ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 6, pp. 1090–1094. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.G. Kazakova, V.A. Demin, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 6, pp. 1033–1036.

MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Preparation of Powder Cellulose

E. G. Kazakova and V. A. Demin

Institute of Chemistry, Komi Scientific Center, Ural Branch of Russian Academy of Science, Syktyvkar, Russia

Received January 28, 2009

Abstract—Powder cellulose was obtained according to the scheme of hydrolysis-bleaching from the wood technical (unbleached) sulfate cellulose. In the first step, from the crude cellulose lignocellulose material was obtained, which in the second step was subjected to delignification by treating with hydrogen peroxide and chlorine dioxide.

DOI: 10.1134/S1070427209060305

Cellulose is one of the basic components of the membrane of all plant cells. At various treatment (chemical, mechanical, etc.) the natural cellulose is comparatively easily decomposed into the fragments, which are characterized by considerably larger stability. The residue after hydrolysis consists of the decomposed into fragments cellulose fibers, which have "maximum" degree of polymerization [1].

X-ray studies showed that these particles have crystal lattice of the cellulose I with the degree of order somewhat higher than in initial cellulose. This gave the basis to Battista [1] for the first time to use for such materials the term "microcrystalline cellulose" (MCC), which found subsequently wide application for the designation of the cellulose hydrolyzed to "maximum" degree of polymerization.

In literature also the term "micro-fine cellulose" (MFC, MNC), which corresponds to the powder cellulose obtained by the hydrolysis and other treatment from the cellulose II. Thus, in the scientific literature there is no uniformity in the designation of the product of hydrolysis of cellulose II that has the high uniformity of particles, but relatively small degree of crystallinity. In the technical literature more frequently is used the more general name "powder cellulose" [2].

Powder cellulose can be produced by different techniques from the crude cellulose under the action of hydrolytic and oxidizing reagents: by hydrolysis, by thermolysis, by oxidizing-hydrolytic and oxidizing-thermal treatment that cause cellulose degradation. The majority of researchers believe that cellulose degradation is connected with the presence of weak C_1–O–C_4 bonds in the amorphous zones of the cellulose macromolecules between the components of different chemical structure. The primary disintegration of cellulose can be also connected with the fragments of acyclic structure, since at the hydrolysis of the cotton cellulose by solutions of HCl, HNO_3 and CH_3COOH at pH 0.5–1.5 at the temperature 95°C a decrease is observed in the content of aldehyde groups with the decrease in the degree of polymerization. Cellulose degradation occurs also under the influence of unspecific oxidizers such as hypochlorites, hydrogen peroxide, peroxyacids, chlorine, ozone, oxygen. The definite choice of reagents depends on the requirements to the powder cellulose [2].

In this work a method is proposed of producing the powder cellulose by the hydrolytic degradation of unbleached technical cellulose followed by bleaching of half-finished product with hydrogen peroxide and chlorine dioxide.

EXPERIMENTAL

As the source material for obtaining the powder lignocellulose we used unbleached sulfate cellulose of deciduous wood produced by the joint stock company "Mondi Syktyvkar LPK" with the degree of polymerization ~1230 and whiteness 35.6%, with the content of cellulose (Kurshner) 77%. Hardness of the initial cellulose is 68 permanganate units.

The hydrolysis of source material was carried out with 10% solution of sulfuric acid during 120 min at a boiling point of the mixture. After hydrolysis the obtained powder lignocellulose material was washed with distilled hot water on a vacuum filter to the neutral reaction, then by acetone, and dried in air.

The weighted quantity of powder cellulose preliminarily dried in air (corresponding to 5 g of absolute dry powder) was placed into a 0.1 l flask the precalculated quantity of water and sodium hydroxide, was added, and then the mixture was stirred and hydrogen peroxide was added to it. The process of delignification was carried out by the stabilized solution of hydrogen peroxide at the temperature 90°C and the hydromodulus from 5:1 to 35:1; the process duration is 120 min; expenditure of H_2O_2 1.25, of sodium hydroxide 0.8% to the mass of absolutely dry material. As stabilizer sodium silicate was used (expenditure of $Na_2SiO_3·9H_2O$ is 5% to the absolutely dry material).

