ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 1, pp. 107−111. © Pleiades Publishing, Ltd., 2009.
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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis of Cyanoethyl Ethers of Cellulose from Flax Fiber Production Waste

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Received July 18, 2008

Abstract—Conditions of preparation of cellulose cyanoethyl ethers with different degrees of substitution, based flax fiber production waste were examined. The chemical structure of the resulting cellulose ethers and variation of the structure of the cellulose materials during cyanoethylation were examined by IR-Fourier spectroscopy and X-ray diffraction analysis. The degree of substitution of cellulose ethers was examined in relation to cyanoethylation conditions and chemical composition of the initial cellulose materials.

DOI: 10.1134/S1070427209010200

Conditions of preparation of cyanoethyl ethers of cellulose with different degrees of substitution based on flax fiber production waste were examined. The chemical structure of the resulting cellulose ethers and variation of the structure of the cellulose materials during cyanoethylation were examined by IR-Fourier spectroscopy and X-ray diffraction analysis. The degree of substitution of cellulose ethers was examined in relation to cyanoethylation conditions and chemical composition of the initial cellulose materials.

Preparation and application of polymer materials based on plant raw materials attracts increased attention in view of today's environmental problems. The reason is that plant raw materials have renewable (naturally replenished) resource base and that plant polymers (cellulose, cellulose ethers) can be easily processed and biodegraded after the use. In this connection, flax fiber production waste (short flax, woody part of the flax stem, flax boon) are regarded as an alternative to cotton as raw material not only for textile industry but also for preparation of polymers thereof, suitable for diversified applications.

At the present time, short flax fibers and flax boon are tested as candidate raw materials to replace flax linter and refined wood cellulose in preparation of sorbents, water-soluble cellulose ethers [1, 2].

Here, we examined cyanoethylation of short flax and flax boon with acrylonitrile. Our aim was to prepare on their basis cyanoethyl ethers of cellulose having a set of useful properties such as high dielectric permittivity, high heat resistance, and microbiological resistance.

EXPERIMENTAL

Short flax and flax boon intended for preparation of cyanoethyl ethers of cellulose were pretreated to remove concomitant compounds, fats, waxes, and pectins by the procedure described in [3]. Fats and waxes were removed by treating cellulose materials with ethanol–benzene mixture in a Soxhlet apparatus. Pectins were removed by treating the materials, freed from fat, with aqueous solutions of HCl and ammonium citrate [4]. The resulting material was a lignin–carbohydrate complex comprising cellulose and lignin. The content of lignin in short flax fibers is 4%, and that in flax boon, 31% [5]. For comparison, we carried out cyanoethylation of cotton linter. The degree of polymerization (DP) of cotton linter cellulose, flax fiber cellulose, and flax boon cellulose was 1500, 3000, and 2600, respectively. The DP of cellulose was determined viscometrically, based on the viscosity of cellulose nitrates in acetone solution by the Mitchell method [6].

In the cyanoethylation reaction we used commercial acrylonitrile (AN) with bp 78°C and dimetylsulfoxide (DMSO) with bp 85°C (at 25 mm Hg). Cyanoethylation was effected by reacting cellulose materials with

Table 1. Cyanoethylation conditions for cellulose materials pretreated with aqueous NaOH at 20°C

Sample no.	NaOH concentration, %	Cellulose:NaOH:AN molar ratio	Nitrogen content, %	Degree of substitution
		Flax fibers, τ = 48 h		
1	2.5	1:0.083:40	5.3	0.7
2	5.0	1:0.20:40	7.2	1.2
3	7.5	1:0.62:40	7.5	1.3
4	10.0	1:1.66:40	9.8	1.8
5	18.0	1:1.8:40	10.0	1.9
6*	5.0	1:0.05:40	13.0	3.0
		Flax boon, τ = 48 h		
7	2.5	1:0.12:40	6.70	1.0
8	5.0	1:0.29:40	6.90	1.1
9	7.5	1:0.43:40	8.45	1.4
10	10.0	1:0.76:40	9.20	1.6
11	18.0	1:0.93:40	9.50	1.7
12*	5.0	1:0.18:40	11.20	2.3
		Cotton linter, τ = 48 h		
13	2.5	1:0.08:40	7.10	1.2
14	5.0	1:0.20:40	10.10	2.0
15	7.5	1:0.62:40	11.50	2.4
16	10.5	1:1.66:40	11.60	2.5

* Sample nos. 6 and 12 were synthesized at T=40°C for 3 h.

acrylonitrile in the presence of an alkaline catalyst by the scheme

$$[C_6H_7O_2(OH)_3]_n + nxCH_2CHCN \xrightarrow{NaOH} [C_6H_7O_2(OH)_{3-x}[OCH_2CH_2CN)_x]_n + nxH_2O.$$

It was of interest to examine cyanoethylation of cellulose materials in relation to amount of the alkaline catalyst NaOH, temperature and time of the reaction, and the diluent DMSO.

