropyl side chains by further add-on of propylene oxide, two criteria are necessary for a macromolecular characterization of HPC, i.e., the DS denoting the average number of cellulosic hydroxyl groups per AGU involved in the reaction and the molar substitution (MS) denoting the average number of propylene oxide molecules added per AGU.[16]

Main Reactions

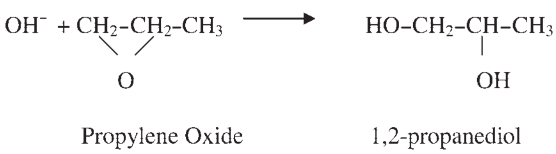
$$\text{Cell–OH} \underset{}{\overset{\text{NaOH}}{\rightleftharpoons}} \text{Cell–O}^- + \text{H}^+ \qquad (1)$$



(2)

Side Reactions

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \qquad (3)$$



(4)

As a part of our ongoing program on chemical modification of cellulose isolated from different sources,[17–20] we were interested to study the derivatization of bamboo cellulose through substitution and grafting reactions. The present communication describes the optimization of hydroxypropylation of cellulose (average DP 816) derived from *Dendrocalamus strictus* bamboo, performed in isopropanol solvent medium by varying the process parameters such as concentration of NaOH and propylene oxide, temperature, and duration of reaction and studying their effect on the hydroxypropoxyl content. Each of these parameters was varied one by one keeping the remaining parameters constant in the reaction. Based on the values of apparent viscosity (η_{app}), the optimized product was characterized rheologically.

EXPERIMENTAL

Materials

D. strictus, a widely distributed and commonly cultivated bamboo in India was used for isolation of the cellulose. Cellulose (yield 35%) with following composition was isolated as per the standard Tappi method (TAPPI T2003 OM-88):

Cellulose 90.09; Hemicellulose 8.91; Lignin 0.44; Ash 0.56; Average D.P. 816.

Other chemicals (NaOH pellets, MCA, methyl alcohol, isopropyl alcohol, potassium hydroxide, perchloric acid, and sulfuric acid) were of laboratory grade.

Methods

Hydroxypropylation of cellulose

The reaction was carried out in two steps—alkalization and etherification of cellulose under heterogeneous conditions. Aqueous NaOH (14–26% w/v) was added to slurry of finely pulverized cellulose (1.0 g) in isopropanol (10 mL) at ambient temperature, with continuous stirring for 1 h. Alkali cellulose, thus, formed was pressed to remove alkali and transferred to a three-necked round-bottom flask of capacity 250 mL, fitted with a coiled condenser and nitrogen inlet. Ice-cold water was circulated in the condenser throughout the reaction. Propylene oxide (11.6–29 mol/AGU), isopropanol (50 mL) and water (2 mL) were added and the reaction was allowed to proceed at desired temperature for fixed duration (2–5 h). After neutralizing the excess alkali with acetic acid the synthesized HPC samples were dissolved in water and precipitated in acetone, filtered, and washed in acetone and dried at 60°C in oven.

Determination of percent hydroxypropoxyl content and MS

The percent hydroxypropoxyl content was determined as reported in the literature.[21] This method involves the hydrolysis of hydroxypropyl group to propylene glycol which in turn is dehydrated to propionaldehyde and the enolic form of allyl alcohol. These products are measured spectrophotometrically after they are reacted with ninhydrin to form a purple color.

Determination of apparent viscosity (η_{app})

Apparent viscosity of the optimized product was determined by a Brookfield Digital Viscometer model "RVTD" (Stoughton, MA), at different shear rates ranging from 3.4 to 34 s^{-1}. All measurements were made at 25 ± 1°C.

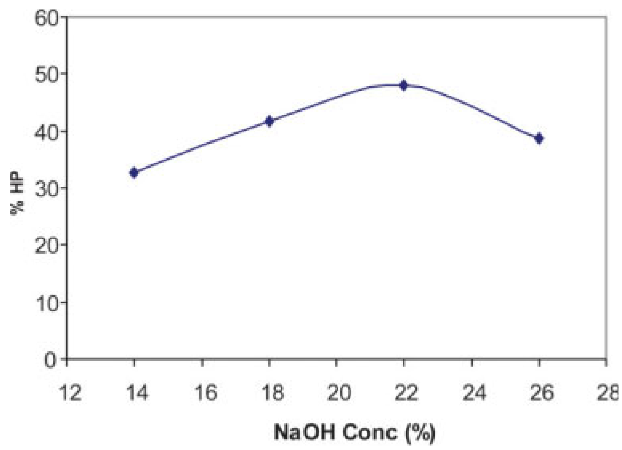


Figure 1 Effect of NaOH concentration on % HP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

IR analysis

The FTIR spectra were recorded on a JASCO FTIR 5300 using KBr pellets.

