Lateral Order Distribution of Native Cellulose

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Introduction

Howsmon and Sisson[1] have discussed the characterization of lateral order distribution in cellulose fibers and suggested how to estimate it. Lately they showed[2] that the lateral order distribution in native cellulose fibers is characterized in the extent of lowering of the "level-off degree of polymerization" after swelling and hydrolysis.

Yurugi[3] and Maeda[4] found that the fractional dissolution in sodium hydroxide solutions of various concentrations after hydrolysis can be another method to estimate the lateral order distribution and they obtained many interesting results about regenerated cellulose fibers.

The present authors[5] have also shown the lateral order distribution in some regenerated cellulose fibers by making use of the method proposed by Yurugi and Maeda.

Every one of these methods is useful to obtain the lateral order distribution but the distributions obtained may be different from each other. So it is desirable to compare these methods and to seek the possible explanation in the phenomena observed.

In this paper the lateral order distributions in native cellulose fibers was obtained by various methods and they were compared with each other and the meaning of distribution was discussed.

Procedure

Cellulose Sample.—For this study the following three native cellulose samples were used:

- (A) Cotton linters pulp, viscose grade, α-cellulose 98.3%, degree of polymerization 610.
- (B) Sulfate wood pulp, viscose grade, α-cellulose 94.3%, degree of polymerization 690.
- (C) Sulfite wood pulp, viscose grade, α-cellulose 93.8%, degree of polymerization 730.

The methods to obtain the lateral order distribution were as follows:

1. The fractional dissolution in sodium hydroxide solutions of various concentrations after methanolysis,
2. The measurement of the drop of the "level-off degree of polymerization",

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[1] J.A. Howsmon and W.A. Sisson, in Otto-Spurlin, "Cellulose and Cellulose Derivatives", Interscience, New York (1954), pp. 251-91.

[2] O. A. Battista, S. Coppick, J.A. Howsmon, F.F. Morehead and W.A. Sisson, *Ind. Eng. Chem*, **48**, 333 (1956).

[3] T. Yurugi, *J. Soc. Chem. Ind., Japan*, **58**, 27 (1955).

[4] H. Maeda, *J. Soc. Textile Cellulose Ind. (Japan)*, **12**, 6 (1956).

[5] S. Mukoyama, *J. Soc. Textile Cellulose Ind. (Japan)*, **11**, 772 (1955).

designated as *D.P.*, after swelling and hydrolysis,

(3) The moisture regain measurement after swelling.

(1) The Fractional Dissolution Method.—Methanolysis.—The purpose of methanolysis was to depolymerize the cellulose without accompanying the recrystallization which would be indispensable in an aqueous acid hydrolysis.

1 N hydrogen chloride in absolute methyl alcohol was used as a methanolysis reagent, which was prepared by blowing dry hydrogen chloride gas in dry absolute alcohol. The methanolysis was performed in an Ehrenmeyer flask in a thermostat kept at 50±0.1°C for forty-eight hours, 6 g. of bone-dry powdered sample being placed in about 250 ml. of reagent. After methanolysis, the sample was filtered, and washed with methyl alcohol until it became chloride-free and then it was dried.

Fractional Dissolution.—Every 0.2 g. of the methanolyzed samples was treated with 20 ml. of sodium hydroxide solutions of increasing concentrations and after being kept at 8±0.1°C for two hours the undissolved residues were filtered, washed with distilled water until the neutral reaction was obtained and dried at 105°C to constant weight.

Lateral Order Distribution.—Solubility Q was defined as follows:

$$Q=1-a\cdot m,$$

where a represents a fraction of residue at fractional dissolution and m a yield at methanolysis.

Summative mass-order relations were given by plotting Q versus increasing concentrations of sodium hydroxide. The lateral order distribution for the original sample was given by differentiating the mass-order curve.

(2) The *D. P.* Method. — Jörgensen[6,7] has pointed out that the *D.P.*'s of native cellulose fibers depend on the extent of preswelling by sodium hydroxide solutions. This phenomenon was applied by Battista et al.[2] to estimate the lateral order distribution of native cellulose fibers.

