

Fine Structural Differences between Natural Cellulose Fibers as Revealed from Chain Length Distributions of Hydrolyzed Materials

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In previous publications ^{1,2}, it was shown that during heterogeneous hydrolyses wood pulps behaved quite differently from cotton and cotton linters. Compared with the latter the degradation of pulps was considerably slower when measured as decrease in average degree of polymerisation (DP). The limit DP values, *i. e.* the constant DP's reached after prolonged time of hydrolysis, was higher for the pulps and greatly dependent upon the severity of the pulping conditions. For pulps swelled in alkaline solutions of increasing strength the rate of fall in DP increased and the limit DP decreased gradually, whereas the hydrolysis behavior of cotton remained unchanged until the alkali concentration was sufficient to cause intracrystalline swelling. A different arrangement in the less ordered regions and especially in the transition regions of the two fiber species was proposed as an explanation for these dissimilarities.

More information regarding these divergences might be acquired from knowledge of the chain length distribution diagrams of fibers degraded to their limit DP's. These diagrams will disclose the spread in length distribution of acid resistant fragments and also, with the reservations outlined below, of the ordered areas in the original fibers. As mentioned, the limit DP of wood fibers is sensitive to treatment with alkaline solutions which cause intercrystalline swelling only. It has recently been shown ³, that at the conditions employed in this investigation, intracrystalline swelling of pulp fibers starts by treatment with 6.5 per cent sodium hydroxide solution. To discover the changes in the intercrystalline domains of wood fibers causing the decrease in limit DP, distribution diagrams will have to be determined for samples swelled in alkaline solutions varying between zero and six per cent. Changes in the size

of ordered regions originating from intracrystalline swelling might be obtained from wood fibers swelled in eight or ten per cent and cotton linters swelled in ten per cent lye.

The present paper deals with such an investigation for a spruce sulfite pulp, an aspen holocellulose and cotton linters. The experimental findings will be seen to support the earlier proposed differences in the fine structural arrangements of purified wood and cotton fibers.

MATERIALS AND METHODS

The spruce pulp was an extracted sulfite pulp of relatively high DP (1650), carefully bleached with sodium chlorite to negligible lignin content. The aspen holocellulose was prepared from air dried chips, which were disintegrated in a Wiley-type mill and screened. The 20–40 mesh fraction was separated and air dried and holocellulose prepared according to the procedure described by Wise *et al.*⁴. Four chlorite treatments were found necessary to bring the lignin content to a low value of about one per cent. The cotton linters was an extracted acetate grade linters from Hercules Powder Co. All extractions were made with alcohol-benzene (1 : 2) for 24 h.

The swelling in sodium hydroxide solutions and the subsequent hydrolysis were as described earlier². Nitration, fractionation of the nitrates in acetone solution and construction of the weight frequency distribution curves were carried out in the manner previously outlined in detail¹. The DP's of the fractions were calculated from the intrinsic viscosities of the nitrates in acetone solutions using the Staudinger equation and $K_m = 10^{-3}$, c in g/l. The fractionation yielded 40–60 fractions of which 30–40 showed different intrinsic viscosities.

EXPERIMENTAL DATA AND DISCUSSION

Fig. 1 shows the weight frequency distribution curves for the hydrolyzed spruce pulp samples previously swelled in 0 (water) — 2—6 and 10 per cent sodium hydroxide solutions, respectively. Fig. 2 gives the similar curves for the aspen holocellulose samples swelled in 0—4—6 and 8 per cent sodium hydroxide and Fig. 3 represents the distribution curves for cotton linters swelled in 0 and 10 per cent lye and hydrolyzed. The loss in material during swelling and hydrolysis as well as the average DP's of the fractionated samples are found in Table 1.

On examination of the changes in the chain length distributions of the spruce pulp it is seen that the water swelled sample exhibits a rather heterogeneous distribution. A high, narrow peak is present at a DP of about 30, then comes another, but lower and broader maximum at about 130–150, followed by a low broad maximum at the 230 level. The most distinctive feature of the curve, is, however, the very long right hand tail extending to DP values of at least 7–800. The amount of material above D.P. 300 comprises almost 30 per cent of the total. The distribution curve for the two per cent

