JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 12, December 2007, p. 3917 - 3920

Structural modifications of cellulose in heterogeneous acetylation process

N. OLARU, D. CIOLACU, D. TAMPU, L. OLARU
Institute of Macromolecular Chemistry "Petru Poni" Aleea Grigore Ghica-Voda 41 A, Iasi – 700487, Romania

Three cellulosic materials with crystalline structures of cellulose I, cellulose II and mixture of cellulose I and III, respectively, are acetylated in a heterogeneous system consisting of a mixture of acetic acid and toluene in order to decrease their hydrophilic character. Different degrees of acetylation are achieved by carrying out the process for various times of reaction. The variation of water affinity of the acetylated fibres estimated from DSC thermograms is studied in relation with the extent of acetylation and with the structural modification of cellulose fibres as revealed by X-ray and FTIR analyses. It was found that two factors are involved in decreasing the hydrophilic character of the studied samples: the change in supramolecular structure and the degree of chemical modification. At lower degrees of acetylation, the reducing of ordered regions in cellulosic material increases the water affinity, while at higher extents of modification, though the decrystallization is more pronounced, water affinity is reduced because of the lower number of free OH groups on the cellulose chain. It was also established that although a decrease of crystallinity is produced for all the studied celluloses, the crystalline forms of the starting celluloses are maintained.

(Received October 8, 2006; accepted December 4, 2007)

Keywords: Cellulose, Heterogeneous acetylation, Supramolecular structure, X-ray, DSC, FTIR

1. Introduction

Natural cellulose fibres are renewable, biodegradable, abundant and low-cost materials that can be useful as reinforcing agents in polymeric composites [1]. They are characterized by specific mechanical properties which can play an important part in strengthening the composites by transfer of stress between the fibre and polymer matrix. Recent papers emphasize the growing interest toward polymer composites using cellulose fibres as reinforcing fillers [2,3]. Some possible ways to refine the compatibility and to improve the surface adhesion between natural fibres and synthetic polymers refer to both physical (like plasma treatments of the fibres [4]) and chemical methods. The latter ones include chemical modification of cellulose fibres in order to increase their hydrophobic character. Cellulose acetylation in heterogeneous media is reported as one suitable procedure to decrease the surface polarity of natural fibres. This process may be performed with [5, 6] or without [7, 8] organic solvents as reaction media.

In this paper, three cellulosic materials with different supramolecular structures are acetylated to various extents in heterogeneous systems containing mixtures of acetic acid and toluene. The aim of this study is the investigation on the variation of water affinity of acetylated celluloses in relation with the change of their crystallinities during the chemical transformation and with their degree of acetylation.

DSC analysis is used to evaluate the hydrophilic character of the polymers, by means of the endothermic peak at about 110 ^{o}C due to the loss of absorbed water.

Structural modification of cellulose fibres is investigated by means of X-ray and FTIR methods.

2. Experimental

The experiments were performed on the following three sorts of cotton cellulose:
- cotton cellulose fibres purified by extraction with benzene – ethanol mixture (sample C I) ;
- C I treated with 18 wt % sodium hydroxide solution, then washed with water and air-dried at room temperature (sample C II) ;
- C I treated with ethylenediamine, then washed with methanol and air-dried at room temperature (sample C III).

Celluloses used as starting materials were activated overnight in glacial acetic acid at room temperature.

Acetylation was performed at 0 ^{o}C with acetic anhydride (16.7 g / g cellulose) in a toluene - acetic acid mixture 4:1 (v/v) at a ratio of solvent mixture to cellulose of 50:1 (v/w), using sulphuric acid as a catalyst (0.5 g / g cellulose). In order to evaluate the structural modifications of cellulose produced during acetylation process, separate samples have been performed for several reaction times: 2, 4, 6, 24 and 28 h. After the desired reaction time elapsed, the acetylation was stopped with an aqueous methanol solution containing the appropriate amount of kalium acetate. The solid product was separated from the reaction system by filtration and then purified by several washings with aqueous methanol 90 % (by volume).