The powdered samples were swollen at 20°C for two hours in sodium hydroxide solutions of various concentrations and then excess solutions was drawn off, the residual sodium hydroxide was neutralized with N/2 acetic acid, washed acid-free with distilled water and then dried from methyl alcohol.

Acid hydrolysis was performed by boiling with 2.5 N hydrogen chloride solution for one and a half hours. Preliminary experiments show that the degree of polymerization of each sample attains to a constant level-off value by this procedure. The *D.P.* was measured using Cuprammonium solvent ($K_m=2\times10^3$).

To obtain the lateral order distribution curve the extent of drop in *D.P.* after swelling and hydrolysis was measured. The relative decrease in *D.P.* ($D.P._{\cdot r}$) is defined as follows:

$$D.P._{\cdot r}=\frac{(D.P.)_0-(D.P.)}{(D.P.)_0-(D.P.)_m},$$

where $(D.P.)_0$ and $(D.P.)_m$ denote the *D.P.* of unswollen sample and of completely mercerized sample respectively. Differential lateral order distribution curves were obtained by plotting $d(D.P._{\cdot r})/d(\mathrm{NaOH})$ versus increasing concentrations of sodium hydroxide.

(3) The Moisture Regain Method.—Rånby[8], Jörgensen[7] and Mitchell[9] have shown the dependence of the moisture regain on the extent of preswelling of native cellulose samples by sodium hydroxide solutions. Sisson and Howsmon[1] suggested that this phenomenon is useful for lateral order measurement.

Samples preswollen in sodium hydroxide solutions of various concentrations were dried over conc. sulfuric acid solution and then transferred to a desiccator with 65 per cent relative humidity at 23°C (over saturated solution of sodium nitrite). When equilibrium at 65 per cent. R.H. was reached (seven days), the samples were weighed and then dried at 105°C to constant weight.

The water content (w) was calculated in per cent of the weight of the dry sample. From the water content w the relative increase in the water content w_r was calculated according to the following relation:

$$w_r=\frac{w-w_0}{w_m-w_0}$$

where w_0 and w_m denote the water contents of unswollen and completely mercerized samples respectively. Differential lateral order distribution was obtained by plotting $dw_r/d(\mathrm{NaOH})$ against increasing concentrations of sodium hydroxide.

Results

(1) The Fractional Dissolution Method.—The samples dissolved a little in the methanolysis reagent. The yield m and the degree of polymerization (*D.P.*) of the methanolyzed samples are collected in Table I.

TABLE I

THE YIELD m AND THE *D.P.* OF THE METHANOLYZED SAMPLE ARE AS FOLLOWS:

Samples	m (%)	*D.P.*
Linters pulp	98.3	150
Sulfate pulp	95.5	120
Sulfite pulp	96.5	140

As shown in Table I, the degree of polymerization of each sample after methanolysis reaches to the leveloff value which has been expected from preliminary experiments.

Summative mass-order curves are shown in Fig. 1 and the lateral order distributions are derived in Fig. 2 from these curves.

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[6] L. Jörgensen, *Acta Chem. Scand.*, **4**, 185 (1950).

[7] L. Jörgensen and E. Ribi, *Nature*, **166**, 148 (1950).

[8] B.G. Rånby, *Acta Chem. Scand.*, **6**, 101 (1952).

[9] R.L. Mitchell, *Ind. Eng. Chem.*, **43**, 1786 (1951).

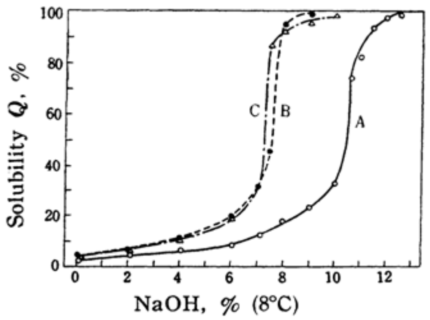

Fig. 1. Solubilities of methanolyzed native celluloses in sodium hydroxide of increasing concentrations.
(A) Cotton linters pulp.
(B) Sulfate wood pulp.
(C) Sulfite wood pulp.