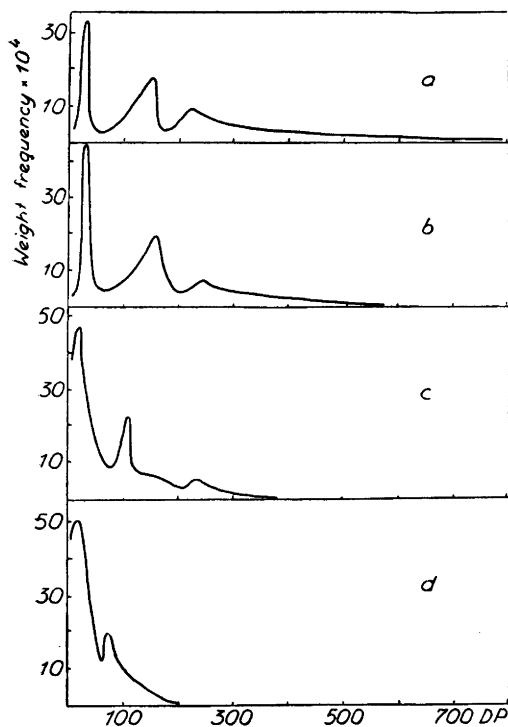


Fig. 1. Weight frequency distribution curves for hydrolyzed spruce pulp previously swelled in: a: Water, b: 2 per cent NaOH, c: 6 per cent NaOH, d: 10 per cent NaOH.

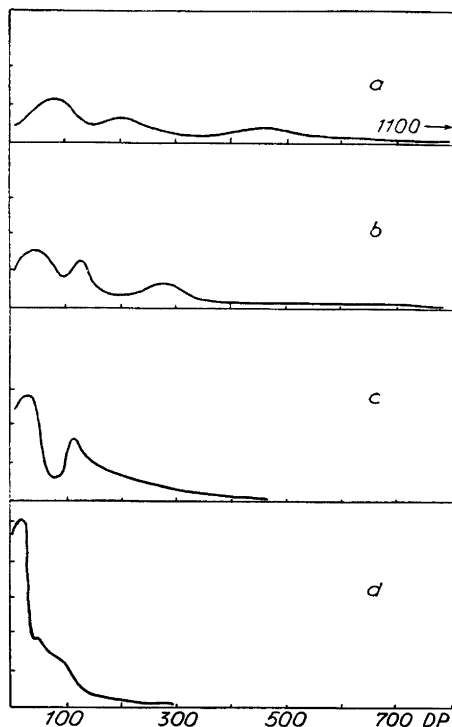
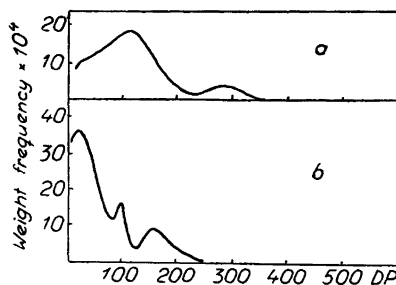


Fig. 2. Weight frequency distribution curves for hydrolyzed aspen holocellulose previously swelled in: a: Water, b: 4 per cent NaOH, c: 6 per cent NaOH, d: 8 per cent NaOH.

sample has a somewhat larger peak at DP 30 and a broader peak at the 150 level as compared with the water swelled sample. The peak at DP 230 has diminished somewhat and the right hand tail comprises now less material and does not extend to the same high DP as it did in the first curve. Chains with DP of over 600 are, however, still present. A pronounced change has occurred in the distribution of the six per cent sample. The maximum at DP 30 has increased considerably and comprises now 55–60 per cent of the material. The broad maxima found at DP 150 in the two previous distributions has moved to a lower DP of about 100–110 and is rather narrow. A small peak is still found at the 230 DP level. The tail to the right has now diminished considerably and comprises only 4–5 per cent of the material. No chains are found with DP above 350–400. As far as the amount of low DP material is concerned the ten per cent sample does not seem to be much different from the six per cent sample. The first maximum contains again about 60 per cent of the total but is somewhat narrower compared with the similar maximum for the six per cent material. The maximum previously at 110 has moved still

Fig. 3. Weight frequency distribution curves for hydrolyzed cotton linters previously swelled in: a: Water, b: 10 per cent NaOH.



further to the left and is found at a DP of 75. The extensive right hand tail has disappeared altogether and the longest chains have a DP of 175–200.

The water swelled aspen holocellulose exhibits a very large breadth of distribution (Fig. 2 a) with no such marked maximums as found for the similar spruce sample (Fig. 1 a). The extensive right hand tail is even more marked, reaching to DP 1100. A flat maximum is found at DP 450. Two broad modes are present in the low DP range, one containing some 20 per cent of the material at a DP of 100 and a smaller one at DP 200. The changes in the distribution caused by swelling in a four per cent lye are not very large (Fig. 2 b). The tail to the right is not so extensive and does not go beyond DP 800 and only ten per cent has a DP above 400. The small maximum previously at 450 is now at DP 275. The two peaks in the low DP range have moved to the left and increased somewhat in size. The first is seen at DP 60 and the second at DP 130. A striking alteration

Table 1. Material dissolved during swelling and hydrolysis and limit DP values for fractionated samples.