The cellulose material was pretreated by two procedures. The former procedure involved pretreatment of the initial fibers and flax boon with an excess of aqueous NaOH of different concentrations (2.5–18.0%) at T = 20°C for 2 h. The latter procedure consisted in pretreatment of the cellulose material with an excess of a mixture of NaOH solutions of different concentrations (2.5–10.0%) in DMSO at the volume ratio of 1.5:1.0 at T = 20°C for 2 h.

Upon activation, pressed cellulose material was treated with acrylonitrile at different reaction temperatures and times under stirring. Upon completion of the reaction the resulting mixture was diluted with acetone, neutralized with 15% aqueous acetic acid solution, washed with water several times, and subjected to ethanol extraction in a Soxhlet apparatus for 12 h. The reaction products were dried in a vacuum desiccator. The degree of substitution of the ethers synthesized was calculated from the nitrogen content determined by the Kjeldahl method [7].

The IR spectra of cyanoethylated compounds of cellulose were measured on an FS–88 Bruker IR-Fourier spectrometer (KBr pellets). The X–ray diffraction patterns of the initial and cyanoethylated cellulose materials were obtained on a DRON-2 instrument, with Ni-filtered CuK_α radiation.

Tables 1 and 2 present the cyanoethylation conditions for short flax fibers, flax boon, and cotton linter. It is seen that the nitrogen content in the cyanoethylated products in the case when the cellulose material was pretreated with an aqueous NaOH varies with the alkali content in the material and tends to increase with increasing cellulose : NaOH molar ratio. This is typical for both short flax fibers and flax boon and cotton linter. Flax fibers are less prone to cyanoethylation than cotton linter, possibly due to a poorer accessibility of the flax structure in the cyanoethylation reaction compared to cotton cellulose. Cyanoehylation of flax boon is an even more difficult

Table 2. Cyanoethylation conditions for cellulose materials pretreated with a 1.5:1 NaOH:DMSO mixture at 20°C , τ = 24 h

Sample no.	NaOH concentration, %	Cellulose:NaOH:AN molar ratio	Nitrogen content, %	Degree of substitution
		Flax fibers		
1	2.5	1:0.037:40	8.2	1.4
2	5.0	1:0.05:40	8.8	1.5
3	7.5	1:0.18:40	12.1	2.6
4	10.0	1:0.30:40	12.1	2.6
5	5.0	1:0.05:40	13.0	3.0
		Flax boon		
6	2.5	1:0.10:40	9.2	1.6
7	5.0	1:0.18:40	10.2	1.9
8	7.5	1:0.30:40	10.4	2.0
9	10.0	1:0.35:40	10.9	2.2
10	5.0	1:0.18:40	11.2	2.3
		Cotton linter		
11	2.5	1:0.037:40	11.3	2.4
12	5.0	1:0.05:40	12.4	2.7
13	7.5	1:0.18:40	12.6	2.8
14	10.0	1:0.30:40	13.0	3.0
15	5.0	1:0.05:40	13.0	3.0

* Sample nos. 5, 10, and 15 were synthesized at T=40°C for 3 h.

task, which can be due to a significant amount of lignin in flax boon.

Cyanoethylation of cellulose materials in the presence of DMSO yielded products in which the nitrogen content was higher than that for cellulose materials pretreated solely with aqueous NaOH. Plots in Figs. 1, 2 more clearly demonstrate how cyanoethylation is affected by DMSO.

Cyanoethylation of flax fibers and flax boon in the presence of DMSO for 24 h at room temperature yielded cellulose ethers with the degree of substitution

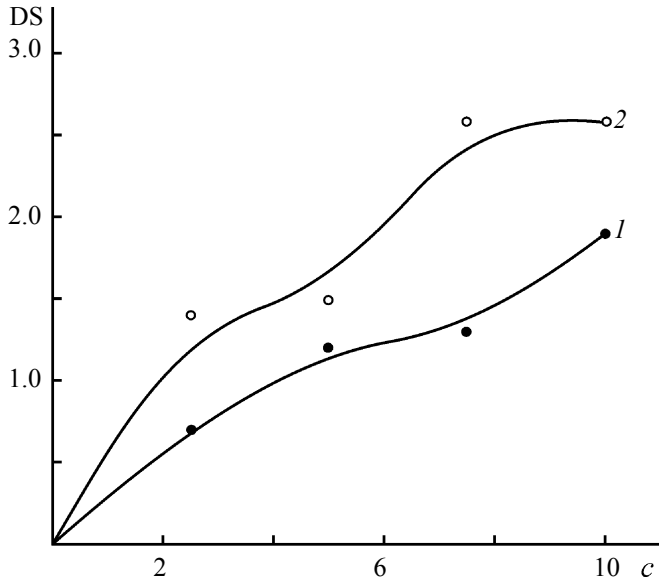

Fig. 1. Degree of substitution DS vs. alkali concentration *c*, %, for flax fiber cyanoethylation. Temperature 20°C; the same for Figs. 2, 4, and 5. (*1*) Aqueous NaOH, τ = 48 h and (*2*) 1.5:1 NaOH : DMSO mixture, τ = 24 h; the same for Fig. 2.