For comparison a series of control experiments was carried out without the stabilizer at the temperature 90°C and the hydromodulus within the range (10–30) : 1, duration 60 min, H_2O_2 expenditure 1.25–2.5, sodium hydroxide expenditure 1.25–2.5% of the absolutely dry material.

Treatment with chlorine dioxide was carried out under the following conditions: concentration of the suspension of powder lignocellulose 10 wt %, treatment duration 60 min, oxidizer ClO_2 consumption 1% of the absolutely dry material.

Alkaline tretament was performed with the solution of sodium hydroxide (expenditure 2% of NaOH of the absolutely dry material) at the temperature 70°C during 60 min.

After bleaching the obtained powder cellulose was washed with the distilled hot water to the neutral reaction, and dried in air.

The content of basic components (cellulose and lignin) in the initial and powder cellulose was determined employing standard procedures [3]: the content of the cellulose by the method of Kurshner; the hardness of cellulose, which characterizes the content of residual lignin in the sample, according to GOST 10070-74. The whiteness of initial and powder cellulose was determined on the color comparator FKTSSH-M, calibrated on the standard models (GOST 30113-94). The degree of polymerization of the initial

Table 1. The results of bleaching of poweder cellulose by hydrogen peroxide

Conditions of bleaching expenditure, % on dry material		Indices of powder cellulose		
H_2O_2	NaOH	yield, %	whiteness, %	hardness, permanganate units
Initial powder lignocellulise			46.3±0.1	61
1.25	1.25	95.1	63.2±0.1	22
2.50	2.50	94.7	66.2±0.1	20

and obtained powder cellulose was calculated from the viscosity of their solutions in cadoxen [4].

The powder lignocellulose obtained by the hydrolysis has degree of polymerization ~200 whiteness 46.3%, cellulose content (Kurshner) 92%. Hardness of the powder lignocellulose after hydrolysis was 61 permanganate units. The residual lignin can be removed by treatment with the usual bleaching reagents (for example, hydrogen peroxide, chlorine dioxide). The yield of powder after hydrolysis by sulfuric acid was 84% of the mass of absolutely dry cellulose.

The samples of the powder lignocellulose obtained by hydrolysis by sulfuric acid were subjected to the delignificating treatment (bleaching) by hydrogen peroxide. The influence of the expenditure of hydrogen peroxide, value of pH, hydromodulus and preliminary alkaline treatment on the indices of the final product was studied.

Influence of the expenditure of hydrogen peroxide. As it follows from the data of Table 1, at the concentration of H_2O_2 1.25% of the absolutely dry material is formed powder product with the yield 95.1% of absolutely dry material, whiteness 63.2% (hardness 22 permanganate units). Under the same conditions, but with expenditure of H_2O_2 2.5% it is possible to obtain powder product with yield 94.7% of the mass of absolutely dry material and with whiteness 66.2%, the hardness 20 permanganate units.

Influence of the pH value. The influence of the value of pH on whiteness and yield of powder cellulose is studied by changing the expenditure of NaOH.

Table 2. The results of bleaching of poweder cellulose by hydrogen peroxide at different pH values (as dependence on NaOH expendure)

Conditions of bleaching		Indices of powder cellulose	
NaOH, % of the mass of dry material	pH_k	yield, %	whiteness, %
Initial powder lignocellulise		–	46.3±0.1
1.00	9.2	95.0	63.0±0.1
1.25	9.5	94.4	65.3±0.1
1.50	9.8	94.2	66.5±0.1
1.75	10.0	94.3	67.2±0.1
2.00	10.3	94.2	67.2±0.1
2.50	10.7	94.0	68.1±0.1

Table 3. Effect of hydromodulus value on the indices of powder cellulose (delignification with stabilized solution of hydrogen peroxide, expenditure of NaOH 0.8%)

