NOTES

Order in Cellulose Fibers

Recently, Ray and Bandyopadhyay[1] have made some interesting observations on the concept of the degree of crystallinity in cellulose fibers and have shown how the method of interpretation of x-ray diffractograms of these fibers containing moisture can lead to contradictory conclusions. In doing so, the authors have rightly stressed the importance of regions of intermediate order in any consideration of the fine structure and moisture effects in these fibers.

The purpose of this note is to point out yet another piece of evidence suggesting the existence of regions of intermediate order. Patil et al.[2,3] have reported the following data (Table I) on the percentages of "crystalline" cellulose I (C_I), cellulose II (C_{II}), and "amorphous" (Am) material in cotton fibers treated with aqueous solutions of various concentrations of NaOH. As concentrations below 10% (w/w) bring about little changes in the C_I/Am contents of the control and as concentrations above 16% (w/w) do not cause any further marked changes in the C_I/C_{II}/Am fractions, the corresponding data are not included in the table. The changes in the percentage content of the three fractions in samples treated with various concentrations of alkali, as compared to the control, are diagrammatically presented in Fig 1. Corresponding to any concentration of the NaOH solution, the *decrease* in C_I fraction and *increase* in C_{II} and amorphous fractions can thus be read off directly from the figure. It may be observed that treatment with 10% (w/w) solution brings about a small increase in the amorphous fraction in the sample, without formation of C_{II}. Further, it is interesting to note that the decrease by 13.4% of C_I on treating the control with 11% NaOH solution is made up of an increase by 7.9% of the amorphous material and an increase by only 5.5% of the C_{II} fraction, indicating that the conversion of C_I fraction into amorphous regions predominates over the transformation to C_{II} fraction. On the other hand, for higher concentrations, it is seen that this order is reversed. It is also observed from the table that while the C_{II} fraction progressively increases on treatment of the sample with solutions of higher concentrations, the increase in the amorphous fraction is only marginal.

Considering that the method employed for estimating the percentages of C_I, C_{II}, and amorphous fractions is fairly accurate, one can conclude that regions of semicrystalline order do exist in cellulose fibers. As envisaged by Howsmon and Sisson,[4] treatment with NaOH solutions of low concentration (<12%) results in bringing about further disorder in these regions, the original crystalline regions being affected only to a small extent. Solutions of higher concentrations bring about a higher conversion to C_{II} fraction, with little increase in the amorphous fraction.

TABLE I
C_I, C_{II}, (C_I + C_{II}), and Am Contents in Samples Treated with Different Concentrations of NaOH

NaOH concentration, %(w/w)	C_I, %	C_{II}, %	(C_I + C_{II}), %	Am, %
Control	69.6	0	69.6	30.4
10	68.0	0	68.0	32.0
11	56.2	5.5	61.7	38.3
12	38.1	19.3	57.4	42.6
13	22.5	32.2	54.7	45.3
16	5.0	46.2	51.2	48.8

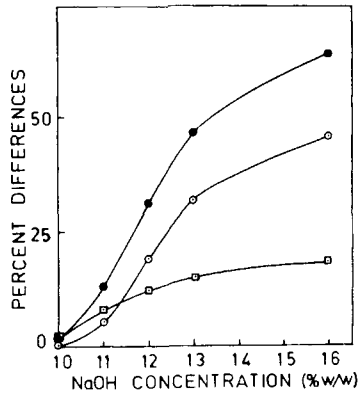

Fig. 1. Decreases in percentages of C_I (●) and increases in percentages of C_{II} (⊙) and Am (⊡) contents on treating cotton fibers with different concentrations of NaOH.

As regards the location of the semiordered regions in the fibers, the structure of these regions can be expected to be such that it gives an x-ray diffractogram which resembles that of C_I, as these regions are envisaged to contribute to "crystalline" areas of the diffractograms by Ray and Bandyopadhyay.[1] Further, in the work of Patil et al.,[2,3] the C_I fraction in the fiber is visualized to get partly converted to C_{II} and partly to amorphous material on alkali treatment. In view of these considerations, it seems more probable that the semiordered regions lie on the periphery of the crystallites in the fibers as proposed by Heritage et al.[5] instead of lying scattered in a random fashion in an amorphous mass. However, more evidence is required to arrive at a definite conclusion in this regard.

References

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