

Microwave-assisted synthesis of eucalyptus cellulose carbamate

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ABSTRACT

Eucalyptus dissolving pulp was derivatized to cellulose carbamate (CC), through heating alkalized cellulose with urea in a microwave oven at 160-320 W for 10-20 minutes. This preliminary study explores the effects of such factors as the energy input and reaction time on the nitrogen content and intrinsic viscosity of the CC samples obtained. The nitrogen content changed from 0.79 to 1.97 % corresponding to relatively low degree of substitution in the range of 0.09-0.24. As the energy input and reaction time increased, the nitrogen content and the intrinsic viscosity of the CC samples increased as well. The formation of CC was confirmed by the IR spectra. Furthermore, according to the observed thermal behavior, the properties of cellulose had changed upon reaction, confirming the esterification of cellulose.

KEYWORDS

Cellulose carbamate, eucalyptus dissolving pulp, microwave heating, urea.

INTRODUCTION

Currently, the manufacture of cellulose derivatives has gained attention due to many relevant applications that contemplate the well-known and excellent properties of their precursor. Regenerated materials –fibers, films, membranes, beads, sponges– and other functional materials can be obtained from different cellulose derivative solutions.[1] In the regenerated cellulose fiber and cellophane industries, the viscose process has long occupied the lead position,[2] however this process generates several dangerous and polluting byproducts. Cellulose carbamate (CC) is a stable cellulose ester which is soluble in aqueous sodium hydroxide.[3] For this reason, its production has been of interest as an environmentally friendly alternative to the viscose process. In conventional synthetic methods of CC, the starting cellulose pulp is usually initially alkalized and aged (partial chain depolymerization). Then it is heated together with urea, and the derivative is obtained through reaction with isocyanic acid that produces urea decomposition when it is heated above its melting point (133 °C).[4]

The use of microwave irradiation as a source of heat in synthetic chemistry offers a fast, facile and interesting way to prepare CC without harmful solvents.[5, 6] It displays a number of advantages over conventional heating, such as non-contact and rapid heating, high reaction rates and high product yields.[7]

The importance of this research and its continuity over time aims to (i) achieve a greater understanding of the structure-property relationship of the resulting cellulose derivatives, and (ii) adapt these products to specific and new applications based on both economic and environmental perspectives.

EXPERIMENTAL

In the present work, CC was prepared from eucalyptus dissolving pulp (98 % α -cellulose) pre-activated with NaOH 18 % w/v. The alkali cellulose was properly impregnated with urea and the mixture was heated using a microwave oven (Whirpool, WMP20Y, 800 W, 10 levels) at 160-320 W for 10-20 minutes. The reaction product was washed with distilled water and a solid material was obtained after oven-drying. Elemental nitrogen content was determined by Kjeldahl method, while intrinsic viscosity of the cellulose pulp and CC in cupriethylenediamine,[8] was measured. The degree of carbamate group substitution (DS) was determined according to $DS = 162.N / (14.100) - (43.N)$ where N = specimen nitrogen content (%); 162 = molar mass (g/mol) of an anhydroglucose unit (AGU); 14 = molar mass (g/mol) of nitrogen atom; and 43 = net increment in molar mass (g/mol) of an AGU on substitution of a hydroxyl (-OH) by a carbamate (-OCONH₂) group.[9]

Moreover, the structure and properties of CC were characterized by FTIR spectroscopy (Shimadzu IR Prestige-21) in the range of $\nu=400-4000$ cm⁻¹. The test specimens were prepared by KBr disk technique. Differential scanning calorimetry analyses (DSC) were performed on Mettler DSC821^o at a heating rate of 10 °C/min under nitrogen atmosphere (50 cm³/min). Alumina 40 μ l capsules were used to enclose 7 \pm 1 mg.

RESULTS AND DISCUSSION

Effects of esterification conditions

The optimal degree of substitution (DS) so that the cellulose carbamate is soluble in aqueous alkali is 0.2-0.3.[10] In the synthesized samples, the DS values obtained were near 0.2 in most of the experimental conditions (see Table 1), whereas the highest value (0.24) was achieved with 20 minutes and 240 W.

In an alkaline system, carbamation proceeds relatively rapidly with a simultaneous drop in the intrinsic viscosity ($[\eta]$) of the original pulp.[11] The $[\eta]$ was reduced by approximately 70 % over the value of 428 ml/g of the cellulose pulp (considering an average value of 130 ml/g). Furthermore, $[\eta]$ increased consistently with DS, which correlates to

the increased molecular mass of the polymer in solution (see Table 1).

