X-Ray Studies on Cellophane[1]

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Synopsis

X-Ray diffractograms of cellophane showed a considerable variation in the intensity corresponding to the 101, 10$\bar{1}$, and 002 planes.   Application of generally accepted procedures for estimating crystalline content in cellulosic materials yields varying results for crystallinity in cellophane.   It is concluded that such procedures are not applicable to cellophane used in this study.

EXPERIMENTAL

The present work on cellophane was carried out in connection with an investigation of the dielectric properties of cellulose of various lateral order structures.[1,2]   The cellophane samples were obtained from Visking Company, Chicago.

Cellophane (regenerated cellulose) used in this study was $3^1/_4$ in. dialysis tubings made from a viscose composition of 7% cellulose by weight, 6% NaOH by weight, and a gamma number of 28.5.[3]   The cellophane tubings contained 20% glycerin by weight, based on total dry weight of glycerin and cellulose.   Significantly, the processing included simultaneous drying and stretching (linearly and transversely) of the plasticized gel tubing (never-dried glycerin and cellulose), "said stretching being within the range of 17% to 23% in the transverse direction and 2% to 8% in the longitudinal direction."[3]   The chemical analysis of the sample has been reported earlier.[2]

X-ray Diffractograms of Cellophane

The apparatus and the procedure for obtaining x-ray diffraction patterns have been described previously.[1]   The cellophane samples were placed in the holder and mounted in the goniometer.   The diffraction intensity was measured from an angle of $2\theta = 10$–$26°$.   Any error due to misalignment of the samples in the holder was corrected by testing the samples again by rotating them through $90°$.

Figure 1 gives the diffractogram of cellophane with glycerin plasticizer; Figure 2 shows the diffractogram of water-washed and air-dried cellophane (to remove the plasticizer); and Figure 3 shows the water-washed, swollen in 95% monoethylamine and then air-dried cellophane.
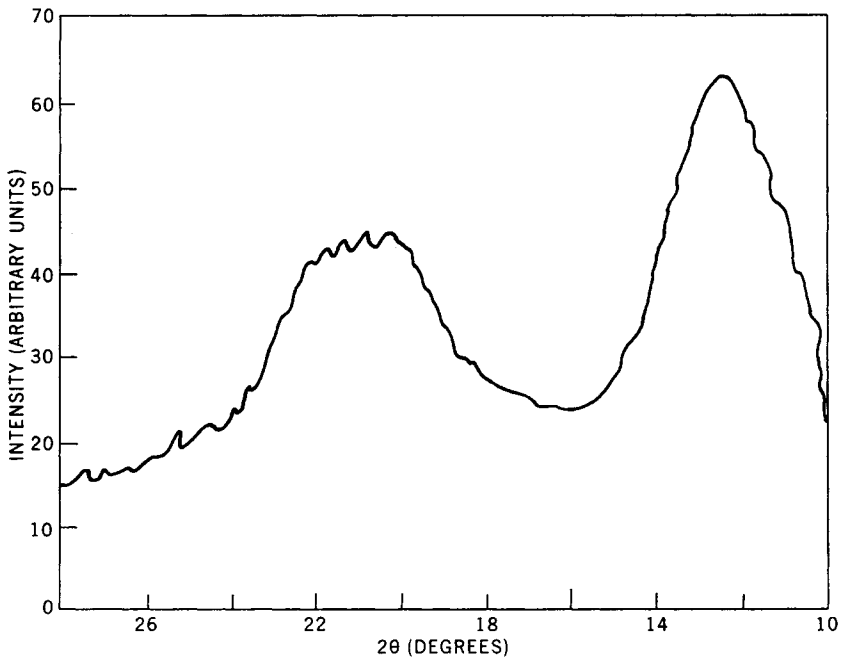
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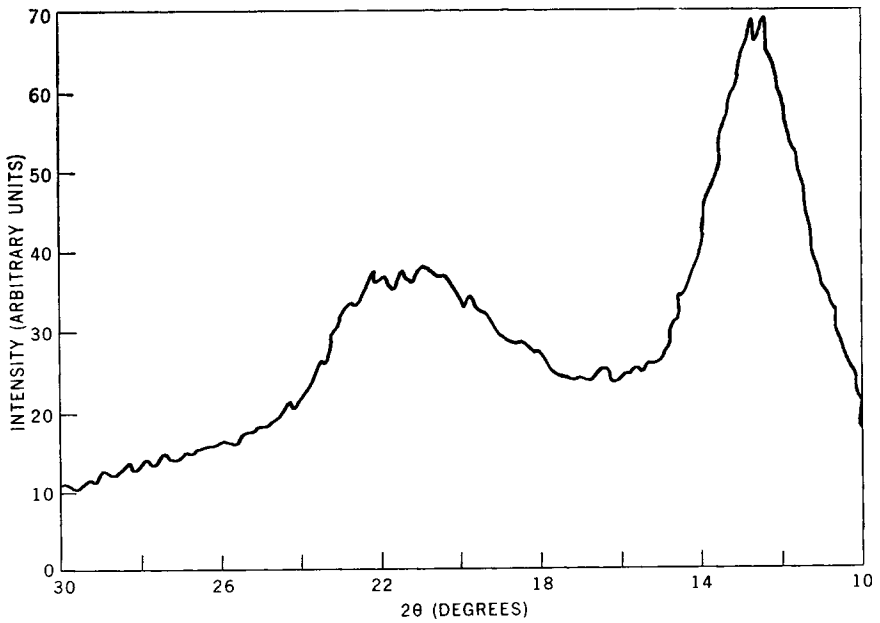Fig. 1. X-Ray diffractogram of cellophane with glycerin plasticizer.

