

Rapid X-Ray Diffraction Technique for Determination of Crystallinity of Cellulosic Materials

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Synopsis

Predominant orientation or texture of cellulosic materials leads to the overestimation of the contribution from crystalline fractions when x-ray diffraction techniques are used for determination of crystallinity of these materials. Therefore it was attempted to determine the fraction of noncrystalline cellulose on the diffractometer by using a recalculating instrument to measure the scattering power at an angle $2\theta = 32^\circ$ from cellulose tablets, and by comparing these result with a reference sample. The method is convenient for process control procedures.

A number of x-ray diffraction techniques have been suggested for the determination of amorphous and crystalline fractions of polymers. All of them are based on intensity separation in debaegram into contributions from crystalline and amorphous regions of polymers,¹⁻⁵ followed by calculation of the ratio of these intensities which are supposed to be proportional to the weight portions of amorphous and crystalline regions.

Such methods are in fact rather efficient, provided all crystallites of the sample under investigation are completely disorient. Unfortunately, predominant orientation or texture may considerably distort the results by overestimation of the contribution from crystalline fractions if in texturing their intensity tends on the average to be augmenting, and vice versa.

Obtaining disoriented samples for any fibrous materials, including cellulose, is a rather difficult problem. Any attempt in obtaining the samples reproducible in terms of density and volume makes the problem more complicated. It is no less easy to verify the absence of orientation, so that either fiber bundles or pressed tablets are used in numerous measurements of cellulosic materials. The major part of fibers in the tablet is arranged parallel to its surface. When an x-ray diffractometer reflecting technique is used, the peaks corresponding to the crystalline regions would increase because all strong reflexes in debaegram of cellulose I and II refer to the zone the axis of which is close to fiber lengthening. With the x-ray passing through, the peak intensities would decrease.

The texture of crystallites in the sample is often neglected when the crystalline and amorphous fractions are to be determined. Most frequently, the index of crystallinity is^{6,7}

$$C.I. = \frac{T_{002} - T_{18.5^\circ}}{T_{002}} \times 100 \text{ for cellulose I}$$

$$C.I. = \frac{T_{10\bar{1}} - T_{15.0^\circ}}{T_{10\bar{1}}} \times 100 \text{ for cellulose II}$$

The height of an individual peak of the polycrystalline sample depends on various factors: texture degree; average crystalline dimensions along the normal axis with reference to the reflecting plane (regarding our data, the change of the mean dimensions determined from broadening of the peaks does not always correlate with the quantitative variations between amorphous and crystalline regions); and structure factors (variable in general as a result of modifications of the structure details).

It is obvious that values similar to the crystallinity index have a quite remote relation to the quantitative fraction of the crystallites. The main source of errors arise from the texture, which leads to overestimating the crystallite fraction when the reflecting technique with pressed tablets is used. At x-ray passed through measurements of thin pressed plates, Shenouda and Viswanathan⁸ found the crystallite fraction of cotton cellulose to be about 50%, associated with errors of the opposite sign.

The amorphous regions of polymers, according to definition, have no predominant orientation, so that it is possible to measure only a fraction of amorphous component of the samples textured differently. The superposed diffraction patterns of three components of cellulosic materials are represented in Figure 1: crystalline modifications I and II and noncrystalline cellulose ob-