Scanning electron microscopy studies

Scanning electron microscopy (SEM) images at 1000 and 5000 magnification were obtained for crude cellulosic material and hydroxypropylated cellulose using Leo 435 VP SEM (Cambridge, England). The fibers were laid down on the aluminum stub using a conductive adhesive tape and were sputter coated with gold.

RESULTS AND DISCUSSION

Effect of NaOH concentration

The effect of NaOH concentration (14 to 26%) on percent hydroxylpropoxyl (% HP) was investigated and its results are illustrated in Figure 1. It was observed that on increasing the concentration of aqueous NaOH from 14 to 22%, the % HP increased to 48.12%. This may be explained in light of better and more uniform accessibility of the cellulose chains within the fiber at such a higher concentration. Further increase in the concentration of alkali up to 26% caused a decrease in % HP which could be attributed to the depolymerization of the cellulose.[16]

Effect of propylene oxide concentration

Using the optimized NaOH concentration of 22%, the effect of propylene oxide (PO) concentration on % HP was examined by varying PO concentration from 11.6 mol/AGU to 29 mol/AGU. The results are plotted in Figure 2. It was observed that % HP

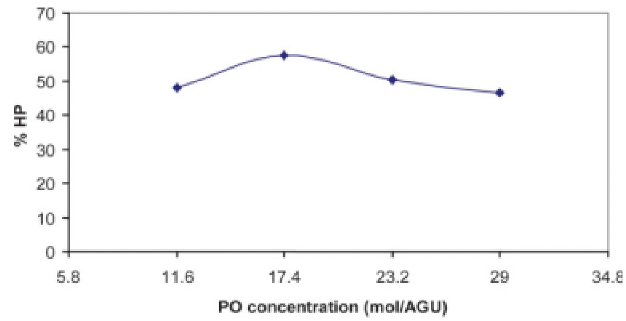


Figure 2 Effect of PO concentration on % HP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increased to 57.37% on increasing PO concentration up to 17.4 mol/AGU. This could be associated with greater availability of PO molecules in the vicinity of cellulose at increased PO concentration. Above this concentration, the side reaction between the PO and water molecules becomes more significant reducing thereby the input of PO. So, further increase in PO concentration resulted in a decrease in % hydroxypropoxyl content.

Effect of temperature

With NaOH concentration of 22% and PO concentration 17.4 mol/AGU, the effect of temperature on % HP was studied by varying the temperature from 30 to 60°C. As shown in Figure 3, an increase in % HP (from 62.48 to 68.33%) was observed with the increase in temperature from 40 to 50°C followed by leveling-off in % HP. The increase in % HP up to 50°C could be linked with the advantageous effect of temperature on main reaction due to lower reaction rate. The leveling-off of % HP beyond 50°C could be attributed to the homopolymerization of PO.

Effect of duration of hydroxypropylation

Conducting the reaction at 50°C, using the optimized concentration of NaOH (22%) and PO (17.4

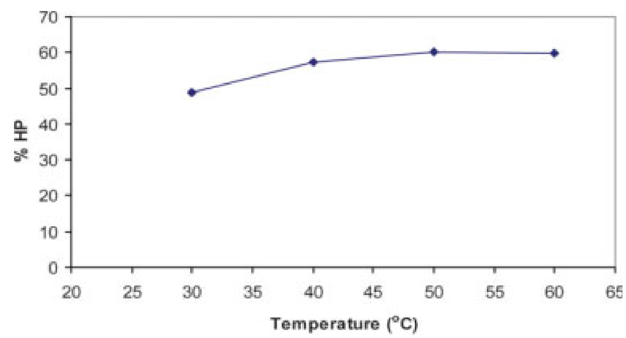


Figure 3 Effect of temperature on % HP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

