Hydrolysis and Fine Structures of Cotton and Wood Pulp Fibers

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The hydrolysis of cellulose fibers has been used repeatedly in recent years to obtain information about the fine structure of fibers. (Nickerson *et. al.*[1], Conrad and Scroggie [2], Philip [3], Conrad and Nelson[4]). The loss of material during the hydrolysis has been used as a measure of the degree of lateral order (crystallinity), and the constant value for the degree of polymerization (limit DP) obtained after a certain time of hydrolysis has been taken as a measure of the size, *i. e.* length, of the regions with high lateral order (crystallite or micelle size). Lately it has been shown that a certain increase in the crystallinity occurs during the hydrolysis (Mark *et. al* [5], Howsmon [6], Hermans [7]). This increase, or recrystallization, is assumed to take place in the transitional areas of the crystallites into the disordered regions, the so-called mesomorphous areas. The length of the crystallite measured by the limit DP will, therefore, not correspond to the original length in the untreated fibers. It will, however, bear a certain relation to the original size in the regions with lateral order, and approximate the size of the crystallites with the addition of the transitional areas.

In order to explain some phenomena encountered during comparative hydrolysis experiments on cotton linters and sulfite pulps, we recently [8] put forth the hypothesis that the regions of high lateral order in the wood fibers are more irregular, not only in size but especially in their dimensions being longer and flatter than the crystalline regions in the cotton linters. We will report here some experiments which strongly indicate that the main difference in the fine structures of cotton and wood pulp fibers is in the extension of the mesomorphous areas in the latter, these being much larger in the pulp than in the cotton fibers. More extensive investigations are in progress and the results will be published later.

The fibers used in the experiments were bleached cotton and sulfite pulps. The pulps had been cooked to varying viscosities followed by a chlorine bleach. The fibers were swelled for 2 hours in sodium hydroxide solutions of different strength at 5° C, carefully washed with icewater, and dried in vacuum oven at 60° C. The water regains were determined at 55 % RH, and the samples were hydrolyzed with 2.5 N H_2SO_4 at 97° C for 6 hours. The average viscosity DP of the hydrolyzed material was found by converting to cellulose nitrate, determining the intrinsic viscosities in acetone solution, and using Staudinger's eq., with a K_m-constant of 10^{-3} (c in g/l), for conversion of the viscosities to DP's.

It can be seen from Table 1, column four, that the limit DP of the cotton remains constant until the alkaline solution is strong enough to cause intramicellar swelling (10 %). At this point a sudden drop in the limit DP, from 140 to 95, takes place, showing that the transformation from Cellulose I (native) to Cellulose II (hydrate) has changed the crystallite size. No change in the size had, however, occured prior to this transformation. The pulps exhibit quite a different behavior. The limit DP for all these samples decreased gradually as the strength of the alkaline solution increased, until at eight per cent concentration a sharp drop occured. No decrease, or only a very small one, resulted when the concentration was increased to the mercerizing strength.

Passing from the disordered to the crystalline regions, the lateral order of the transitional area will increase. Alkaline solutions of increasing concentration will

Table 1. Hydrolysis and water regain data for fibers swelled in alkaline solutions of varying concentrations.

Material	Swelled in NaOH sol. conc. in weight %	Water regain, relative values (regain with water swelling = 1.0)	Limit DP
Bleached cotton	0	1.0	140
	2	1.0	140
	4	1.05	140
	6	1.05	140
	8	1.08	140
	10	1.44	95—100
Pulp of high viscosity	0	1.0	400
	2	1.0	330
	4	1.0	275
	6	1.03	170
	8	1.16	60
	10	1.21	60
Pulp of medium viscosity	0	1.0	300
	2	1.0	275
	4	1.0	250
	6	1.0	180
	8	1.21	65
	10	1.20	55
Pulp of low viscosity	0	1.0	195
	2	1.0	190
	4	1.0	175
	6	1.07	125
	8	1.36	55—60
	10	1.36	45—40

swell and cause disorder to a larger and larger part of these regions until, at last, the crystallite themselves swell and are partly destroyed. The constant limit DP of the cotton shows that the mesomorphous region is negligible in this material, or is of such a low order that even water will penetrate it. In the pulp fibers, this area is of considerable size and contains probably a large variation of order, shown by the gradual decrease in limit DP. The length of the transitional area is several times that of the crystallite, which probably should be regarded only as a nucleus from which the large mesomorphous regions extend. It is interesting to note, that the length of the wellarranged crystallites of Cellulose I (after swelling in 8 % NaOH) is almost the same as those of Cellulose II (after swelling in 10 % NaOH), in contrast to the findings for the cotton fibers.

Table 2. Recalculated water regains for the low viscosity pulp.

Swelled in % NaOH	Material dissolved Weight %	Recalculated relative water regain: 55% RH
0	0	1.0
2	2.0	1.04
4	3.5	1.08
6	6.5	1.19
8	10.0	1.53
10	13.5	1.57

The relative water regains of the cotton follow the same course as previously found by Urquhart and Williams [9], *i. e.* almost constant regain until swelled in 10 % NaOH, when a sudden increase occurs. This is in agreement with the hydrolysis data, namely, that no large change takes place in the fine structure until swelled in 10 % NaOH. The regains of the pulps, as presented in Table 1, are confusing and not as was to be expected from the hydrolysis data. However, we have to take into account that two effects may counteract each other. The swelling and destruction of the mesomorphous regions will tend to increase the water absorption. At the same time, the loss of materials, which occurs in pulp in contrast to cotton, will cause the absorption to diminish. More correct values might be arrived at by assuming that the part which was brought in solution belonged to the disordered regions and formed Cellulose-hydrate II ($C_6H_{10}O_5 \times 1\,^1/_2\ H_2O$) at 55 % RH. On this assumption the regains in Table 2 are recalculated for the low viscosity pulp. It is now seen that the regains follow the course which might be expected, namely a gradually increase in swelling up to 6 % NaOH, followed by a sharp jump at 8 % NaOH, and very little further change when the strength is increased to 10 %.