Heterogeneous Hydrolytic Degradation of Cellulose

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Introduction

As it is well-known, cellulose is a chain molecule consisted of glucosidic anhydrides linked together through 1- and 4-positions. Recently, E. Husemann[1] investigated hydrolysis of purified ramie in 0.5 *M* $KHSO_4$ solution for 2-1200 hours at 60°. Chain length distribution of the nitrates of both slightly and extremely hydrolyzed products indicated a uniform splitting of the glucosidic bonds, but the chain length distribution of intermediately hydrolyzed products showed an increase in uniformity especially in the products of a degree of polymerization (D. P.) of 400-500. He concluded that wood cellulose as well as cotton and ramie cellulose has weak bonds at intervals of about 500 glucose units which split 5000 times faster than the usual glucosidic bonds. G. V. Schulz[2] also stated the same conclusion and the others supported him. Since 1946, E. Pacsu[3] suggested the presence of hemiacetal bonds at intervals of 260 glucose units which split on mild hydrolysis faster than the usual glucosidic bonds. E. Heuser,[4] according to his unpublished work, also found that a uniform splitting took place upon hydrolysis of cotton cellulose in H_3PO_4, but of Aspen wood cellulose, molecules of a chain length of about 500 glucose units were accumulated, as Schulz *et al.* recognized.

If cellulose has such acid-weak bonds in its linkages, and cellulosic materials are submitted to acid treatments such as sulphite cooking, acetylation or nitration, the chain length distribution of the samples treated should be different from the case where uniform splitting takes place. We showed, in our previous work,[5] that the fractional precipitation of cellulose nitrate with acetone-ligroin gave superior results to that of fractional solution with acetone-ethanol or ethyl acetate-ethanol, or fractional precipitation with acetone-water. The distribution becomes broad and it seems that high-molecular as well as low-molecular fractions are considerably separated enough. We applied this fractional procedure to purified cotton, wood cellulose and heir hydrolyzed products and attempted to prove the presence of the weak bonds and investigated heterogeneous hydrolysis of cellulose as a model experiment of cooking.

Experimental Procedures and Results

Samples studied were purified surgery cotton and red pine (Pinus densiflora S. *et* Z.) pulp for viscose rayon grade. 4 g. of conditioned samples were weighed and imbibed in 300 cc. of 3.5 *N* HCl for 4-120 hours at 30°. At the end of each specified hydrolysis period, they were taken out, washed thoroughly, dried in air and then dried under vacuum in $CaCl_2$ desiccator. Table 1 shows

Table 1

Results of Heterogeneous Hydrolysis of Cotton and Wood Pulp in 3.5 *N* HCl at 30°

Time	Purified Cotton Residue, %	D. P.	Wood Pulp Residue, %	D. P.
0	—	1080	—	950
4	99.7	889	—	—
24	99.1	466	98.8	488
48	—	—	98.7	400
72	98.9	318	98.5	343
120	98.7	282	98.3	321

the weight loss and D. P. change of the samples by these mild hydrolysis. In spite of the large changes in D. P. the weight loss is very little, because of recrystallization[6] of splitted, disorganized and strained chains. Then these degraded samples were nitrated with the acid mixtures of HNO_3, H_3PO_4 and P_2O_5 (60:35:5) for 6 hours at 0°. The nitrates were washed with water for 24 hours and stabilized with methanol refluxing for 30 minutes. About 2 % of methanol soluble products were obtained. As nitrogen content and viscosity of the stabilized products increased with this treatment, the methanol

(1) E. Husemann, *Makromol. Chem.*, **1**, 140 (1947); E. Husemann and M. Goecke, *ibid.*, **2**, 293 (1948); **4** 194 (1949).
(2) G. V. Schulz and G. Sing, *J. Polymer Sci.*, **3**, 385 (1948).
(3) P. C. Mehta and E. Pacsu, *Textile Research J*, **18**, 387 (1948).
(4) E. Heuser, Tappi, Monograph Series No. 6, 8-74 (1948).
(5) K. Matsuzaki and H. Sobue, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **54**, 289 (1951).
(6) O. A. Battista, *Ind. Eng. Chem.*, **42**, 507 (1950); J. A. Howsmon, *Textile Research J.*, **19**, 152 (1949).