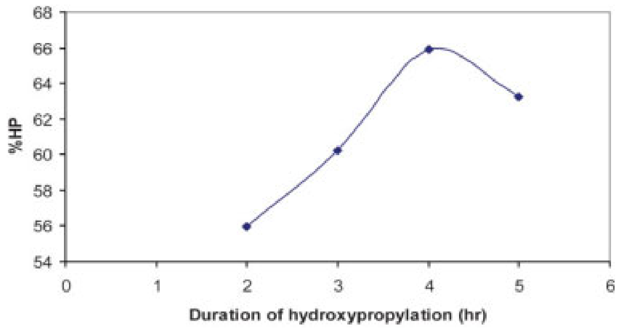


Figure 4 Effect of duration of hydroxypropylation on % HP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

mol/AGU), the effect of duration on % HP was investigated by performing hydroxypropylation at different length of time (2 to 5 hr). As illustrated in Figure 4, on increasing the hydroxypropylation time from 2 to 4 hr, % HP was found to increase from 55.98 to 65.89%. However, further increase in the time resulted in slight decrease in % HP. The increment in % HP on increasing the duration of hydroxypropylation up to 4 h is due to the direct consequence of the favorable effect of time to induce better contact between the PO and the hydroxyl groups both originally present in the system and newly formed, owing to the low rate of hydroxypropylation. The decrease in % HP on prolonging the hydroxypropylation time may probably be due to the deactivating effect of the additional side chains.[16]

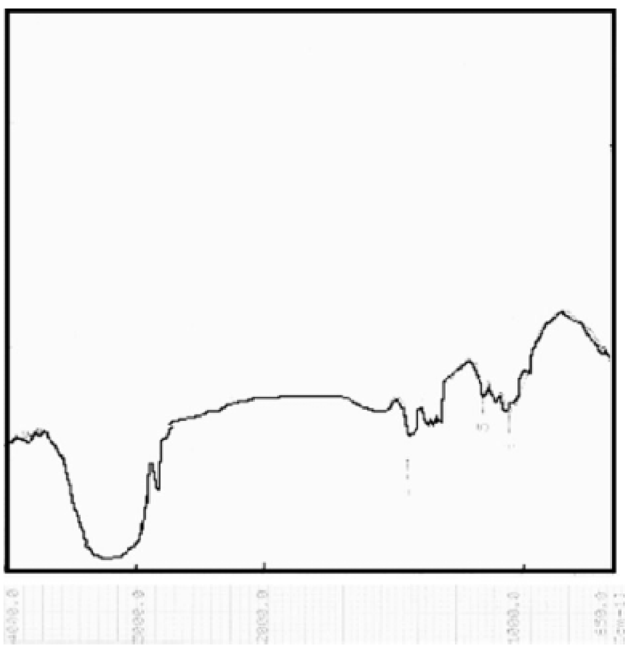


Figure 6 FTIR spectra of cellulosic material derived from bamboo.

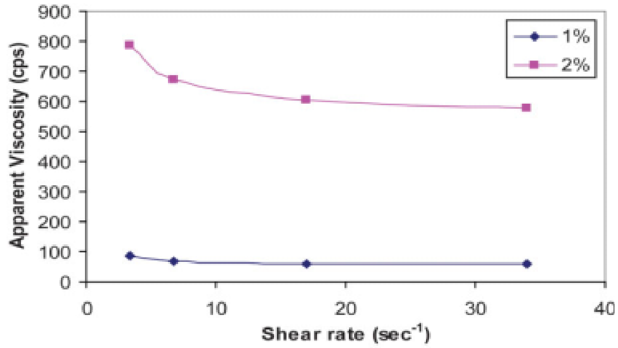


Figure 5 Effect of shear rates on the apparent viscosities of the aqueous solutions (1 and 2%) of the optimized HPC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The optimum reaction conditions obtained for hydroxypropylation of cellulosic material derived from bamboo (*D. strictus*) were NaOH concentration 22%, propylene oxide concentration 17.4 mol/AGU, temperature 50°C, duration of hydroxypropylation 4 h. The hydroxypropoxyl content of optimized HPC sample is 65.89%.

IR characterization

The FTIR spectra of the cellulosic material derived from bamboo and the optimized HPC sample (hydroxypropxyl content 65.89%) were recorded and are shown in Figures 6 and 7. Besides the typical signals of cellulose backbone (υ_{OH} 3398 cm^{-1}, υ_{CH} 2890 cm^{-1}, and 1419 cm^{-1}, υ_{COC} 1060 cm^{-1}, $\upsilon_{\beta\text{-linkage}}$ 890 cm^{-1}), the FTIR spectra of the optimized HPC displays a shoulder at 2974 cm^{-1}, which was assigned to the —CH stretching of the methyl group characteristic for the hydroxypropyl group,

