

Crystallization of Cellulose

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Synopsis

Crystallization of cellulose from low DP acetylated hydrolyzed bagasse pulp has been studied. The morphology of the crystals obtained after crystallization at 50°C for different intervals of time (5, 20, and 40 days) revealed needle-shaped, elongated, ribbonlike fibrous crystals. The electron diffraction pattern obtained on these crystals was typical of cellulose II lattice.

INTRODUCTION

Crystallization of cellulose into its microcrystals after hydrolyzing cellulose by mineral acids was studied by several investigators.¹⁻⁷ Battista⁷ could recover single cellulose microcrystals of size 100 Å wide by hydrolyzing cellulose from cotton linters and wood pulp by 2.5 NHCl at boiling temperature. However, the study of single crystals recovered from the solution of cellulose triacetate has been reported by few investigators. They reported cellulose crystals as platelets,^{8,10-13} ribbons,^{12,13} and fibrous crystals,⁹⁻¹¹ according to the preparative procedure. To quote a few, Ranby and Noe⁸ reported lamellar crystals from water-soluble low substituted cellulose acetate having a DP of 97. Hexagonal and rhombic-shaped crystals of cellulose II obtained by saponification of cellulose formate and cellulose acetate, which were prepared from filter paper, were observed by Munekata and Soube.⁹

Maeda et al.¹⁰ could succeed in crystallizing cellulose from hydrolyzed cotton, mercerized cotton, and high tenacity rayon having DPs of 400, 200, 100, and 50, respectively, and they concluded that crystallization occurs in the form of extended chain fibrous crystals from high molecular weight cellulose.

Ramesh et al.¹¹ characterized the ellipsoidal crystals of cellulose II obtained from cellulose acetate with a DP of 345 by electron diffraction technique. Buleon and Chanzy¹³ reported platelets, ribbons, and fibrous crystals of cellulose II from dilute aqueous solution of cellulose triacetate prepared from cellulose acetate.

The present paper reports the morphology and characterization of cellulose crystals obtained from acetylated hydrolyzed bagasse pulp (DP 344).

EXPERIMENTAL

Bleached bagasse pulp (BP) having DP 715 obtained from a paper mill was hydrolyzed by 2.5 NHCl at boiling temperature for 15 min. The degree of

polymerization of hydrolyzed bagasse pulp was determined following the method described in ASTM Standard¹⁴ using cupriethylene diamine as solvent for cellulose and applying the equation given by Battista.¹⁵ The hydrolyzed bagasse pulp having DP 344 was then acetylated by standard acetylation method using perchloric acid as catalyst¹⁶ for 4 h to the maximum degree of substitution of 2.8.

The cellulose triacetate thus obtained was then dissolved in cyclohexanone to get 0.5% solution and then further hydrolyzed by 60% v/v acetic acid at 50°C for different intervals of time varying from 7 to 40 days. The crystals thus formed were washed with cyclohexanone and acetic acid and finally with distilled water. The crystals were suspended in distilled water, and a drop of crystal suspension was placed on carbon-coated copper grids for examination under transmission electron microscope (TEM).

The electron diffraction (ED) patterns from these crystals were recorded using the method described earlier.¹⁷ The *d* spacings of the reflections were measured.

RESULTS AND DISCUSSIONS

The specimens obtained after crystallization of cellulose for a number of days varying from 7 to 40 days were observed under TEM. The needle-shaped crystals of cellulose after crystallization of 50°C for 7 days are shown in Figure 1. The length of the crystals is about 350 Å, which is coincidentally