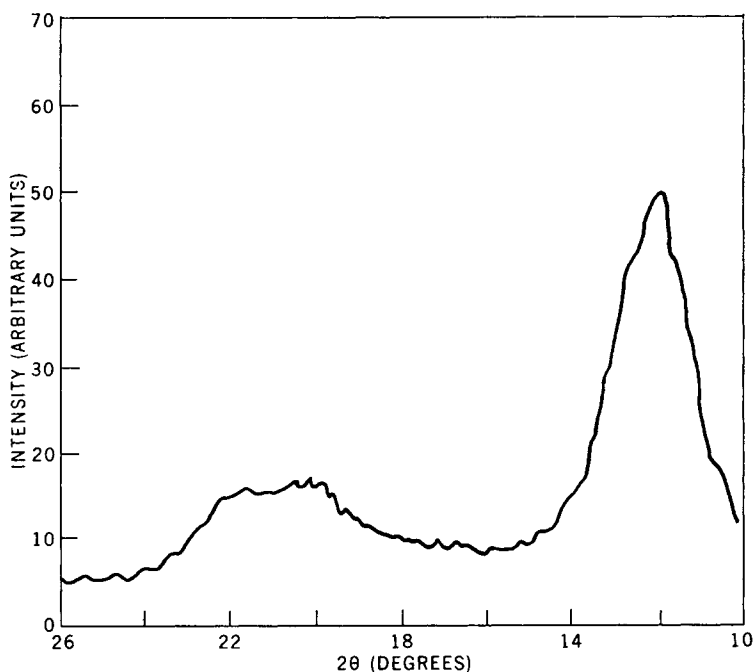Fig. 2. X-Ray diffractogram of cellophane washed with water.

Fig. 3. X-Ray diffractogram of cellophane swollen in water-washed 95% EtNH₂ and then air dried.

Several interesting points emerge from these figures:

(1)   Cellophane is regenerated cellulose, i.e., cellulose II.   In the case of cellulose II, the molecules are displaced relative to one another along the a-axis.   In cellulose IV, the molecules are displaced relative to one another on the b-axis.[4]   In the case of cellulose I, II, III, and IV (Fig. 4),[2] the intensity in the 002 plane is predominant, and in cellulose II, the intensity in 10Ī plane is shifted toward the intensity on 002 plane.   Comparing the x-ray pattern of cellulose II in Figure 4 and those for cellophane in Figures 1, 2, and 3, it is seen that, in addition to the shift of 101 intensity toward 002, a reversal of intensity also is observed.

(2)   Figures 2 and 3 show that even after cellophane was swollen in water and 95% ethylamine (EtNH₂) and then air dried, samples still retained the same patterns as for unwashed cellophane (Fig. 1).   This is because, as Shiner and Brounstein[3] demonstrated, the dried tubings exhibited only very little circumferential shrinkage when soaked in water and therefore retained substantially all the stretch imparted in drying.

Further study of the x-ray diffractogram was done in the following manner.   A sufficient number of rectangular pieces (3.5 × 2.5 cm) of washed and 95% EtNH₂-treated cellophane was stacked to form a pile 1 cm thick.   The stack of cellophane film was placed on the holder and mounted in the goniometer in such a way that the primary beam was allowed to fall on the surface formed by the edge of the pile.   Figure 5 shows the x-ray

diffractogram. The plane of the surface containing the x-ray beam was then rotated through 90° and the x-ray diagram was again recorded (Fig. 6).