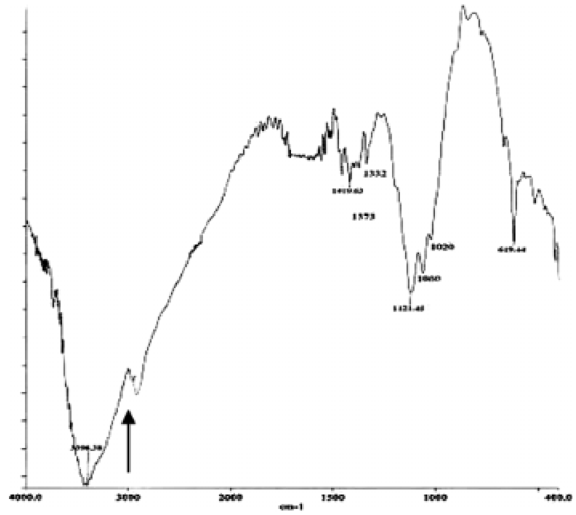


Figure 7 FTIR spectra of optimized HPC sample.

furnishing thereby the evidence that hydroxypropylation has occurred.

Surface morphology

SEM images at magnification 1000 and 5000 were obtained for parent and hydroxypropylated cellulosic material and are presented in Figures 8 and 9. A comparison of these images depicts the transformation in surface morphology of bamboo cellulose on hydroxypropylation. The parent bamboo cellulose exhibits a relatively smooth surface compared with HPC. Moreover, the deposition of PO on the surface and in the intercellular region of the bamboo cellulose fiber is clearly visible.

Rheological characterization

Consideration of the end uses for HPC makes it immediately apparent that the rheological properties of the HPC solutions are of prime importance. Rheological properties of the optimized HPC were, therefore, studied in which apparent viscosity (η_{app}) of its 1 and 2% aqueous solution was determined and influence of different shear rates on the apparent viscosity was also examined. The apparent viscosity of 1 and 2% solutions, at shear rate 3.4 s^{-1}, was 85 cps and 785 cps, respectively. The trend of η_{app} of 1 and 2% solutions as a function of shear rates is shown in Figure 5. It is evident that η_{app} is a decreasing function of the shear rate. Thus, the solution of the optimized product exhibited non-Newtonian pseudoplastic behavior.

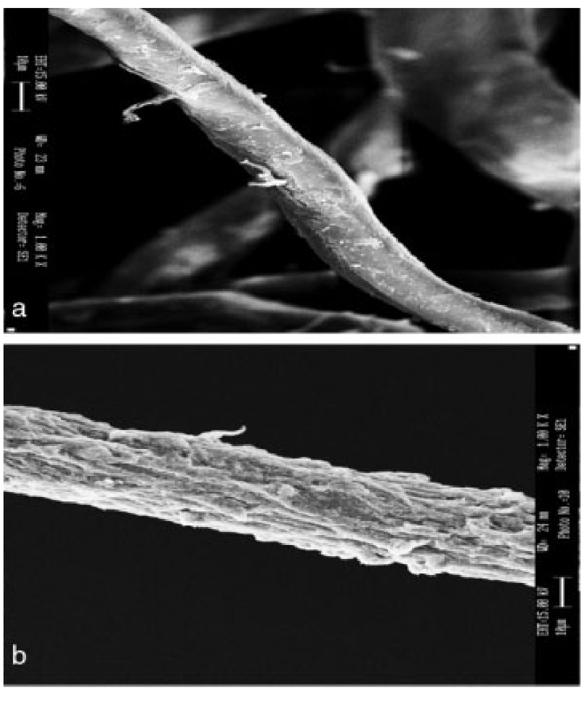


Figure 8 Scanning electron micrographs at 1000 magnification of parent cellulosic material (a) and HPC (b).

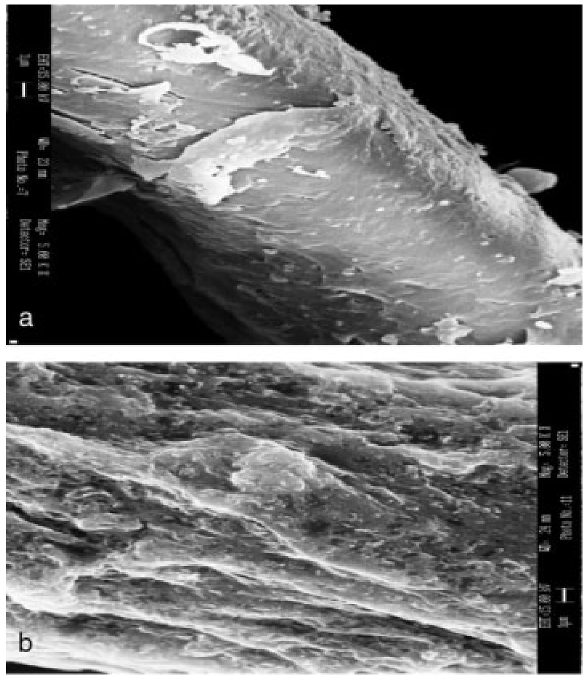


Figure 9 Scanning electron micrographs at 5000 magnification of parent cellulosic material (a) and HPC (b).