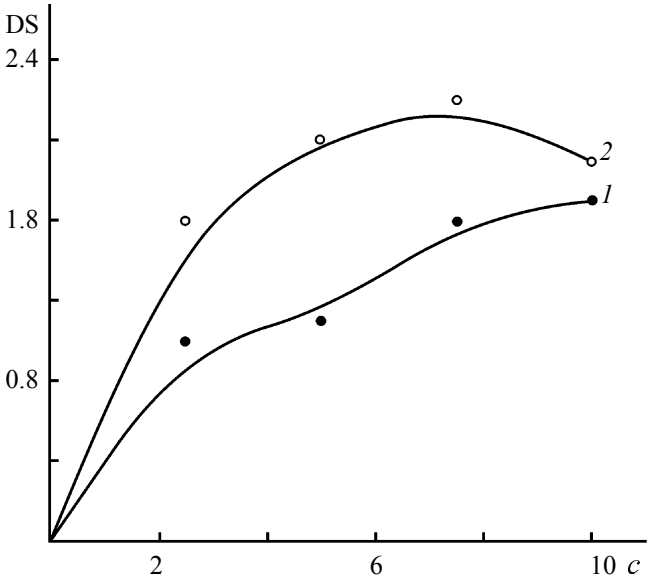

Fig. 2. Degree of substitution DS vs. alkali concentration *c*, %, for flax boon cyanoethylation.

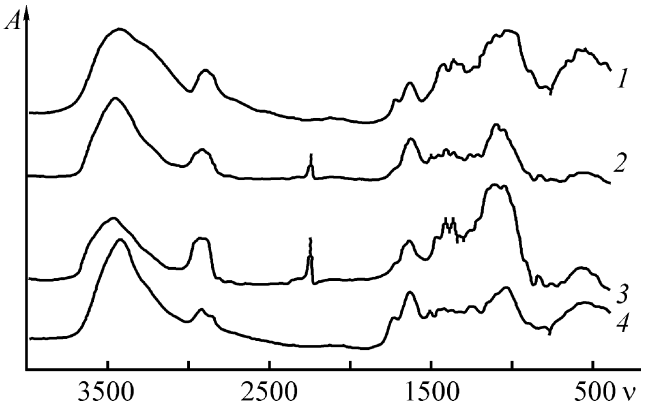

Fig. 3. IR absorption spectra of (*1*) flax boon, (*2*) cyanoethylated flax boon, (*3*) initial flax fibers, and (*4*) cyanoethylated flax fibers. (*A*) Intensity, rel. units, and (ν) wavenumber, cm^{-1}.

of 2.6 and 2.2, respectively. The choice of DMSO as the cyanoethylation reaction component was dictated by the fact that DMSO is a polar aprotic solvent in which there is no hydrogen bonding between the solvent molecules and solute ions [8].

Donor–acceptor interaction of DMSO molecules with the hydrogen atom of the hydroxy group in the glucose unit, being protonated can result in a rupture of the hydrogen bonds linking the cellulose macromolecules and a formation of a fiber structure with large inner surface area [9]. This can intensify cellulose cyanoethylation in the presence of DMSO, which was specifically the case in this study. Cyanoethylation of cotton linter in the presence of DMSO yielded cellulose ethers with the degree of substitution of 3.0. Highly efficient cyanoethylation of cotton linter is due to better accessibility of its structure compared to that of cellulose of flax fibers and flax boon.

The rate of cyanoethylation of the cellulose materials examined is strongly dependent on the reaction temperature. At 40°C, in the presence of DMSO cyanoethylation yields trisubstituted cellulose ethers from flax fibers and cotton linter under substantially decreased amount of alkaline catalyst and reaction time. In the case of flax boon under the same conditions we obtained cynoethyl ethers of cellulose with the degree of substitution of 2.3. Thus, cellulose cyanoethylation in the presence of DMSO goes at a smaller amount of alkaline catalyst. This can decrease the amount of acrylonitrile spent for side reactions and also yield highly substituted cellulose ethers within a smaller period both at heating and room temperatures.