The degree of substitution (DS) of cellulose acetates was determined by the usual saponification method [9].

The X-ray diagrams for celluloses and cellulose acetates were recorded on a diffractometer Rontgen-Universal HZG 4/A with CuKα radiation.

FTIR spectra were recorded with a spectrophotometer FTS 2000 Series DIGILAB, in the frequency range 4000 – 400 cm^{-1}, with a resolution of 4 cm^{-1}.

DSC analysis was carried out on a differential calorimeter Mettler DSC 12E at a heating rate of 10 ^{o}C / min. Before analysis, all the samples have been preserved for 5 days at a temperature of 20 ^{o}C and a relative humidity of 65 %.

3. Results and discussion

The degrees of substitution of the obtained cellulose acetates as well as the DSC data and the crystallinity indexes are listed in Table 1.

In Figs. 1 – 3 are presented the X-ray diagrams for cellulose samples C I, C II and C III, as well as for the corresponding acetates obtained after 4 and 24 h of esterification. From these diffractograms, the crystallinity indexes (Cr.I.) have been determined as a ratio between the crystalline domain area (S_{cr}) and the total (crystalline + amorphous, S_{tot}) one.

Diagrams in Fig. 1 show considerably reduced intensities of the peaks (2θ angle) at 14.7^{o}, 16.5^{o}, and 22.6^{o}, characteristic of the cellulose I planes 101, $10\bar{1}$, and 002, respectively, indicating a significant consumption of ordered region of cellulose I after partially esterification for 4 hours. This effect is even more pronounced for the sample acetylated for 24 h.

Also, X-ray diffractograms of C II and its acetylated derivatives II 4 and II 24 depicted in Fig. 2 proved similar structural modifications for this allomorph: the intensities of the specific peaks of cellulose II (at 2θ angle 12.4^{o}, 20.3^{o}, and 22^{o}, for the planes 101, $10\bar{1}$, and 002, respectively) are progressively diminished during acetylation.

In Fig. 3 it is observed that C III consists of a mixture of cellulose I and cellulose III allomorphs. The peak of the plane 002 of cellulose I (at 2θ angle 22.6^{o}) is superposed with the peaks of the planes $10\bar{1}$ and 002 (at 2θ angle 21.5^{o}). Also, beside the peaks corresponding to the planes 101 and $10\bar{1}$ of cellulose I (at 2θ angle 14.7^{o} and 16.5^{o}, respectively), the peak of the plane 101 of cellulose III is visible, at 2θ angle 12.75^{o}. The X-ray diagrams show that a small modification of supramolecular structure after partial esterification, for 4 h, appears.

Although a decrease of crystallinity is observed for all the studied celluloses, however, the crystalline forms of the starting cellulose are maintained. This fact suggests that the acetylation occurs not only in amorphous areas, but also on crystalline surfaces of the cellulosic material.

Table 1. DS of acetylated samples, specific areas (S_x) calculated from DSC data and crystallinity indexes (Cr.I.).

Sample	DS	S_x (DSC) (cm^2/mg)	Cr.I. (S_{cr}/S_{tot})100
C I	-	2.753	77.17
I 2	0.35	2.811	76.30
I 4	0.47	3.292	59.37
I 6	0.62	3.872	-
I 24	1.79	2.642	47.06
I 28	1.85	2.606	-
C II	-	3.940	62.92
II 2	0.44	3.901	74.32
II 4	0.64	3.913	67.75
II 6	0.81	3.925	-
II 24	1.55	3.010	53.85
C III	-	3.006	57.50
III 4	0.10	3.012	60.00
III 24	0.57	3.272	56.33

