Some Observations on the Concept of the Degree of Crystallinity in Cellulose Fibers with Reference to Moisture Effects

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Synopsis

A conceptual effort has been made here to reconcile two approaches of defining the degree of crystallinity by the x-ray diffraction method, (a) one as proportion of x-ray diffracting matter in the entire fibrous material, and (b) another as the extent of qualitative perfection of the crystalline region only, since these two approaches often lead to opposite conclusions from the same set of observations.

INTRODUCTION

A reappraisal of the concept of the degree of crystallinity in cellulose fibers seems to be necessary in view of some of the latest experimental information in the field of fiber structure. As is well known, x-ray pattern of cellulose fibers is diffuse, and diffuse x-ray scatter[1] can arise not only from the noncrystalline portions of a fiber but also from chain twisting and lattice distortions[2] in the crystalline regions themselves. The breadth of the diffraction line is interpreted in terms of either paracrystalline disorder or mosaic structure formed by dislocations.[3]

Molecular arrangement in cellulose structure has been proposed to be paracrystalline by several workers.[1,2] Kulshreshtha et al.[4,5] found evidence of paracrystalline structure in ramie and jute fiber. They also found that lattice structure of cotton and related celluloses of plant or bacterial origin is paracrystalline.[6]

It has been shown by electron microscopy that the elementary fibril is a morphologic entity that occurs as a universal building unit in all native cellulosic materials. Two types of ideas have been put forward concerning the internal structure of microfibrils. Ranby,[7] Preston[8] and Ellefsen et al.[9] conclude that each microfibril contains a single crystalline core of the order of size of the microfibril itself. Freywyssling,[10] Muhlcthaler,[11] and Manley,[12] on the other hand, maintain that electron-microscopic evidence points to the presence in microfibrils of linear bodies 35 Å wide. Heyn,[13] from electron-microscopic study of cotton, found that crystalline-amorphous areas are along the length and that the diameter of the microfibril varies from 30 to 60 Å. Stockmann[14] observed that among the crystallization conditions known to produce extended chain structure,

crystallization with simultaneous polymerization appears most plausible mechanism for forming elementary fibrils. The mechanism yields a structure distinguished by uniformity of lateral order along the fibrillar axis, the lateral order being paracrystalline.

The degree of crystallinity in such a structure as measured by the x-ray method takes into account the contributions of all regions having degrees of order suitable enough to diffract x-rays. It has been found that the so-called single crystals of cellulose showed a maximum crystallinity of about 70–80%[15] only and an accessibility as high as 50–60% in deuterium exchange studies with heavy water. Thus, the crystalline fraction as designated by the x-ray method may be accessible to an extent of about 40%. From infrared studies, Mann and Marrinan[16] found that 28% of the OH groups of crystalline regions of untreated bacterial cellulose are hydrogen bonded in an amorphous manner. After deuterating and rehydrogenating ramie fiber, Okajima and Kai[17] found that ramie could be divided into amorphous, intermediate, and crystalline regions. The intermediate region has an important role in determining the effect of moisture on the degree of crystallinity in cellulose fibers.

In recent years, however, while reporting the effect of moisture on the degree of crystallinity, several authors sometimes ignored this aspect of fiber structure and came to different conclusions as discussed in the next section. It is therefore felt necessary to clarify the ideas on which different conclusions were based so that conflicting conclusions are not made for the same sets of experimental observations.

RELATED EXPERIMENTAL OBSERVATIONS

We shall confine ourselves mainly to the results obtained in connection with the effect of moisture on the molecular arrangement in cellulose fibers. Investigating on the structure of dry and wet celluloses, Antzenberger et al.[18] found that wet ramie gave a sharper x-ray pattern. Kouris et al.[19] found that the crystallinity index became lower when undried pure cellulose fibers were dried indirectly by the method of solvent exchanges. Antwuorinen[20] found a decrease in crystallinity index with increase in humidity in cotton linters, etc. Kantola et al.[21] studied the degree of crystallinity of some sheet-like celluloses of different moisture contents and found lower degrees of crystallinity for samples having higher moisture contents.

