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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

A New Procedure for Preparing Microcrystalline Cellulose

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Abstract—A procedure was developed for preparing microcrystalline cellulose, involving hydrolytic treatment of technical-grade (unbleached kraft) wood pulp, followed by oxidative delignification of the resulting lignocellulose powdered material with chlorine dioxide.

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Microcrystalline cellulose (MCC) is a product of partial hydrolysis of natural cellulose with dilute mineral acids. It has the most ordered microcrystalline structure, the highest homogeneity among the known cellulose materials, and the "limiting" degree of polymerization (150–250). The classical procedure for preparing MCC is hydrolytic treatment of cellulose with 2.5 M HCl [1]. Despite higher degree of crystallinity due to preferential dissolution of the amorphous part in the course of hydrolysis, MCC is capable of breakdown into finer structural fragments in liquid media, and under ultrasonic treatment it disintegrates into nanoparticles approximately 40 nm thick [2]. Microcrystalline cellulose exhibits high reactivity in carboxymethylation, acetylation, and oxidation. It finds growing use in pharmaceutical, food, and chemical industries. The raw material for preparing MCC is usually cotton cellulose.

The commercial product prepared from wood raw material is so-called powdered pulp. Degradation of glycoside bonds in cellulose is performed by not only hydrolytic but also oxidative hydrolytic procedures, e.g., with concentrated hot solutions of sodium hypochlorite. The product is suitable for industrial use only.

Certain reported procedures allow preparation of purer cellulose suitable for food and pharmaceutical industries. These procedures involve degradation of pulp with ozone [3] or with nitric, sulfuric, peroxymonosulfuric, peroxyacetic, and other acids [4]. As a rule, to obtain a pure and white product, hydrolysis is performed with bleached wood pulp, in particular, with kraft pulp produced from deciduous or coniferous wood, which involves inefficient consumption of reagents (a part of bleached technical-grade pulp dissolves in the course of hydrolysis). In addition, with common mineral acids (sulfuric, hydrochloric), MCC has low whiteness and yellow or gray tint.

In this study we considered a new procedure for preparing microcrystalline cellulose by hydrolytic degradation of unbleached technical-grade pulp, followed by bleaching of the intermediate product with chlorine dioxide.

EXPERIMENTAL

As raw material we used unbleached deciduous kraft pulp produced by Mondi–Syktyvkar Wood Processing Combine, Joint-Stock Company.

Hydrolysis of unbleached pulp was performed with 10% sulfuric acid and 1% hydrogen peroxide. In the second case, the active species is peroxymonosulfuric acid (PMS, Caro's acid) formed by the reversible reaction

$$H_2O_2 + H_2SO_4 \rightleftarrows H_2SO_5 + H_2O.$$

The treatment was performed at 100°C for 120 min. The hydrolytic treatment of unbleached deciduous kraft pulp yielded lignocellulose powder (LCP) which

Table 1. Quality characteristics of lignocellulose powders depending on the treatment procedure

Treatment	Hardness, p.u.	Kürschner cellulose content, %	Yield, %	DP	Whiteness, %
Unbleached pulp	68	–	–	1230	35.6
10% H_2SO_4	61	92.6	83.9	180	46.3
PMS	11	92.1	81.7	140	55.7

Table 2. Effect of ClO_2 consumption on the whiteness and relative lignin content of MCC

ClO_2 consumption, %	Yield, %	Whiteness, %	c/c_0[a]	Degree of delignification, %
0.0	–	46.3	1.000	–
0.5	96.9	55.5	0.317	68.3
1.0	96.0	61.9	0.217	78.3
1.5	95.9	68.9	0.121	87.9
2.0	95.7	72.5	0.110	89.0
2.5	94.9	75.2	0.090	91.0
3.5	94.9	80.0	0.070	93.0

[a] (c/c_0) Relative lignin content; c_0 corresponds to 68 p.u.

was bleached with chlorine dioxide for preparing MCC. Bleaching of LCP with chlorine dioxide was performed under the following conditions: LCP suspension concentration 10 wt %, treatment duration 60–120 min (at high ClO_2 consumptions, the treatment was prolonged until the chlorine dioxide was completely taken up), and temperature 70°C; the oxidant (ClO_2) consumption was varied within 0.0–3.5% based on absolutely dry matter.

Alkaline extraction was performed with NaOH consumption of 2% based on absolutely dry matter, at 70°C for 60 min.