Table 1. Degree of substitution and intrinsic viscosity of cellulose carbamate synthesized under different experimental conditions. (a) carbonized; (b) eucalyptus dissolving pulp 428 ml/g.

Cellulose carbamate sample	Reaction conditions		DS	[η] ^(b) [ml/g]
	Energy input [W]	Time [min]		
CC-160-10	160	10	0,09	121
CC-160-15		15	0,17	128
CC-160-20		20	0,20	132
CC-240-10	240	10	0,15	125
CC-240-15		15	0,21	134
CC-240-20		20	0,24	139
CC-320-10	320	10	0,20	133
CC-320-15		15	0,22	135
CC-320-20		20	(a)	-

The effect of time and energy input in the nitrogen content of the synthesized samples was studied. Figure 1 shows that the nitrogen content increases as both reaction variables increase. The sample synthesized at the highest time and power input was carbonized, possibly because in these experimental conditions, the pyrolysis of cellulose and/or other components might occur.

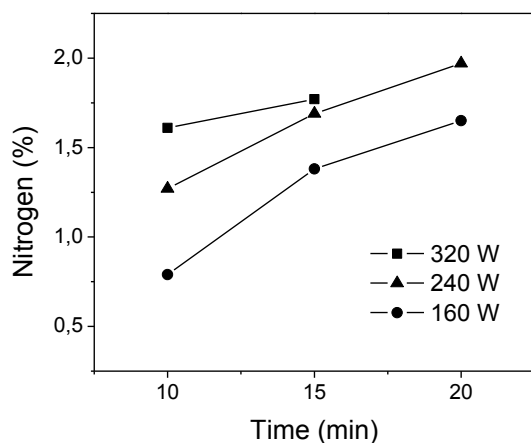


Figure 1. Nitrogen content of cellulose carbamate samples synthesized under different experimental conditions.

Structural and thermal properties

A qualitative analysis of CC samples by FTIR spectroscopy and DSC was performed. Figure 2 shows the FTIR spectra of the original pulp and the CC samples with different nitrogen contents obtained with 10 minutes of reaction at 240 W and 320 W. Compared with cellulose (A), it can be clearly seen the appearance of a new absorption peak at 1719 cm^{-1} corresponding to the stretching vibration of the carbonyl group (C=O) in the base of urethane.[12] This indicates that urea had reacted with the

hydroxyls groups of cellulose to form cellulose carbamate. Furthermore, the absorption band at 1719 cm^{-1} gradually rose with the increasing nitrogen content of the CC. The intensity of the band at 1425 cm^{-1} (C-H rocking of the ring) results in an increase after the esterification of cellulose, which corresponds to the decrease in the signal corresponding to hydrogen bonds.[13]

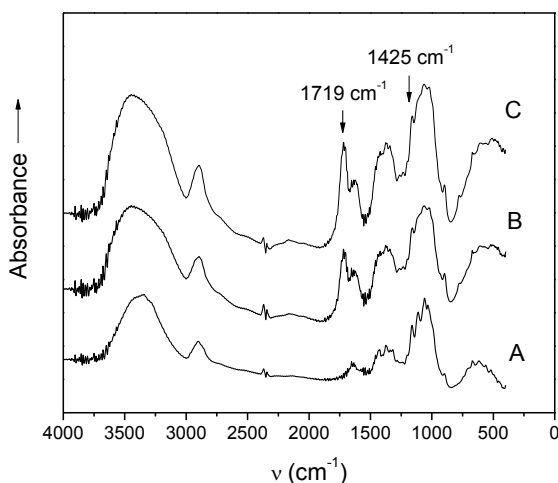


Figure 2. FTIR spectra of cellulose (A) and cellulose carbamates with different nitrogen content: 1.27%, CC-240-10 (B) and 1.61%, CC-320-10 (C).

The thermal stability of cellulose fibers is affected by their crystalline order, which decreases after substitution of hydroxyl groups presented in cellulose with organic acids.[14] Therefore, the thermal stability of cellulose esters is lower than that of original cellulose. Figure 3 shows the thermograms obtained. An endothermic peak around 100 °C can be observed for cellulose as well as for the CC samples synthesized at 240 W after different times. This is due to the evaporation of moisture, which was relatively smaller for cellulose than for the CC samples. The DSC thermograms also show the endothermic peaks of CC at approximately the same maximum temperature value (~346 °C) which is slightly lower than that of cellulose pulp, which appears at 350 °C (see Fig. 3). It is well documented in the literature that this main endotherm is primarily due to the depolymerization of cellulose with the formation of levoglucosan and its evaporation.[15] The CC samples also show a broad endothermic peak at approximately 272 °C, which increases in size with increasing DS (or N%). This endotherm at lower temperature is due to thermal cleavage of the urethane bond under elimination of isocyanate acid.[16] The exothermic peak at approximately 370 °C is present in the CC samples with the highest nitrogen contents (C and D). This peak would be due to possible crosslinking reactions occurring during thermal degradation,[14] or char formation.[15]