Material	Dissolved during swelling, %	Dissolved during hydrolysis, %	Total dissolved, %	Limit DP
Spruce pulp, swelled in:				
water	0	16.1	16.1	270
2 % NaOH	2.5	14.1	16.6	220
6 » NaOH	11.8	16.4	28.2	105
10 » NaOH	16.3	17.8	34.1	50
Aspen holocellulose, swelled in:				
water	0	—	—	315
4 % NaOH	30.4	20.0	50.4	240
6 » NaOH	32.6	19.2	51.8	130
8 » NaOH	28.6	28.1	56.7	60
Cotton linters, swelled in:				
water	0	7.3	7.3	135
10 % NaOH	2.2	13.1	15.3	75

has occurred in the distribution curve of the six per cent sample. The long right hand tail has diminished considerably and reaches to DP 450 only. The main maximum is found at DP 30—35 and comprises 45 per cent of the total. Another maximum with a pronounced skewness to the right is seen at DP 100—110. The distribution is not too different from that of the six per cent spruce material. In the latter more material is concentrated in the first maximum (Fig. 1 c). This similarity is even more marked when the two fibers have undergone intracrystallin swelling, as for the eight per cent aspen and ten per cent spruce material (Fig. 1 d and Fig. 2 d). The peak at DP 25—30 comprises 55—60 per cent of the total. No other peak is found in the curve. †

The water swelled cotton linters (Fig. 3 a) show a chain length distribution which in one respect differs markedly from those exhibited by the corresponding purified wood fibers. The long tail to the right so peculiar to the distribution of those fibers is not found in the curve for cotton linters. A rather small maximum is seen at DP 275 and the longest chains have a DP of about 375, compared with 800—1100 for the wood fibers. A broad maximum with its peak at a DP of 110—125 comprises almost 85 per cent of the material. This part of the curve is somewhat similar to the distribution of the aspen holocellulose (Fig. 2 a). However, in the latter it includes 45 per cent only, of the total. In contrast to the spruce pulp (Fig. 1 a) the water swelled samples of cotton and aspen holocellulose (Fig. 2 a and Fig. 3 a) do not show any maximum in the very low DP range of 25—30. The distribution curve for the intracrystalline swelled cotton linters (Fig. 3 b) is rather similar to those of the corresponding wood fibers (Fig. 1 d and Fig. 2 d). A broad maximum comprising about 60 per cent of the chains is found at DP 25—30. Another minor peak is seen at DP 100 and still another low maximum at DP 130. The material does not seem to contain chains with DP above 250.

Cellulose chains may terminate within acid resistant aggregates and consequently the chain length distribution diagrams would not be identical with the length distribution of these fragments. However, the maximum length of the acid resistant fragments correspond at least to the length of the longest cellulose chains, and accordingly the amount of long chain material is a good indication of the amount of the longest aggregates. It is also reasonable to assume that pronounced peaks in the chain length diagrams correspond to similar peaks in the size distribution of the fragments. Regarding peaks in the lowest DP range it could be reasoned that these very short chains mostly end within aggregates. However, this does not necessarily always have to be the case. When comparing the size distribution of acid resistant fragments with that of the ordered domains in the fibers one must consider the changes which take place during hydrolysis. "The recrystallization" occurring when the cellulose chains are disrupted⁵⁻⁷ might be expected to lead to a certain increase lengthwise in these domains. This increase might, however, be small and not serious if we realize that we are dealing with highly approximate values.

Interpreted on this basis it is evident that the purified, not alkali swelled wood fibers contain acid resistant aggregates of considerable length including cellulose chains with 800—1100 glucoseanhydride units or 4—5000 Å long,

which is several times the frequently considered average size of crystalline regions, 5—600 Å⁸⁻¹⁰.

Upon swelling in alkaline solutions these long aggregates are made acid susceptible and a gradual decrease in their length takes place upon treatment in two, four and six per cent lyes.