soluble products would probably have low nitrogen content and low D. P. Also, almost all of combined H_3PO_4 is removed by this treatment. Acetone solution (1%) of the stabilized nitrates was then fractionally precipitated with ligroin and the weight and D. P. of each fraction were determined. The results are tabulated in Tables 2-9.

As a number of samples have high molecular weight, high-molecular fractions were at first precipitated, dissolved in acetone again and re-fractionated. Integral chain length distribution curves were plotted and by graphical differentiation differential chain length distribution curves were also plotted. The curves are illustrated in Figs. 1-4.

Since two main fractions were separately fractionated for a number of samples, integral and differential distribution curves should be obtained from the summation of the curves for the two main fractions. But, as the procedure which enables to obtain continuous integral curves from the step-wise experimental data contains an arbitrary factor, we plotted integral curves for these samples simply rearranging all fractions in the order of D. P. without plotting the curves for the two main fractions separately.

Table 2

Fractionation of Nitrate of Purified Cotton. Sample 5.002 g., Yield 97.3 %. av. D. P. 1080, N 12.86 %(7)

High-molecular Fractions			Low-molecular Fractions		
Fraction	Weight %	D. P.	Fraction	Weight %	D. P.
1	2.20	500	1	2.91	90
2	0.78	910	2	1.31	140
3	12.76	935	3	2.68	230
4	1.80	1085	4	5.37	335
5	5.88	1160	5	3.54	495
6	2.32	1255	6	3.31	595
7	8.24	1465	7	2.58	680
8	2.60	1580	8	12.44	750
9	11.20	1605	9	3.19	1205
10	7.43	1740	total	37.33	
11	7.43	1950			
total	62.64				

Table 3

Fractionation of Nitrate of 4-hrs. Hydrolyzed Purified Cotton. Sample 5.004 g., Yield 96.3 %, av. D. P. 889, N 13.09 %

High-molecular Fractions			Low-molecular Fractions		
Fraction	Weight %	D. P.	Fraction	Weight %	D. P.
1	2.10	290	1	4.53	95
2	1.15	340	2	5.25	160
3	0.72	410	3	2.66	215
4	1.18	535	4	6.30	275
5	8.50	560	5	5.42	360
6	4.90	790	6	4.39	445
7	16.36	850	7	5.67	480
8	1.99	885	8	13.05	630
9	4.28	1050	9	3.38	820
10	1.52	1075	10	2.69	1005
11	3.96	1330	total	53.34	
total	46.66				

(7) Details of the fractional procedures are given in the following issue: *The Science of Forest Products*, **5**, 53 (1950).

Table 4

Fractionation of Nitrate of 24-hrs. Hydrolyzed Purified Cotton. Sample 3.030 g., Yield 97.2 %, av. D.P. 466, N 12.96%

Fraction	Weight %	D. P.
1	6.17	75
2	1.65	160
3	3.99	170
4	3.76	190
5	3.91	210
6	10.57	280
7	3.70	345
8	0.74	345
9	7.07	365
10	15.71	430
11	5.76	490
12	12.36	675
13	19.88	750
14	4.73	885

Table 5

Fractionation of Nitrate of 72-hrs. Hydrolyzed Purified Cotton. Sample 3.051 g., Yield 97.2 %, av. D. P. 318, N 13.1 %

Fraction	Weight %	D. P.
1	10.58	55
2	1.17	110
3	5.74	130
4	4.32	155
5	7.41	200
6	1.56	230
7	13.70	245
8	1.81	300
9	3.35	315
10	5.93	330
11	13.41	340
12	6.41	430
13	17.80	535
14	6.81	630