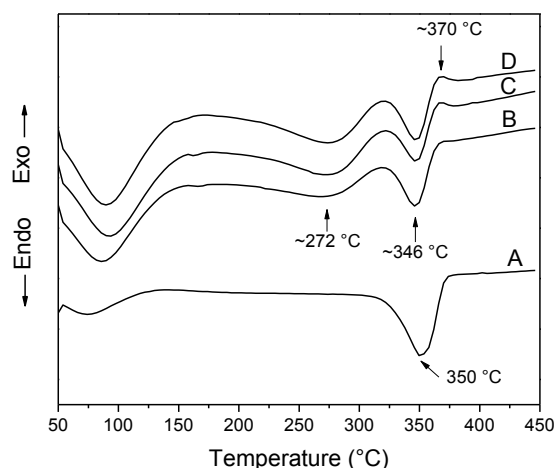


Figure 3. DSC curves of cellulose (A) and cellulose carbamates with different nitrogen content: 1.27%, CC-240-10 (B), 1.69% CC-240-15 (C) and 1.97% CC-240-20 (D). Heating rate, 10 °C/min; Nitrogen flow, 50 cm³/min.

CONCLUSIONS

Cellulose carbamates were successfully prepared from mixtures of urea and eucalyptus dissolving pulp through microwave heating. Reaction time and power input play important roles in the carbamation of cellulose. The time and power input appropriate for an optimal degree of substitution were found to be between 10-15 minutes and 240-320 W respectively. In addition, by using these experimental conditions, the carbonization of cellulose is avoided. FTIR analysis showed that a sharp peak appeared in the spectra of the samples synthesized at 1719 cm⁻¹, indicating the generation of CC. The DSC of the eucalyptus pulp and CC samples indicated that the thermal stability of the cellulose derivative is comparable to that of the raw material. Also and according observed thermal behavior, cellulose had changed upon reaction, confirming the esterification of cellulose.

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REFERENCES

- [1] Klemm, D.; Heublein B.; Fink, H. P.; Bohn, A. *Angewandte Chemie International Edition*, 2005, **44**, 3358-3393.
- [2] Bywater, N. *Lenzinger Berichte*, 2005, **89**, 22-29.
- [3] Kotek, R. In: *Handbook of Fiber Chemistry*, Regenerated cellulose fibres, M. Lewin Ed., Taylor & Francis Group, New York, 2007.
- [4] Segal, L.; Eggerton, F. V. *Textile Research Journal*, 1961, 460-471.
- [5] Loth, F. 2005, US 2005/0107602 A1.

- [6] Guo, Y.; Zhou, J.; Wang, Y.; Zhang, L.; Lin, X. *Cellulose*, 2010, **17**, 1115-1125.
- [7] Kappe, C. O. *Angewandte Chemie International Edition*, 2004, **43**, 6250-6284.
- [8] Marx, V. M.; *Die Makromolekulare Chemie*, 1955, **16(1)**, 157-176.
- [9] Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. In: *Comprehensive Cellulose Chemistry: Functionalization of Cellulose*, Appendix to Volume 2, Weinheim: WILEYVCH, 1998.
- [10] Turunen, O. T.; Fors, J.; Huttunen, J. I. *Lenzinger Berichte*, 1985, **59**, 111-117.
- [11] Laszkiewicz, B.; Domasik, B. *Journal of Thermal Analysis*, 1989, **35**, 2235-2242.
- [12] Nada, M. A.; Kamel, S.; El-Sakhawy, M. *Polymer Degradation and Stability*, 2000, **70**, 347-355.
- [13] Yin, C.; Li, J.; Xu, Q.; Peng, Q.; Liu, Y.; Shen, X. *Carbohydrate Polymers*, 2006, **67**, 147-154.
- [14] Jandura, P.; Riedl, B.; Kokta, B. V. *Polymer Degradation and Stability*, 2000, **70**, 387-394.
- [15] Soares, S.; Camino, G.; Levchic, S. *Polymer Degradation and Stability*, 1995, **49**, 275-283.
- [16] Mormann, W.; Michel, U. *Carbohydrate Polymers*, 2002, **50**, 201-208.