The permanence of the x-ray diagrams has been established for wood pulp fibers swelled in alkaline solutions of this strength range³. No new maxima are observed in the distribution curves for samples swelled in lyes of these concentrations compared with the water swelled samples. This is especially pronounced for the spruce pulp. These findings indicate strongly that the very long aggregates found in the unswelled fibers consist of well arranged "crystalline" regions interconnected by throughgoing chains grouped in arrangements of somewhat lower order but still able to resist or greatly delay attack under the hydrolysis conditions applied. No such arrangements are present in the intercrystalline areas of cotton linters. The distribution diagrams for linters do not change upon swelling in lyes of these intermediate concentrations.

The resistance of the long aggregates is greatly dependent upon the conditions during hydrolysis. It has been shown² that the limit DP value change with the pulping conditions. We have also found that hydrolysis with stronger acids, especially if they exert greater swelling than the sulfuric acid applied in this investigation, will yield a lower limit DP. On the contrary weaker acids or milder conditions, *e. g.* lower temperature, lead to higher limit DP values for the wood fibers.

As mentioned wood pulp swelled in a six per cent lye still retains an unchanged x-ray diagram. Samples swelled in 6.5 per cent alkaline solutions will show sign of intracrystalline swelling. In six per cent samples all but the crystalline domains, as defined by x-ray diffraction, should therefore have undergone swelling, and in consequence the greater part of the intercrystalline acid resistant arrangements destroyed. The intercrystalline domains in the six per cent pulp fibers should hence be available for acid attack similar to that experienced by the linters. It was also found that the drop in DP for a six per cent wood pulp closely followed the course of cotton linters².

The length distributions of the acid resistant fragment in six per cent wood fibers and in linters show, however, a great variance. In the wood fibers an accumulation of very small fragments with a length of 100—200 Å is observed. No such accumulations is found in the linters. In spruce this part amounts to 60 per cent and in aspen to 45 per cent of the total. It seems reasonable to assume that regions of this dimension make out a considerable part of the highly ordered domains in wood fibers.

Several important differences in physical properties of wood fibers and cotton may be intimately connected with this large amount of very small crystalline regions in the former material. The easier mercerizing^{3,11} of wood pulps compared with cotton might be due to an easier intracrystalline swelling of small crystalline regions when interconnected by long cellulose chains. In spite of similarity in amount of crystalline materials¹² the water regains of pulps is higher than for cotton, and this could very well be related, to the larger surface of many small compared with the smaller surface of fewer and larger crystallites. The higher constant rate of loss in material during hydrolysis of wood fibers may also be traced to their larger crystalline surface.

For all three materials, spruce, aspen and cotton fibers, the hydrolysis of the intracrystalline swelled samples leads to a considerable accumulation of small fragments 100—200 Å long only. In all three cases fragments of this size amount to about 60 per cent of the total. For the wood fibers this accumulation is a result of a continuous change as it was found that the intercrystalline swelled samples contained already an agglomeration of these very small aggregates. For the linters the appearance of a large amount of small fragments is much more abrupt.

Considering the small differences in loss of material during hydrolysis of intracrystalline and intercrystalline swelled materials (Table 1) it might be assumed that the accumulation of these small fragments has been brought about through division of the larger ordered domains. This assumes that intracrystalline swelling has made the ordered regions acid susceptible at certain places, where the cellulose chains now may be disrupted. A final consequence of such a hypothesis would be that the areas exhibiting a true crystalline order are very small (100—200 Å), and that it is the arrangement in the regions between these small true crystallites which differs in various fibers, being of a highly gradual and diversified nature in wood fibers and exhibiting more abrupt changes in cotton fibers.

It is in this connection interesting to note that the average length of the hydrolysis products of regenerated cellulose fibers^{13,14} compare well with the pronounced peak in the fragment size of the intracrystalline swelled materials.

The theory put forward above is in need of much more definite experimental evidence before it in any way should be regarded as established. The interpretation of the chain length distribution data do, however, strongly support and advance the earlier proposed fine structural difference between wood fibers and cotton.

SUMMARY

Spruce sulfite pulp, aspen holocellulose and cotton linters have been swelled in alkaline solutions varying from zero to ten per cent concentration and subsequently hydrolyzed. Chain length distribution determinations have been carried out on the hydrolyzed materials. Evaluation of the distribution curves show that the fine structure of purified wood fibers differs from that of cotton linters by

- 1) the presence of well arranged chains interconnecting the highly ordered regions and resistant towards acid hydrolysis if not swelled in alkaline solutions
- 2) the presence of a large amount of very small highly ordered regions.

Upon hydrolysis all intracrystalline swelled fibers show an accumulation of very small fragments, 100—200 Å long. These are most probably formed through division of longer well ordered regions suggesting a subdivision of the latter into smaller perhaps more fundamental units.

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