The whiteness of pulp, LCP, and MCC was evaluated on an FKTsSh-M color comparator calibrated against reference samples [GOST (State Standard) 30113–94]. The cellulose hardness characterizing the content of residual lignin in the sample was determined according to GOST 10070–74 (permanganate units, hereinafter p.u.), and the cellulose content, by the Kürschner method. The degree of polymerization (DP) of the initial pulp and powders obtained was calculated from the viscosity of their solutions in Cadoxen [5]. In the samples obtained, we also determined the relative lignin content (by the photometric method) [6].

To evaluate changes occurring in the cellulose structure in the course of hydrolysis, we used an XRD-6000 X-ray diffractometer (Shimadzu).

The sample characteristics before and after hydrolysis are given in Table 1. The initial unbleached deciduous kraft pulp had hardness of 68 p.u., whiteness of 35.6%, and DP of approximately 1230. After hydrolysis with sulfuric acid, the hardness decreased by approximately 10%, the whiteness increased to 46.3%, and DP decreased to 180.

Hydrolysis of the pulp with PMS leads to lower degree of polymerization (DP 140) at higher whiteness of the lignocellulose powder (55.7%). Simultaneously the pulp undergoes delignification owing to oxidation of the major fraction of lignin (degree of delignification 84%). The yield of lignocellulose powder in hydrolysis with sulfuric acid is 83.9%, and with PMS, 81.7%. The Kürschner cellulose content is within 92.1–92.6%.

Then the LCP samples obtained by hydrolysis with sulfuric acid were subjected to delignifying treatment (bleaching) with chlorine dioxide taken in an amount of 0.0–3.5 wt % based on absolutely dry matter, with 0.5% step (Table 2).

Table 3. Effect of pH in the course of chlorine dioxide treatment on MSS whiteness (whiteness of initial LCP 46.3%)

NaOH consumption, %	pH_{fin}	Yield, %	Whiteness, %
0.00	2.0	98.1	57.8
0.25	2.6	98.0	61.7
0.50	3.6	97.5	62.7
0.75	4.6	97.1	62.0
1.00	5.7	97.0	61.1
1.50	9.4	96.8	60.5
2.00	10.7	96.6	62.9
2.50	11.5	95.6	62.6

As seen from Table 2, at a ClO_2 consumption of 0.5%, 68% of lignin is removed, and the whiteness increases by approximately 9%. At the highest ClO_2 consumption, 3.5%, the degree of delignification is 93% of the lignin content of the lignocellulose powder.

It is well known that, in the step of pulp treatment with chlorine dioxide, the mechanism of redox transformations of ClO_2 depends on pH. The maximal degree of delignification of common kraft pulp is attained at pH ~3–4, and the maximal whiteness in the final steps of bleaching, at pH ~6–7 [7]. In pulp bleaching with chlorine dioxide for the production of paper, alkaline medium is not recommended because of faster decomposition of ClO_2 (to chlorate) and possible degradation of cellulose fiber. In bleaching of pulp with the limiting DP, there is no problem with possible degradation, but the bleaching rate can increase. Therefore, in the next series of experiments we examined the effect of pH (by varying the NaOH consumption) on the MCC whiteness in bleaching with chlorine dioxide (the ClO_2 consumption in this series was 1 wt % based on absolutely dry matter; Table 3).

Depending on pH in the step of treatment with chlorine dioxide, the MCC whiteness changes. Two maxima are observed: at pH ~3.6 (whiteness 62.7%) and ~11 (whiteness 62.9%) (Fig. 1, Table 3). In the neutral medium, the whiteness of microcrystalline cellulose is lower by 4–5%.

The most efficient in bleaching of kraft pulp fibers are schemes in which the treatments with an electrophilic reagent in acid solution and with a nucleophilic reagent in alkaline solution alternate [8]. However, to date no quantitative experimental data have been available in the literature on lignocellulose powders. Therefore, it is of practical and scientific interest to examine the effect exerted by alkaline extraction of lignocellulose material on the results of treatment with chlorine dioxide, i.e., to compare the results of treatment in two (hydrolysis with H_2SO_4–bleaching with ClO_2) and in three steps (hydrolysis with H_2SO_4–alkaline extraction–bleaching with ClO_2). The effect of preliminary alkaline extraction of LCP on the MCC whiteness after bleaching with ClO_2 is illustrated by Fig. 2.