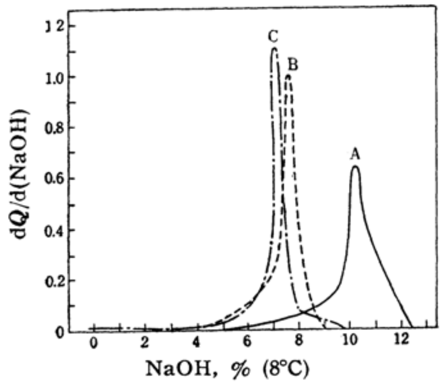

Fig. 2. Lateral order distribution curves obtained by the fractional dissolution method.

From Fig. 2 it will be seen that the linters pulp is more highly ordered relative to sulfate and sulfite pulp, but between the latter two no difference in their distribution is observed. Each of the distribution curves has a sharp peak, suggesting that the samples are mainly composed of crystalline regions of uniform perfection.

(2) **The *D.P.* Method.**—In Fig. 3 the *D.P.*'s after swelling and hydrolysis are plotted against increasing concentrations of sodium hydroxide. From these data the lateral order distribution curves are derived in Fig. 4.

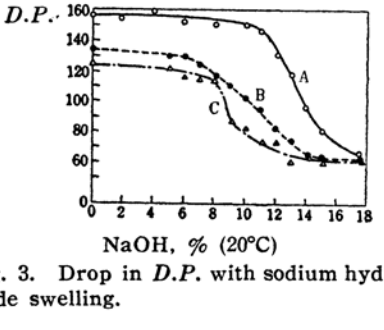

Fig. 3. Drop in *D.P.* with sodium hydroxide swelling.

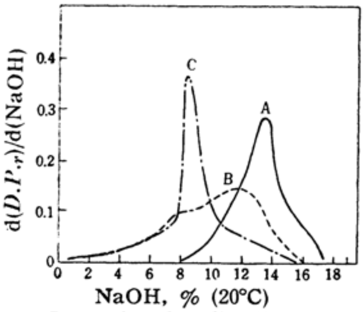

Fig. 4. Lateral order distribution curves obtained by the *D.P.* method.

As shown in Fig. 3, the *D.P.*'s of original pulps are in the range of 135 to 160, whereas mercerized pulps exhibit almost the same *D.P.*'s of about 65.

It is interesting to note that the lateral order distribution of sulfate pulp in Fig. 4 is different from that in Fig. 2. In Fig. 2 the distribution curve of sulfate pulp has a sharp peak of the same order as the sulfite pulp, whereas in Fig. 4 sulfate pulp has a broad distribution extending between the peaks of curve of sulfite pulp and that of linters pulp. In general the distribution curves in Fig. 4 are more flat than those in Fig. 2.

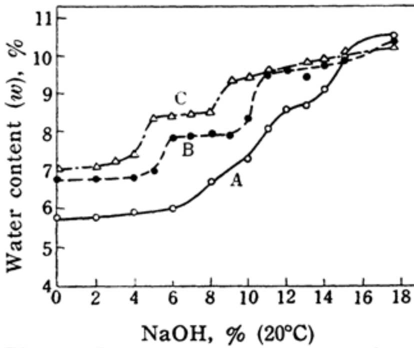

Fig. 5. Increase in moisture regain with sodium hydroxide swelling.

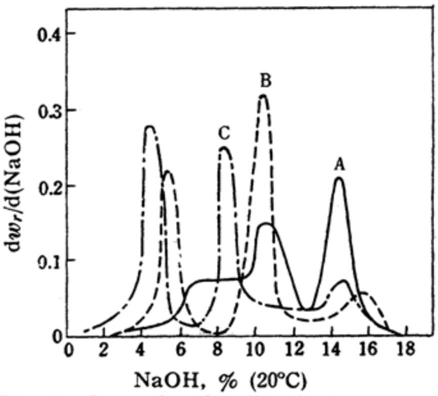

Fig. 6. Lateral order distribution curves obtained by the moisture regain method.

(3) The Moisture Regain Method.—In Fig. 5 water contents at 65 per cent R.H. for the preswollen samples are plotted against increasing concentrations of sodium hydroxide.

From these data the lateral order distribution is derived by the procedure described previously. They are shown in Fig. 6.

The distribution curves in Fig. 6 are different from those in Fig. 2 and Fig. 4; they have two peaks respectively, one of which is of lower order than the other which is of the same order as that in Fig. 4.