Table 6

Fractionation of Nitrate of 120-hrs. Hydrolyzed Purified Cotton. Sample 3.048 g., Yield 96.3 %, av. D. P. 282, N 12.93%

Fraction	Weight %	D. P.
1	9.76	45
2	1.28	115
3	7.71	130
4	3.62	155
5	5.94	175
6	1.27	215
7	13.83	235
8	1.43	290
9	2.59	300
10	5.42	305
11	17.13	320
12	6.24	400
13	15.26	480
14	8.53	620

Table 7

Fractionation of Nitrate of Wood Pulp. Sample 5.056 g., Yield 95.3 %, av. D. P. 950, N 12.9 %

Fraction	Weight %	D. P.
1	4.84	2360
2	8.11	2020
3	4.17	1910
4	9.16	1720
5	5.15	1630
6	9.82	1170
7	8.67	1010
8	2.11	690
9	15.77	545
10	1.74	425
11	2.92	335
12	5.44	295
13	10.77	170
14	11.36	45

Table 8

Fractionation of Nitrate of 48-hrs. Hydrolyzed Wood Pulp. Sample 2.869 g., Yield 95.0 %, av. D.P. 400, N 12.9%

Fraction	Weight %	D. P.
High-molecular Fractions		
1	6.77	1095
2	3.05	950
3	2.65	820
4	8.83	650
Low-molecular Fractions		
1	0.97	940
2	9.03	555
3	6.60	480
4	16.50	370
5	16.63	305
6	9.71	170
7	8.18	80
8	5.07	80
9	2.51	40
10	3.50	—

Table 9

Fractionation of Nitrate of 120-hrs. Hydrolyzed Wood Pulp. Sample 2.805 g., Yield 95.8 %, av. D.P. 321, N 12.9 %

Fraction	Weight %	D. P.
High-molecular Fractions		
1	2.05	920
2	3.88	735
3	6.51	530
Low-molecular Fractions		
1	0.77	720
2	6.92	415
3	5.03	385
4	12.63	300
5	22.07	270
6	7.13	230
7	7.27	140
8	7.15	105
9	18.59	30

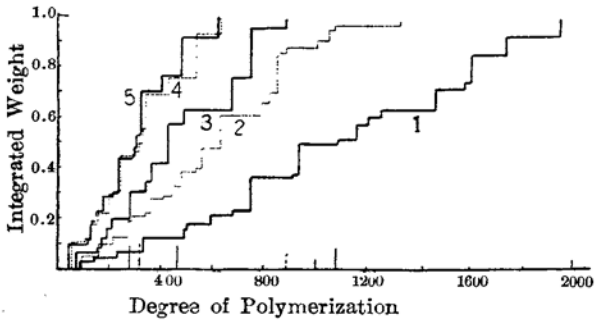

Fig. 1.—Integral chain length-weight distribution curves of hydrolyzed cotton (3.5 *N* HCl, 30°): 1, original; 2, 4 hrs. hydrolyzed; 3, 24 hrs. hydrolyzed, 4, 72 hrs. hydrolyzed, 5, 120 hrs. hydrolyzed

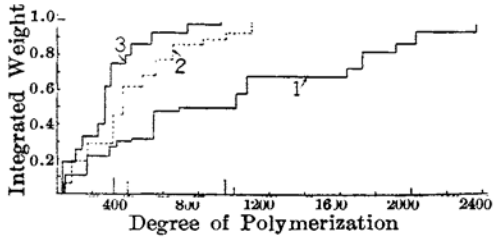

Fig. 2.—Integral chain length-weight distribution curves of hydrolyzed wood pulp (3.5 *N* HCl, 30°): 1, original; 2, 48 hrs. hydrolyzed; 3, 120 hrs. hydrolyzed.