Conditions of delignification		Indices of powder cellulose	
hydro-modulus	expenditure of H_2O_2, % of the mass of dry material	yield. % of the mass of dry material	whiteness, %
Initial powder lignocellulise		–	46.3±0.1
20	1.25	95.9	72.3±0.1
30	1.25	95.5	72.3±0.1
5	2.50	96.3	69.5±0.1
10	2.50	95.6	72.9±0.1
20	2.50	95.0	76.6±0.1
30	2.50	94.3	79.7±0.1
35	2.50	94.1	78.7±0.1

Analysis of the data listed in Table 2 shows that with an increase in the expenditure of NaOH and corresponding increase in pH value an insignificant decrease in the yield is observed and a uniform increase in the whiteness of the powder cellulose (by 5%), which reaches 68.1%.

Influence of hydromodulus. The data on the effect of hydromodulus in the range 5–35 at the delignification by H_2O_2 on the indices of powder cellulose are presented in Table 3 (H_2O_2 with stabilizer) and in Table 4 (H_2O_2 without stabilizer).

At low hydromodulus (5 and 10) and the expenditure of hydrogen peroxide 2.5% on the powder the lingocellulose of whiteness 69.5 and 72.9% is obtained, yield 96.3 and 95.6%, respectively. The use of hydromodulus 20 and 30 leads to an increase in the whiteness to 76.6 and 79.7%, respectively. An increase in the hydromodulus to 35 somewhat decreases whiteness of powder cellulose to 78.7%.

As can be seen from the data listed in Table 3, at the expenditure of hydrogen peroxide 1.25% the increase in the hydromodulus from 20 to 30 does not affect practically the whiteness of powder cellulose which remains equal to 72.3%.

Study of the influence of hydromodulus on the results of bleaching by hydrogen peroxide without the stabilizer (Table 4) showed that at the expenditure of hydrogen peroxide 1.25% on the mass of absolutely dry material an increase in the hydromodulus from 10 to 20 noticeably increases whiteness of powder cellulose (by 4.4%), in the range 20 to 30 the additional effect is low (0.7%). Increase of the hydromodulus within the same range (from 10 to 30) at the expenditure of hydrogen peroxide 2.5% results in the whiteness of powder cellulose 66.2–72.2%.

Table 4. Effect of hydromodulus value on the yield and whiteness of powder cellulose

Conditions of delig-nification		Indices of powder cellulose		
hydro-modulus	expenditure of H_2O_2, % of the mass of dry material	expenditure of NaOH, % of the mass of dry material	Yield, % of the mass of dry material	whiteness, %
Initial powder lignocellulise			–	46.3±0.1
10	1.25	1.25	96.1	63.2±0.1
20	1.25	1.25	95.8	67.6±0.1
30	1.25	1.25	95.6	68.3±0.1
10	2.50	2.50	95.1	66.2±0.1
20	2.50	2.50	94.6	72.2±0.1

Table 5. Effect of preliminary treatment with sodium hydroxide solution of the whiteness of powder cellulose

Scheme of treatment	Step I		Step II		Indices of powder cellulose	
	NaOH, % of the mass of dry material	pH_k	Na_2SiO_3, % of the mass of dry material	pH_k	yield, % of the mass of dry material	whiteness, %
Alkali–hydrogen peroxide	2	10.7	–	9.2	93.0	68.7±0.1
Alkali–hydrogen peroxide	2	10.7	5	10.7	93.0	71.3±0.1
Hydrogen peroxide	–	–	–	9.4	95.1	66.3±0.1
Hydrogen peroxide	–	–	5	10.6	94.7	69.8±0.1

Table 6. Effect of bleaching conditions on the whiteness of powder cellulose

Scheme of bleaching	Step I	Step II		Step III		Indices of powder cellulose	
	expenditure of reagents, % of dry material						
	NaOH	ClO_2	–	H_2O_2	NaOH	yield, %	whiteness, %
Alkali–chlorine dioxide–hydrogen peroxide	2.0	1.00	–	1.25	1.25	90.0	88.6±0.1
Alkali–chlorine dioxide–hydrogen peroxide	2.0	1.00	–	1.25	0.80	89.5	90.1±0.1
		H_2O_2	NaOH	ClO_2			
Alkali–hydrogen peroxide–chlorine dioxide	2.0	1.25	1.25	1.00	–	90.4	82.9±0.1
Alkali–hydrogen peroxide–chlorine dioxide	2.0	1.25	0.80	1.00	–	89.9	86.2±0.1