We sought to prove the chemical structure of the synthesized derivatives of flax fiber and flax boon cellulose using IR spectroscopy. Figure 3 presents the IR spectra of the initial and cyanoethylated samples. The spectra of all the samples exhibit absorption bands near 3500 cm^{-1}, characteristic for free hydroxy groups in cellulose and for those linked by intra– and intermolecular hydrogen bonds. The absorption bands near 2918 cm^{-1} are assigned to vibrations of the CH and CH_2 groups of the polymers. The IR spectrum of flax boon contains an absorption band near 1512 cm^{-1}, characteristic for aromatic lignin moieties. This band is not observed in the IR spectrum of flax fibers, which can be associated with a minimal amount of lignin in the fibers. In the IR spectra of cyanoethylated samples of flax and flax boon

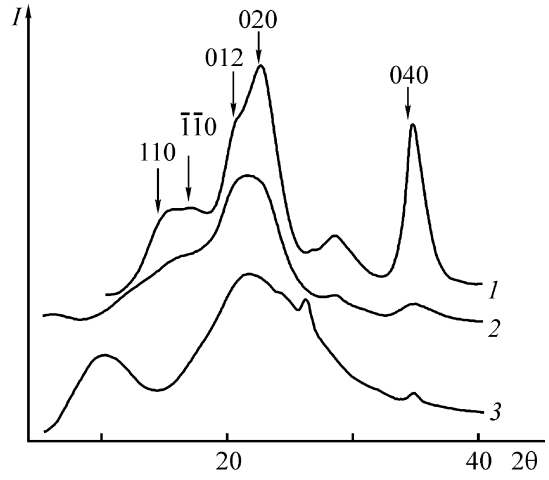

Fig. 4. X–ray diffraction patterns of (*1*) flax fibers, (*2*) flax fibers activated with 10% aqueous NaOH in the presence of DMSO for 24 h and 20°C, and (*3*) activated flax fibers treated with acrylonitrile for 24 h at 20°C. (*I*) Intensity, rel. units and (2θ) Bragg's angle, deg; the same for Fig. 5.

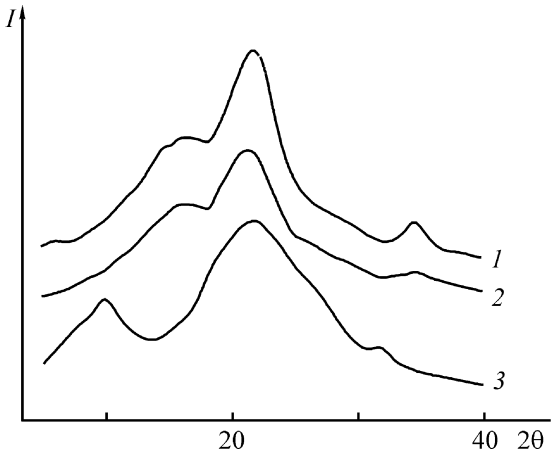

Fig. 5. X–ray diffraction patterns of (*1*) flax boon, (*2*) flax boon activated with 10% aqueous NaOH in the presence of DMSO for 24 h and 20°C, and (*3*) activated flax boon treated with acrylonitrile for 24 h at 20°C.

there are absorption bands near 2253 cm^{-1}, characteristic of stretching vibrations of the cyanoethyl group, that suggests formation of cyanoethyl ethers of cellulose. Cyanoethylation of flax boon and formation of the reaction products does not involve removal of lignin, as confirmed by the IR spectrum.

To examine how the structure of the flax fiber and flax boon cellulose varies in the course of the cyanoethytlation, we applied X-ray diffraction analysis. Figures 4 and 5 show the X-ray diffraction patterns of the initial and cyanoethylated flax fiber and flax boon samples. The patterns of the initial samples exhibit clear reflexes near 2θ of 23, 15, and 35°. They are characteristic of highly ordered natural cellulose fibers with the crystallinity index close to 80. Upon treatment of the cellulose materials with 10% aqueous NaOH or its mixture with DMSO for 24 h the crystalline reflexes get much broader. The 004 reflex has a negligible intensity. This suggests a significant decrease in the degree of crystallinity of cellulose. The X-ray diffraction patterns of the cyaloethylated flax fibers and flax boon substantially differ from those of the initial materials. The patterns exhibit clear reflexes near 2θ of 10 and 23°, identical to those for block samples of cyanoethyl cellulose.

CONCLUSIONS

(1) Cyanoethylation of short flax fibers and flax boon yields cyanoethyl ethers of cellulose with the degree of substitution of 2.3–3.0.

(2) The decisive influence on the structure and degree of substitution of the resulting cellulose ethers is exerted by the chemical composition of the cellulose material, the amount of alkaline catalyst, the presence of dimethylsulfoxide, and the reaction temperature.

(3) Flax fiber production waste is suitable for preparation of polymer materials.

This study was financially supported by the Program "Scientific Principles of Resource and Energy Saving in Mineral, Technogenic, and Renewable Raw Materials Processing", Department of Chemistry and Material Science, Russian Academy of Sciences.

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