In case of cotton fibers, Heyn[22] observed that a crystallization process must take place during direct drying of the water-wet fibers. Legrand[23] studied the crystallinity of viscose rayon at different humidities and found a decrease in crystallinity with humidity. In their infrared spectroscopic studies, Mann and Marrinan[16] found that there was an increase in crystallinity of about $3 \pm 1\%$ when a viscose film was dried after being in water, and this agreed with the amount of resistant OD groups when the film was similarly treated with D_2O. Ray[24,25] studied the effect of humidity on the degree of crystallinity of some cellulose fibers and found that the degree of crystallinity decreased with humidity.

Creely and Tripp,[26] on the other hand, studied cellulose samples at three relative humidities and found an increase in crystallinity in going from the dry to the humid state. Seitsonen and Mikkonen[27] observed that a decrease in x-ray intensity takes place after drying pulp specimens initially kept in humid air.

THE CONCEPT NEEDED FOR
INTERPRETATION OF RESULTS

It is found that when the perfection of the crystalline regions is considered, an increase in perfection with humidity was observed, as was evident in the increase in sharpness of the x-ray patterns. But when the degree of crystallinity based on the integrated intensity, after Hermans,[28] was considered, a decrease was observed. This difference in the mode of assessment of the change had, it appears, given rise to the different conclusions reached by the cited authors. As a matter of fact, it was pointed out in an earlier communication[29] that the data from which we concluded that the degree of crystallinity decreased with moisture would indicate a higher perfection according to the method of interpretation followed by Creely and Tripp.[26] Thus, the interpretation becomes clear when the contribution of the intermediate region is properly taken care of. Actually, when the disorder in the crystalline region is accounted for by Ruland's[30] method, the same figures were obtained for the degree of crystallinity in the native and mercerized forms of ramie.[31]

EXPLANATION OF RESULTS

To reconcile the various experimental features, we conceive of a fiber structure in which some regions diffract x-rays and simultaneously are amenable to the attack of moisture. Water molecules might enter such regions and push the cellulose molecules farther apart; these regions, instead of contributing to coherence of x-ray reflections, will add to the continuous background scattering. The change of the badly ordered regions into amorphous ones could make the x-ray interference peaks narrower and the amorphous background more intense. This would explain the decrease in the proportion of fibrous matter that diffracts x-rays, and the simultaneous increase in the perfection of the remaining crystalline regions.

On this basis, a better agreement is possible between the calculated and experimental intensity curves in the wet state of ramie fiber as observed by Antzenbergers et al.[18] The existence of intermediate regions has been found by many workers. In rayon fiber, Heritage et al.[32] ascribed to 14% of the material a state of intermediate order which would diffract x-rays but did not give a sharp infrared band. Again, by the process of powdering cellulose fiber by ball mill, Viswanathan et al.[31] found a reduction in the disorder parameter; according to them, this was due to the formation of small but perfect crystallites resulting from the removal from the original crystallites of the distorted peripheral layers.

The decrease of the degree of crystallinity is also explainable on the basis of the structure of the elementary fibrils. Ahmed and Rapson[33] checked the experiment of Manley[34] on hydrolysis by infrared technique and found that accessibility did not remain unchanged after hydrolysis as found by Manley gravimetrically. The change of accessibility on hydrolysis suggests that there are regions of different accessibilities in cellulose fiber. This was explained in terms of Manley's[34] concept of protofibrils and accessibility data by proposing a nonuniform distribution of disorder in molecular chain folding.

The conception of the transformation of the less ordered region also finds a support in Stockmann's[35] theory that the elementary fibril in native cellulosic

materials possesses an energy-elastic deformation mechanism and built-in stress which strives to shrink the fibril longitudinally. Whenever the intermolecular cohesion is weakened, a structure transformation of the paracrystalline fibril is conceived; this consists of the creation of distinctly disordered and distinctly well-ordered phases. By a phase separation principle, Stockmann explains the two contradicting features: higher disorder with higher degree of perfection of crystalline order (decrease of (002) peak width).

CONCLUSIONS

It is thus clear that, if by the degree of crystallinity we identify the x-ray diffracting percentage of the entire fibrous matter, the results may well be expressed in terms of Hermans'[28] approach; on the otherhand, when the structure of the diffracting matter is to be assessed in terms of degree of perfection, Stockmann's[35] concept may be adopted. For practical purposes, the former gives a quantitative estimate while the latter is a qualitative measure of the crystalline region. If this is kept in mind, there would be no confusion.

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