Discussion

As previously pointed out by Howsmon and Sisson[1], there are various methods to obtain the lateral order distribution of cellulose. In the present experiment the following methods were adopted: the fractional dissolution method, the *D.P.* method and the moisture regain method.

Among them the fractional dissolution method gives the most distinct distribution curve. In this method the samples were depolymerised before the alkali treatment, so that the solubilities of samples into sodium hydroxide solutions of various concentrations were determined simply by the degree of perfection of the separated crystalline regions.

In the other two methods the swelling in sodium hydroxide solution was performed in the original state, so that the swelling was restricted by many other morphological factors. These restrictions give rise to broadening of the distribution range as shown in the curve of sulfate pulp obtained by the *D.P.* method.

The difference between sulfate and sulfite pulps, which is the so-called "sulfate effect"[10], is observed in Fig. 4 and Fig. 6, but no difference in Fig. 2. This fact shows that the depolymerization before the alkali treatment reduces the higher resistance of sulfate pulp against the swelling in the aqueous sodium hydroxide solution. In other words, the lateral order of the crystalline regions in sulfate pulp is the same as that in sulfite pulp and some other morphological factors probably affect to increase the resistance of sulfate pulp against the swelling. Thus it is apparent that the "sulfate effect" is not due to the difference in the crystalline regions.

The crystallinities of sulfite wood pulp and cotton were found to be 65 and 70 per cent respectively by Hermans[11] from X-ray diffraction measurement. It is interesting to compare its result with the summative mass-order curves in Fig. 1. In Fig. 1, the concentrations of sodium hydroxide at which the solubility curves rise sharply are 7 per cent for sulfite pulp and 10 per cent for linters pulp, and the solubilities at these concentrations are the same value of about 30 per cent. This fact suggests that the crystallinity obtained by X-ray diffraction method shows the quantity of such uniform crystalline regions irrespective of their lateral orders. The difference between cotton linters pulp and wood pulp is considered to be remarkable in the crystalline regions as shown in Fig. 2; that is, the crystalline regions of wood cellulose are less perfect than those of cotton cellulose.

In Fig. 6 each of the distribution curves has two peaks, one of which appears at almost the same concentration of sodium hydroxide as that in Fig. 4, while the other occurs at lower concentration. To understand the meaning of these circumstances the mechanism of mercerization must be considered. Nukushina[12] has recently reported that the decrystallization precedes the phase transition when native cellulose fibers are treated with the alkali of increasing concentrations. The present authors have confirmed this fact with respect to linters pulp by making use of X-ray diffraction. In their experiment, linters pulp started to decrystallize at 10 per cent sodium hydroxide and to induce the phase transition at 13 per cent sodium hydroxide at 20°C. The lower ordered peak of the distribution curve of linters pulp may be attributed to this decrystallization, for the decrystallization in general gives rise to increase in moisture regain. The same line of argument will be possible with respect to wood pulps, too.

If these views are accepted, the conclusion may be drawn that the fractional dissolution method will be the best method to obtain the lateral order distribution of native cellulose fibers. Thus the following concept will be accepted; that is the native cellulose fibers consist of a large proportion of uniform crystalline regions separated by amorphous regions of fairly high order, and the crystalline regions in wood cellulose are less perfect than those in cotton cellulose.

Summary

To obtain the lateral order distribution of native cellulose fibers the fractional dissolution method, the *D.P.* method and the mois-

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[10] B.G. Rånby and H.F. Mark, *Svensk Papperstidning*, **10**, 374 (1955).

[11] P.H. Hermans and A. Weidinger, *J. Polymer Sci.*, **4**, 135 (1949).

[12] Y. Nukushina, *J. Soc. Textile Cellulose Ind. (Japan)*, **12**, 158 (1956).

ture regain method were adopted. Among these three methods the fractional dissolution method gives the most correct distribution. The other methods give somewhat different distribution curves, the meanings of which were discussed. The structural difference between wood pulp and linters pulp is due to the difference in the degrees of perfection of crystalline regions, whereas no difference between sulfate pulp and sulfite pulp is observed in their crystalline regions.

One might conclude that the fractional dissolution method is the best method to obtain the lateral order distribution in both native and regenerated cellulose fibers.

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