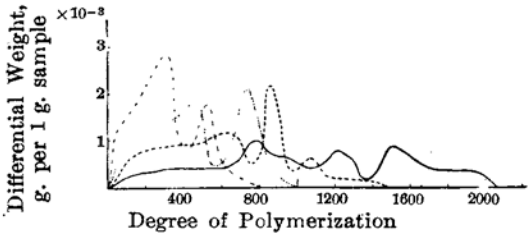

Fig. 3.—Differential chain length-weight distribution curves of hydrolyzed cotton: —— original; ---- 4 hrs. hydrolyzed; ..... 24 hrs. hydrolyzed, ----- 120 hrs. hydrolyzed.

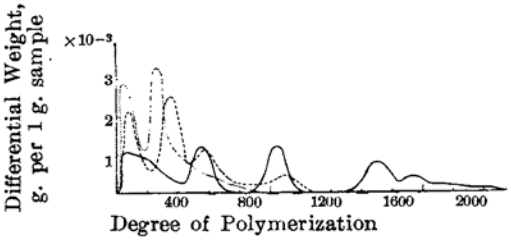

Fig. 4.—Differential chain length-weight distribution curves of hydrolyzed wood pulp: —— original; ---- 4 hrs. hydrolyzed; ..... 120 hrs. hydrolyzed.

Discussion

From Figs. 1-4, the difference between the chain length distributions of purified cotton and wood cellulose is evident, although these two samples have been degraded with several purification treatments. Wood cellulose has more low and high molecular weight fractions and more nonuniform distribution of chain length than purified cotton. The difference does not disappear even if the hydrolysis proceeds. The weight loss is little due to recrystallization and it is evident that the short recrystallized splitted chains are also included in the samples. These short chains of lower D. P. than 200 increase rapidly, as hydrolysis proceeds. Several maxima in the chain length distribution curves of purified cotton and pulp shifts to low molecular weight as the reaction proceeds. It seems as if these maxima are not so distinct as to give a positive proof of the presence of the weak bonds which would split 5000 times faster than the usual bonds and exist at regular intervals of 500 or 260 glucose units. If those acid-sensitive bonds exist in cellulose molecules, more rapid accumulation of chains of 500 or 260 glucose units would be expected. The heterogeneous degradation of cellulose can be explained well with its submicroscopic structure as follows.

In cotton and wood cellulose, crystalline

regions of relatively uniform length exist between amorphous regions. On hydrolysis, acid diffuses into the amorphous regions where the chains are splitted. Therefore the D. P. becomes lower and lower as the hydrolysis proceeds giving rise to several maxima in the differential distribution curves corresponding to several times the length of crystalline regions. Chain length of the crystalline regions at the beginning of the hydrolysis seems to be 200-300. Although the reason for the discrepancy between this value and that measured with x-ray method (120) is not yet clear, it is probable that the chain length of the crystalline regions grows long by the recrystallization of the splitted chains or acid-resistant crystalline regions may have different D. P. from that determined with x-ray method.

As previously mentioned, the nonuniformity of chain length distribution of wood pulp does not disappear upon hydrolysis. This indicates that the submicroscopic structure of wood pulp is not uniform. On one side, its amorphous regions are easily attacked with acid, but on the other, the crystalline regions or mesomorphous regions are more resistant to acid than that of cotton. This nonuniformity of crystalline structure of wood pulp would be closely related with the difference in chain length distribution and reactivity of cotton when submitted to micellar reactions as hydrolysis, xanthation or acetylation.

Summary

Purified cotton and wood pulp were hydrolyzed in 3.5 *N* HCl for 4-120 hours at 30°. The hydrolyzed products were nitrated with the mixtures of H_3PO_4-HNO_3-P_2O_5 at 0° for 6 hours. Acetone solutions of the nitrates were fractionally precipitated with ligroin, and chain length distribution curves were plotted. These curves show no positive proof of the presence of the weak bonds which split 5000 times faster than the usual glucosidic bonds. These are well explained with the submicroscopic structure of cellulose.

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