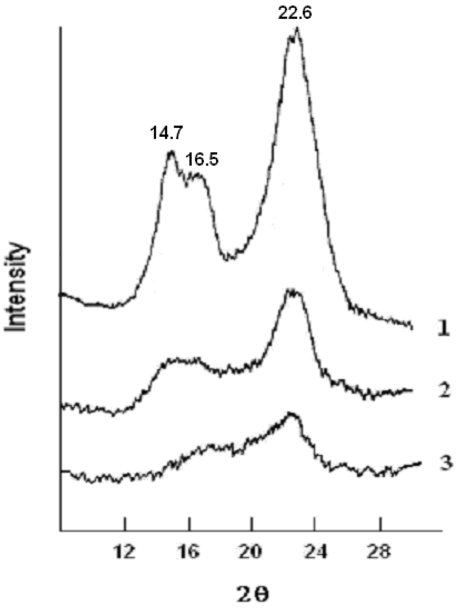

Fig. 1. X-ray diffractograms for samples C I (1), I 4 (2) and I 24 (3).

The most important features of the DSC curves are the endothermic peaks occurring in the range 40 – 150 ^{o}C, which are due to the loss of absorbed water. The specific areas of these peaks, S_x in cm^2/mg (Table 1), may be a measure of the hydrophilic properties of the samples. Thus, for cellulose I, it can be seen that during the first 6 h of acetylation a progressive increase of water affinity is recorded, simultaneously with the decrease of crystallinity indexes. At longer reaction times (24 h), hydrophilic character of acetylated cellulose I (sample I 24) decreases because of higher DS value which provides lower content of free OH groups, although the crystallinity index is the lowest one in this case.

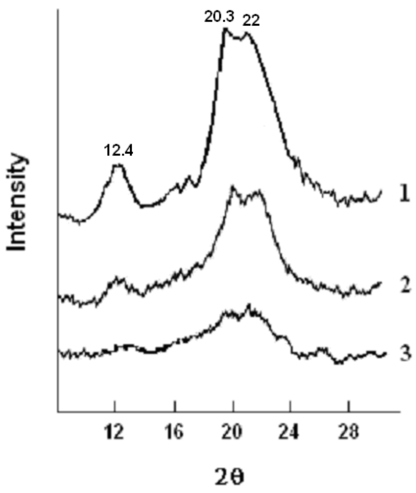

Fig. 2. X-ray diffractograms for samples C II (1), II 4 (2) and II 24 (3).

The same behaviour may be noticed in the case of the other two cellulose allomorphs. For cellulose II and its acetylated samples, the hydrophilic character is maintained for the acetates with DS up to 0.8 at about the same level as for the unmodified cellulose and the water affinity is considerably decreased for cellulose acetate II 24 with DS 1.55.

Thus, it can be concluded that for heterogeneous acetylation of cellulose in the studied media containing toluene, the hydrophilic character of the acetylated polymers is influenced by both morphological structure and the degree of chemical transformation, these two properties proving somewhat opposite tendencies from the point of view of the water affinity of the polymer. At lower DS values, this character is controlled by the crystallinity, while at higher levels of chemical transformation it is mainly determined by the extent of acetylation.

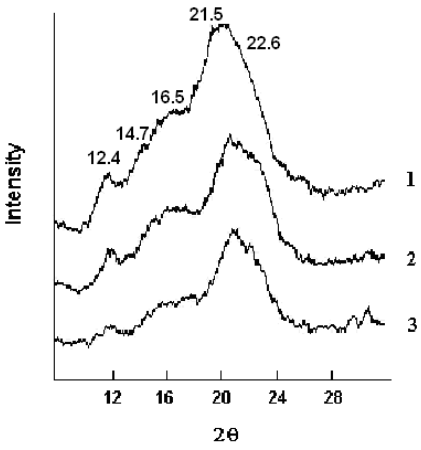

Fig. 3. X-ray diffractograms for samples C III (1), III 4 (2) and III 24 (3).