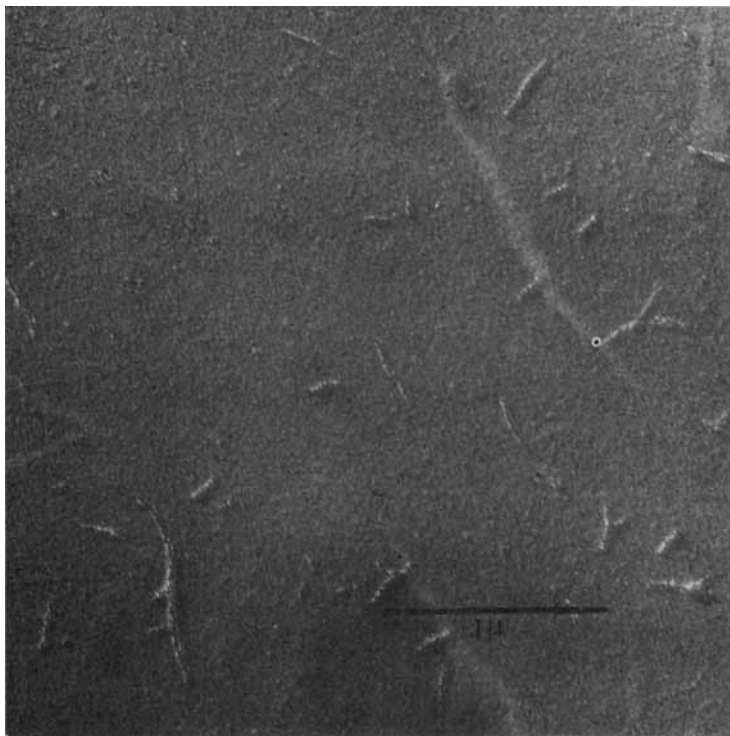
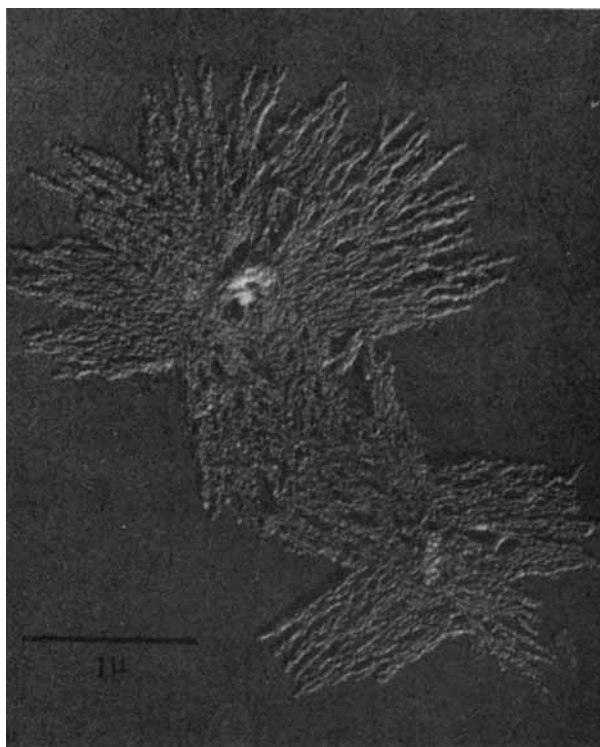
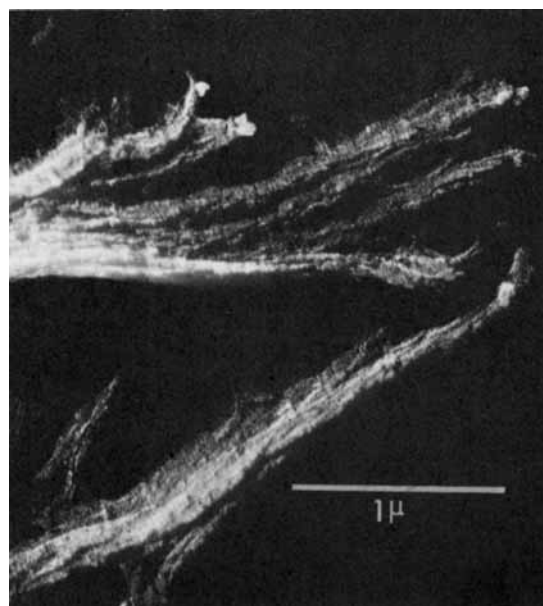


Fig. 1. TEM of cellulose crystals grown at 50°C for 7 days. Note the needle-shaped crystals.



(a)



(b)

Fig. 2. TEM of crystals obtained after crystallization at 50°C for different intervals: (a) long elongated ribbonlike crystals after 20 days; (b) fibrous crystals after 40 days.