Influence of alkaline treatment . At the stage of the hydrolytic degradation of unbleached pulp by acid (at producing powder lignocellulose) the residual lignin can transform by two pathways: The destruction due to cleavage of ether bonds and condensation. The partially destroyed lignin in this case can remain in the powder cellulose and it is possible to extract it by alkali. The decrease in the content of lignin in the lignocellulose material can positively affect the results of its bleaching, but, as shown in the survey [5], two consecutive treatments in the alkaline medium can be not very effective (it will increase the expenditure of alkali at the low effect of delignification). The data on the influence of alkaline processing on the delignification of powder cellulose by H_2O_2 are presented in Table 5.

As at the bleaching of usual sulfate cellulose of the deciduous wood [5], the preliminary alkaline treatment insignificantly increases whiteness of powder cellulose at the subsequent bleaching by hydrogen peroxide (also in the alkaline medium). An increase in the whiteness of powder cellulose as a result of the preliminary treatment with NaOH is 1.5% (with sodium silicate) and 2.4% (without the stabilizer).

At the bleaching of powder cellulose by chlorine dioxide or by hydrogen peroxide alone, it is practically impossible to reach complete delignification and high whiteness even at the large expenditure of the reagents. Therefore we carried out study of the combined bleaching the powder lignocellulose using the most effective combinations of treatment: chlorine dioxide–hydrogen peroxide [5] in opposite sequence (Table 6).

The introduction of sodium silicate at the bleaching by hydrogen peroxide increases the whiteness of powder cellulose by 1.5%, maximum whiteness reached is 90.1%. The yield of powder cellulose at the combined bleaching is 90%, i.e., the losses are somewhat less than in the five-stage bleaching of deciduous sulfate cellulose in joint stock company “Mondi Syktyvkar LPK” (about 89%). At the opposite sequence of stages (alkali–peroxide–chlorine dioxide) the whiteness of powder cellulose is 86.2%. Thus, the most effective scheme of the bleaching of lignocellulose material is alkali–chlorine dioxide–hydrogen peroxide.

CONCLUSIONS

(1) The effective method of producing powder cellulose from the unbleached deciduous sulfate cellulose is processing according to the scheme: hydrolysis–bleaching. In the first stage from the crude cellulose powder lignocellulose is obtained, in the second stage te latter is subjected to delignification by treatment with hydrogen peroxide and then by chlorine dioxide.

(2) The introduction of stabilizer (sodium silicate) at the stage of bleaching of hydrogen peroxide increases the final whiteness of powder cellulose by 1.5–2.3%.

REFERENCES

1. Battista, O.A., *Tsellyuloza i ee proizvodnye* (Cellulose and its Derivatives), vol. 2, Moscow, 1974, p. 412.
2. Demin, V.A. and Shereshovets, V.V., *Khimiya drevesiny i lesokhimiya* (Chemistry of Wood and Forest Chemistry), Komi Sci. Center, Russ. Acad. Sci., 1993, no. 129, p. 78.
3. Obolenskaya, A.V., El’nitskaya, Z.P., and Leonovich, A.A., *Laboratornye raboty po khimii drevesiny i tsellyulozy* (Laboratory Textbook on the Chemistry of Wood and Cellulose), Moscow, 1991.
4. Bolotnikova, L.S., Danilov, S.N., and Samsonova, T.I., *Zh. Prikl. Khim*., 1966, vol. 39, no. 1, p. 176.
5. Demin, V.A., Shereshovets, V.V., and Monakov, Yu.B., *Usp. Khim*., 1999, vol. 68, no. 11, p. 1029.