FTIR spectra of C I and its acetylated samples I 2 and I 24 (here selected for examples and illustrated in Fig. 4) confirm the comparative behaviour of the studied samples from their hydrophilic properties point of view. As compared with FTIR spectrum of untransformed cellulose I, those of acetylated I 2 and I 24 show specific acetyl bands appearing at 1740 – 1748 cm^{-1} (carbonyl C=O stretching of ester), 1371 – 1379 cm^{-1} [C–H in –O(C=O)–CH$_3$] and 1249 – 1258 cm^{-1} (C–O stretching of acetyl group) [10]. From the spectra it also can be observed the presence of the peaks at about 1641 – 1647 cm^{-1}, due to the water contained in polymer. To get a measure of the affinity for water of the investigated samples, the ratio between the intensity of this band and the intensity of C-O stretching vibration of the cellulose backbone at about 1053 – 1062 cm^{-1} has been calculated. This ratio has the highest value for sample I 2 (0.467) and decreases for I 24 (0.434), which is in good agreement with X-ray and DSC data presented in Table 1. That means lower water affinity for the more substituted sample, although its crystallinity is decreased.

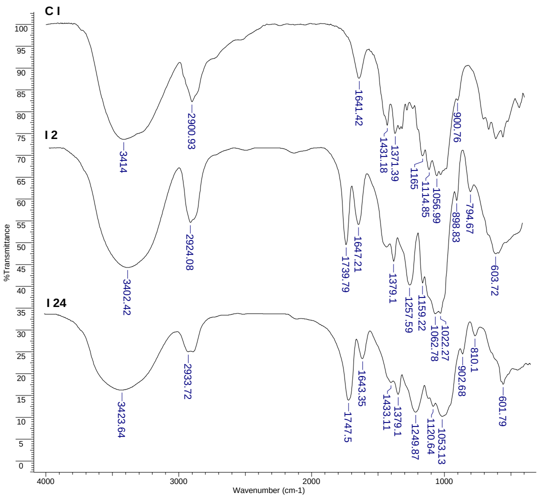

Fig. 4. FTIR spectra of unmodified cellulose I (C I) and of its acetylated samples for 2 h (I 2) and 24 h (I 24).

An estimation of the extent of acetylation can be given by the ratio between the intensity of the acetyl C=O stretching of ester at 1740 – 1748 cm^{-1} and the intensity of C-O stretching vibration of the cellulose backbone at about 1053 – 1062 cm^{-1}. This ratio was found to be 0.587 and 0.887 for samples I 2 and I 24, respectively.

4. Conclusions

Heterogeneous acetylation of cellulose in the studied media containing acetic acid and toluene led to modification of the hydrophilic character of the acetylated cellulosic fibres. This property is influenced by both morphological structure and the degree of chemical transformation. At lower DS values, this character is controlled by the crystallinity, while at higher levels of chemical transformation it is mainly determined by the extent of acetylation.

References

[1] L. Czarnecki, J. L. White, J. Appl. Polym. Sci. **25**, 1217 (1980).
[2] A. S. Hermann, J. Nickel, U. Riedel, Polym. Degrad. Stab. **59**, 251 (1998).
[3] W. G. Glasser, R. Taib, R. K. Jain, R. Kander, J. Appl. Polym. Sci. **73**, 1329 (1999).
[4] N. Olaru, D. Onac, Gh. Cobiliac, Proc. 5-th Eur. Work. Lignocell. & Pulp, Aveiro, Ed. Univ. Aveiro, Portugal, 1998, p. 255.
[5] L. J. Tanghe, L. B. Genung, J. W. Mench, in Methods in Carbohydrate Chemistry, Ed. R. L. Whistler, Academic Press, New York & London, 1963, p. 193.
[6] J. Geurden, Pure & Appl. Chem. **14**, 507 (1967).
[7] G. Frisoni, M. Baiardo, M. Scandola, Biomacromol. **2**, 476 (2001).
[8] M. O. Adebajo, R. L. Frost, Spectrochim. Acta Part A **60**, 2315 (2004).
[9] L. J. Tanghe, L. B. Genung, J. W. Mench, in Methods in Carbohydrate Chemistry, Ed. R. L. Whistler, Academic Press, New York & London, 1963, p. 201.
[10] H. P. Rensch, B. Riedl, J. Wood Chem. Technol. **13**, 167 (1993).

---

[*] Corresponding author: oocristina@yahoo.com