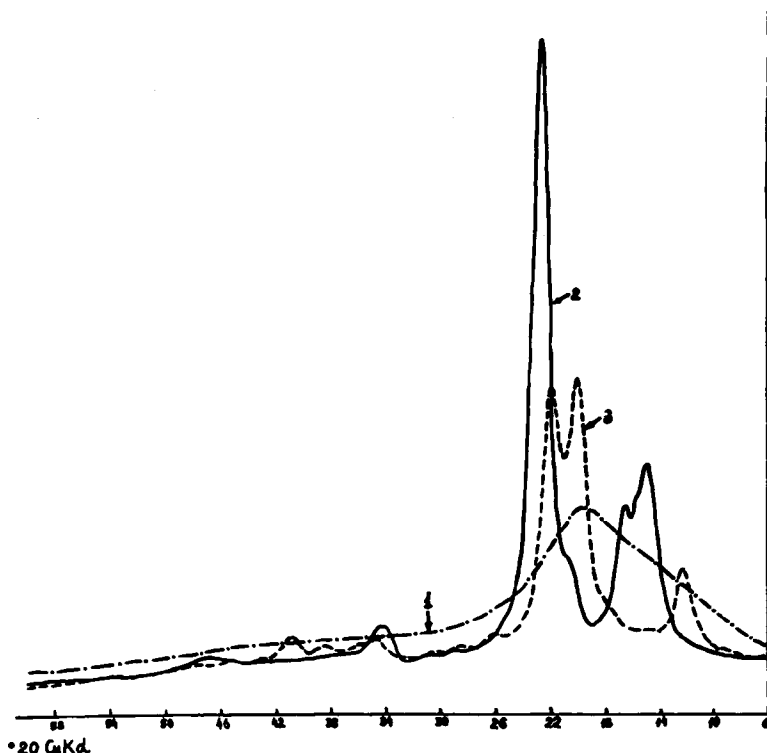


Fig. 1. Diffraction patterns of pressed tablets of noncrystalline cellulose (1), cellulose I (2), and cellulose II (3). The contributions of 10% and 15% of amorphous component are deduced from the curves for cellulose I and II, respectively.

tained with the $\text{CuK}\alpha$ under identical conditions. The 0.3 g samples pressed at 2000 kg/sq. cm within 5 min consisted of flat 12-mm diameter tablets. There is a remarkable difference in intensity between amorphous and crystalline modifications at $2\theta = 32^\circ$ ($\text{CuK}\alpha$). The measured intensity presents a background for the crystalline modifications since even low peaks with respective interplanar spacing in the process of thorough measurements of oriented samples of cellulose I and II were not recorded.⁹ At the same time, the intensity for the "tail" of the amorphous halo still widely differs from this background.

It was attempted to determine the fraction of noncrystalline cellulose on the diffractometer by using a recalculating instrument to measure the scattering power at an angle $2\theta = 32^\circ$ from identical cellulose tablets under stabilized conditions and by comparing these results with a reference sample.

A kraft pine cellulose powder beaten dry for 3 hr with a Vibromill⁷ served as a reference sample for amorphous cellulose. As standard crystalline cellulose, a powder of cotton cellulose with the leveling of D.P. obtained on acid hydrolysis was used. It was assumed that such a standard sample contains 10% of an amorphous component since the samples of cotton fibers have about $30 \pm 3\%$ of noncrystalline cellulose at such a graduation (Fig. 2), which is in good agreement with values obtained by different methods reported in the literature.

Reliable measurements require a high stability of x-ray generator and measuring circuit. Such requirements can be easily met by using a modern diffractometer. Evaluation of errors based on calculation statistics shows that with measurements within a period of 100–400 seconds, the error value would be

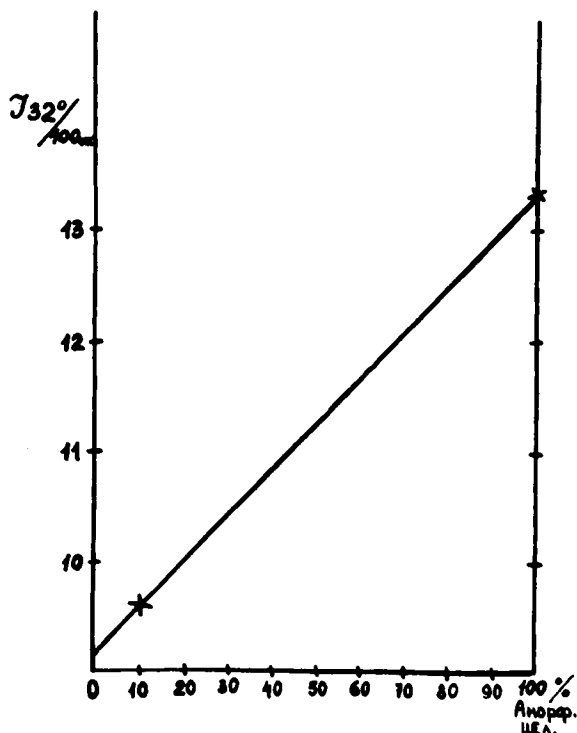


Fig. 2. Graduating diagram for determination of amorphous fraction of cellulose. Vertical axis, intensity for 32° angle expressed in 1000 impulses per 100 seconds.

as high as 2-3%. The estimation of reproducibility by different measurements made for one or different tablets of the same sample lies within these limits.