It was found that preliminary extraction with an aqueous NaOH solution (NaOH consumption 2 wt % based on absolutely dry matter) allows the whiteness of powdered cellulose to be increased by approximately 10%. As seen from Fig. 2 (curve *1*), as the ClO_2 consumption is increased to 2 wt % based on absolutely dry matter, the whiteness increases by approximately 27% (from 55.5 to 82.5%). With a

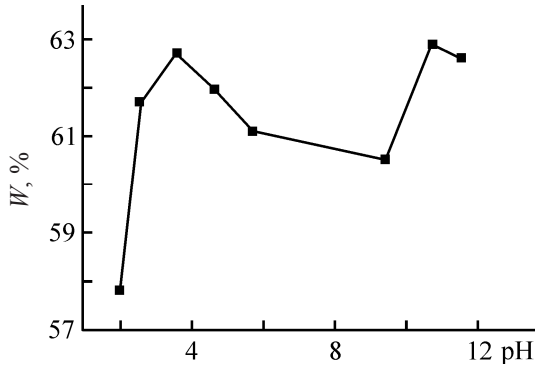

Fig. 1. Effect of pH of the medium in which the treatment is performed on MCC whiteness *W*.

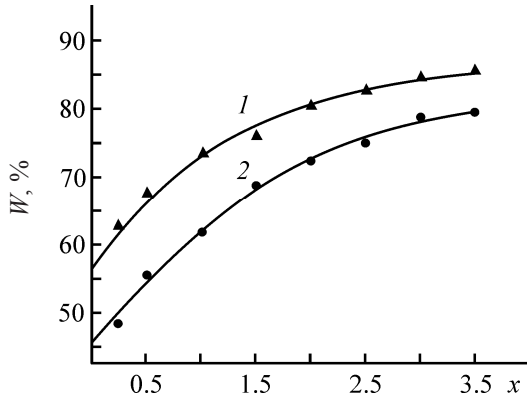

Fig. 2. Effect of the treatment procedure on the MCC whiteness *W*. (*x*) Chlorine dioxide consumption. (*1*) Alkaline extraction + ClO_2 bleaching and (*2*) ClO_2 bleaching.

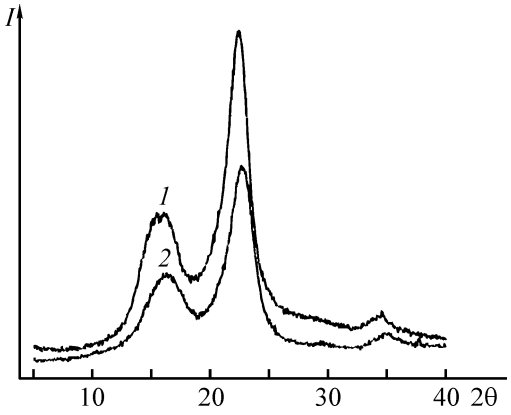

Fig. 3. Diffraction pattern of (*1*) MCC and (*2*) initial (technical-grade) pulp. (*I*) Intensity and (2θ) Bragg angle.

further increase in the ClO_2 consumption from 2 to 3.5%, the whiteness changes insignificantly (from 82.5 to 86.1%). The maximal MCC whiteness in this series was 86.1%.

Changes in the supramolecular structure of cellulose, occurring in the course of hydrolysis, were characterized by X-ray diffraction. The diffraction patterns (Fig. 3) show that the crystal lattice of cellulose I is preserved. To calculate the so-called crystallinity index (or ordering index), we used the Ant–Vuorinen method [9]

$$K_{rel} = 1 - (h_{am}/h_{cr}),$$

where K_{rel} is the crystalline ratio; h_{am}, height over the baseline of the minimum of the diffraction pattern between 18° and 19° (2θ), expressed in arbitrary units; $h_{cr} = H - h_{am}$, H is the height over the baseline of the maximum of the diffraction patterns between 22° and 23° (2θ), expressed in the same arbitrary units.

The crystallinity index of the initial pulp is 0.70, and after the hydrolysis it increases to 0.83.

CONCLUSIONS

(1) A new scheme was developed for preparing microcrystalline cellulose from unbleached deciduous kraft pulp by the hydrolysis–bleaching scheme. In the first step, lignocellulose powder is obtained from technical-grade pulp, and in the second step, this powder is delignified with chlorine dioxide to obtain microcrystalline cellulose.

(2) It is appropriate to use alkaline extraction in preparing microcrystalline cellulose from technical-grade pulp by the hydrolysis–alkaline extraction–bleaching scheme. By so doing, the cellulose whiteness can be additionally increased by 10%.

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