CONCLUSIONS

The optimum reaction conditions obtained for hydroxypropylation of cellulosic material derived from bamboo (*D. strictus*) (average D.P. 816) were NaOH concentration 22%, propylene oxide concentration 17.4 mol/AGU, temperature 50°C, duration of hydroxypropylation 4 h. Using these reaction conditions, a water-soluble HPC (soluble content 82% and hydroxypropoxyl content 65.89%) of low viscosity could be prepared. The apparent viscosity of 1 and 2% solutions of optimized HPC at shear rate 3.4 s^{-1} are 85 cps and 785 cps, respectively. The characterization of the optimized HPC with the aid of FTIR and SEM furnished the evidence of hydroxypropylation.

Authors are thankful to the Director, Forest Research Institute, Dehra Dun for encouragement.

References

1. Clasen, C.; Kulicke, W.-M. Prog Polym Sci 2001, 26, 1839.
2. Barkalow, D. G.; Young, R. A. J Wood Chem Technol 1985, 5, 293.
3. Spasojevic, L. D.; Majdanac, L. J.; Petrovic, S. D.; Hrabar, J. P.; Nesovic, V. M.; Galovic, Z. M.; Cvetkovic, M. D. Cell Chem Technol 1997, 31, 297.
4. Akaranta, O.; Otaigbe, J. O. E.; Onu, C. O.; Odozi, T. O. Cell Chem Technol 1988, 22, 315.
5. Patra, C. M.; Singh, B. C. J Appl Polym Sci 1994, 52, 1557.

6. Patnaik, S.; Sarangi, S.; Mohanty, A. K.; Singh, B. C. J Appl Polym Sci 1989, 37, 2099.
7. Ghosh, P.; Ganguly, P. K. J Appl Polym Sci 1994, 52, 77.
8. Samal, R. K.; Bhuyan, B. L. J. Appl Polym Sci 1994, 52, 1675.
9. Khalil, E. M. A.; El-Wakil, N. A. Cell Chem Technol 2000, 34, 473.
10. Vieira, M. C.; Heinze, T. h; Cruz, R. A.; Mendoza, A. M. Cellulose 2000, 9, 203.
11. Ramos, L. A.; Frollini, E.; Heinze, T. h. Carbohydr Polym 2005, 60, 259.
12. Cruz, R. A.; Mendoza, A. M.; Vieira, M. C.; Heinze, T. Die Angewantde Makromol Chem 1999, 273, 86.
13. Tewari, D. N.a MONOGRAPH ON Bamboo,International Book Distributors: Dehra Dun, 1995; pp 251–272.
14. The Wealth of India: 'A Dictionary of Indian Raw Materials & Industrial Products: Raw Materials'; Ambasta, S. P., Ed.; CSIR Publication: New Delhi, 1988; Vol. II B.
15. Just, E. K.; Majewicz, T. G.Cellulose ethers. Encylopedia of Polymer Science and Engineering;Krischwitz, J. I., Ed; John Wiley and sons Inc.: New York, 1998; p 3.
16. Klemm, D.; Phillip, B.; Heinze, T.; Heinze, U.; Wagenknetch, W.Comprehensive Cellulose Chemistry; Wiley-VCH: Weinheim, 1998; Vol. 2, p 207.
17. Khullar, R.; Varshney, V. K.; Naithani, S.; Heinze, T.; Vieira-Nagel, M.; Gupta, P. K.; Naithani, S.; Soni, P. L. Cell Chem Technol 2007, 40, 545.
18. Khullar, R.; Varshney, V. K.; Naithani, S.; Soni, P. L. J Nat Fibers 2006, 5, 138.
19. Khullar, R.; Varshney, V. K.; Naithani, S.; Heinze, T.; Soni, P. L. J Appl Polym Sci 2005, 96, 1477.
20. Varshney, V. K.; Gupta, P. K.; Naithani, S.; Khullar, R.; Bhatt, A.; Soni, P. L. Carbohydr Polym 2005, 63, 40.
21. Jhonson, D. P. Anal Chem 1969, 41, 859.