The fraction of amorphous cellulose which has been determined by this method varies for wood pulps in the range from 35% to 60% depending on the kind of the raw material, methods of pulping, bleaching, etc. These variations are within 50-80% for regenerated cellulose fibers.

Figure 3 illustrates the advantages of the suggested method. The fraction of the amorphous component has been evaluated as follows: for 1, 15%; 2, 22%; 3, 55%; where 1 = sulfite aspen pulp transformed to cellulose II by treatment with 18% caustic soda (NaOH) followed by hydrolysis up to the leveling of degree of polymerization; 2 the same procedure for the kraft pine pulp; 3 = kraft pulp fibers treated with 18% NaOH but without any hydrolysis. It is noticeable that in the third case as compared with two previous ones, not only the contribution of the amorphous component is growing but also the intensity is connected with crystallites. It is evident that the orientation degree for the crystallites in tablets made of fibers is higher than that of powder resulting in gain (instead of decline) of the peaks attributed to crystallites. These distortions have no effect on the measurement at $2\theta = 32^\circ$ value with $\text{CuK}\alpha$.

Another advantage in this case is that the amorphous fraction can be estimated by using the same scale regardless whether or not we deal with cellulose I and II or their mixtures.

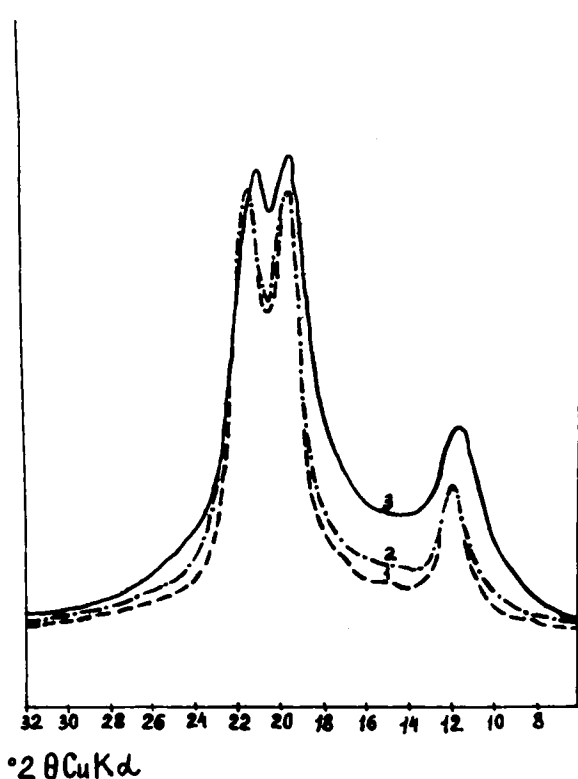


Fig. 3. Diffraction patterns of three samples of cellulose II with different amorphous content. For explanation, see the text.

The measurements according to the suggested technique are comparatively simple: the tablet scattering power is measured for a period of 100–400 seconds and the fraction of amorphous component is evaluated according to a graduation scheme of the type given in Figure 2. It is recommended to remeasure the standard samples in 1–2 hr in order to check the graduation. The method is convenient for process control procedures.

References

1. J. L. Matthews, H. S. Peiser, and R. B. Richard, *Acta Cryst.*, **2**, 85 (1949).
2. W. Ruland, *Acta Cryst.*, **14**, 1180 (1961).
3. W. O. Statton, *J. Appl. Polym. Sci.*, **7**, 803 (1963).
4. N. T. Wakelyn and P. R. Young, *J. Appl. Polym. Sci.*, **10**, 1421 (1966).
5. F. H. Chung and R. W. Scott, *J. Appl. Cryst.*, **6**, 225 (1973).
6. L. Segal, J. J. Greely, A. E. Martin, Jr., and L. M. Conrad, *Text. Res. J.*, **29**,(10), 786.
7. D. F. Caulfield and R. A. Steffes, *Tappi*, **52**, 1361 (1969).
8. S. G. Shenouda and A. Viswanathan, *J. Appl. Polym. Sci.*, **15**, 2259 (1971).
9. J. Mann, L. Roldan-Conzales, and H. J. Wellard, *J. Polym. Sci.*, **42**, 165 (1960).

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