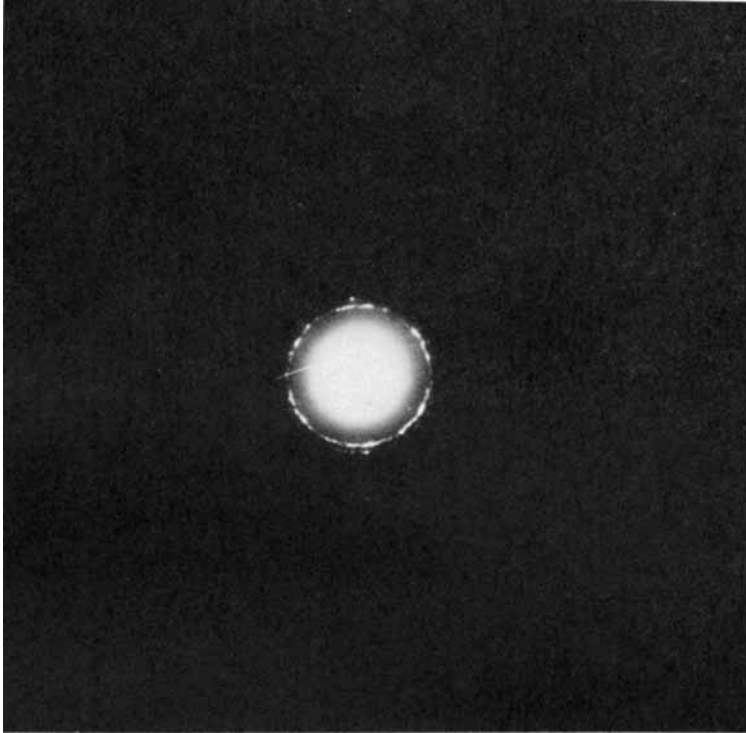


Fig. 3. Electron diffraction pattern of cellulose single crystals.

equal to the length of crystallites in native cellulose reported. These types of needle-shaped crystallites were also observed after repeated enzymatic hydrolysis of cellulose for several cycles.¹⁸ After 20 days of crystallization at 50°C long elongated ribbonlike crystals were observed [Fig. 2(a)], which eventually exhibited fibrous structure after 40 days [Fig. 2(b)]. The ED pattern recorded on these crystals revealed typical cellulose II pattern (Fig. 3). The d spacings of reflections were 4.1 and 4.42 Å, corresponding to (002) and (10 $\bar{1}$) interferences of cellulose II. These observations are similar to those of Buleon and Chanzy,¹³ who observed ribbonlike crystals which further agglomerated into elongated fibrous crystals.

The well-defined ribbons and fibrous crystals obtained from low molecular weight cellulose (DP 344) leads to the contradiction of hypothesis of Maeda et al.,¹⁰ who proposed that crystallization of high molecular weight cellulose (DP 400) results in extended chain fibrous crystals. Our observations along with observations made by some earlier investigators show that the crystals of cellulose are platelets, ribbons, and fibrous crystals, depending on the experimental conditions and duration of crystallization process. However, starting material of different molecular weight cellulose does not decide the morphology of crystals during crystallization.

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References

1. B. G. Ranby, *Discuss. Faraday Soc.*, **11**, 158 (1951).
2. S. M. Mukherjee and H. J. Woods, *Biochem. Biophys. Acta*, **10**, 499 (1953).
3. R. H. Marchessault, F. F. Morehead, and M. J. Koch, *J. Colloid Sci.*, **16**, 327 (1961).
4. F. F. Morehead, *Text. Res. J.*, **20**, 549 (1950).
5. S. M. Mukherji, J. Sikorski, and H. J. Wood, *Nature*, **167**, 821 (1951).
6. O. A. Battista and P. A. Smith, *Ind. Eng. Chem.*, **54**,(9), 20 (1962).
7. O. A. Battista, *Microcrystal Polymer Science*, McGraw-Hill, New York, 1975.
8. B. G. Ranby and R. W. Noe, *J. Polym. Sci.*, **51**, 337 (1960).
9. S. Munekata and H. Soube, *J. Polym. Sci.*, **B5**, 1043 (1967).
10. H. Maeda, H. Kawada, and U. T. Kawai, *Makromol. Chem.*, **131**, 169 (1970).
11. R. Ramesh, C. K. Patel, and R. D. Patel, *Makromol Chem.*, **171**, 179 (1973).
12. H. Bittiger and E. Husemann, *J. Polym. Sci.*, **B10**, 549 (1972).
13. A. Buleon and H. Chanzy, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 833 (1978).
14. ASTM DS 539-53, ASTM Standards Part-25, ASTM, Philadelphia, 1967, p. 123.
15. O. A. Battista, *Ind. Eng. Chem., Anal. Ed.*, **16**, 351 (1944).
16. E. M. Buras, Jr., S. R. Hobart, C. Hamalainen, and A. S. Cooper, Jr., *Text. Res. J.*, **27**, 214 (1957).
17. K. M. Paralikar and S. M. Betrabet, *J. Appl. Polym. Sci.*, **21**, 899 (1977).
18. K. M. Paralikar and S. P. Bhatawdekar, *J. Appl. Polym. Sci.*, **29**, 2573 (1984).

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