Finally, washed cellophane film was cut into tiny pieces (<1 × 1 mm) and the pieces were placed on a rectangular aluminum holder. Figure 7 shows the cross-section of the holder with the sample and the diffractogram
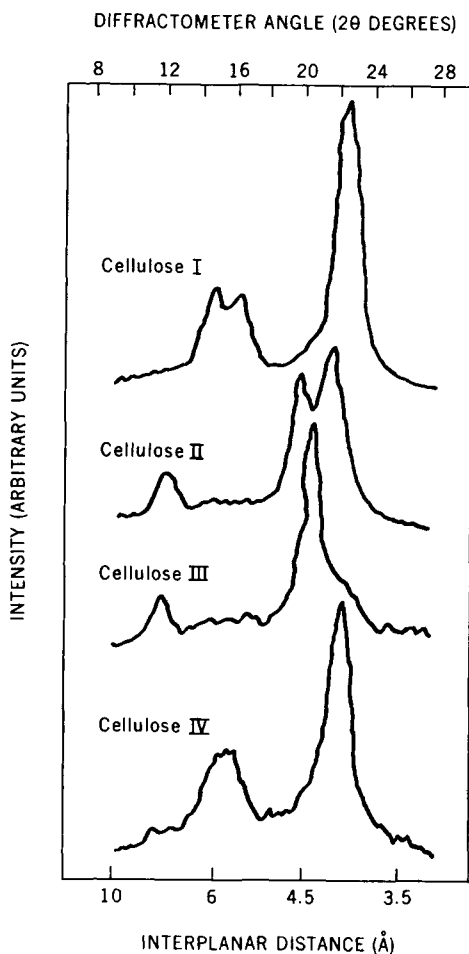
DIFFRACTOMETER ANGLE (2θ DEGREES)

Fig. 4. X-Ray diffractograms of cellulose I, II, III, and IV.

obtained in this manner is given in Figure 8. The collection of small pieces in the holder was not compacted but merely tumbled in the container to obtain random orientation of the small bits of cellophane.

Figure 5 is similar to Figures 1, 2, and 3; Figure 6 is similar to that of cellulose II. Figure 8 shows no sharp intensity in either the 101 or 002 plane. Instead, two broad and weak peaks are observed.
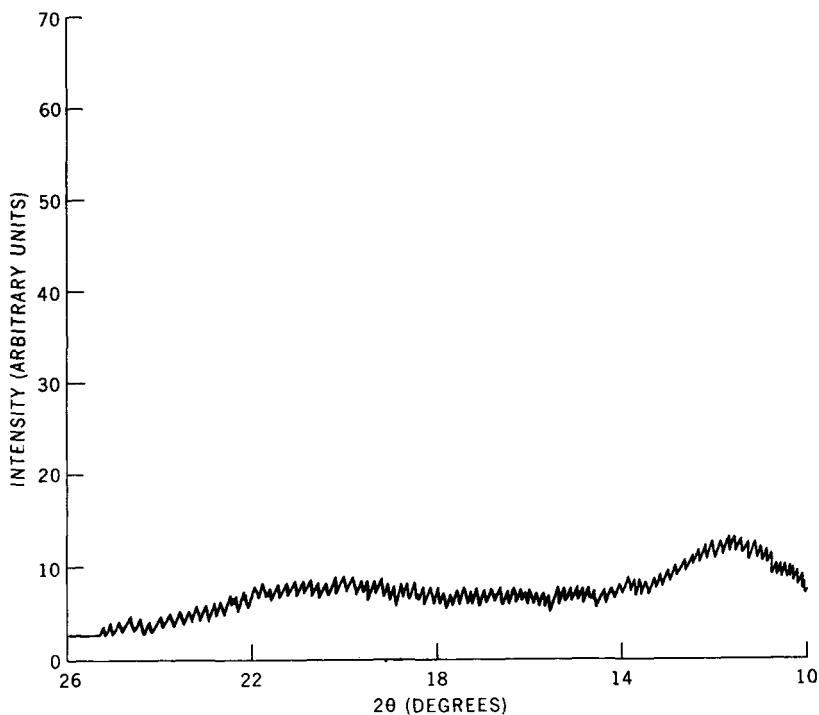
Fig. 5. X-Ray diffractogram obtained in a manner that the x-ray beam was incident on a surface formed by the edge of a pile of cellophane films (3.5 × 2.5 cm).

Hermans and Weidinger,[5] while studying the x-ray investigation on the crystallinity of cellulose quantitatively, used uncoated cellophane sheets of varying number (each 0.09 mm thick) piled on top of each other. They also took exposures for cellophane rolled to form a little rod about 12 layers in diameter and for a pellet made by molding thin cellophane shavings obtained by scratching a sheet with a sharp knife. The magnitude of the compressive stress used in making the pellet was not given. They observed the absence of a peak in 101 plane in the sheets and found that this peak reappeared in the pellet. They also observed that the intensity of the peak $10\bar{1} + 002 + 021$ dropped from 0.24 in the sheet to 0.21 in the roll and to 0.12 in the pellet. Hermans and Weidinger considered this phenomenon to be a striking illustration of the necessity of their procedure of randomizing orientation in all fiber samples through pellet formation.

DISCUSSION AND CONCLUSIONS

The x-ray diffraction technique for the determination of crystallinity of a material is based on the interpretation that the crystalline region gives rise to sharp peaks, while noncrystalline regions scatter x-rays in a diffuse manner. The relative integrated intensities of the discrete reflections and the background depend on the proportions of the two components present.
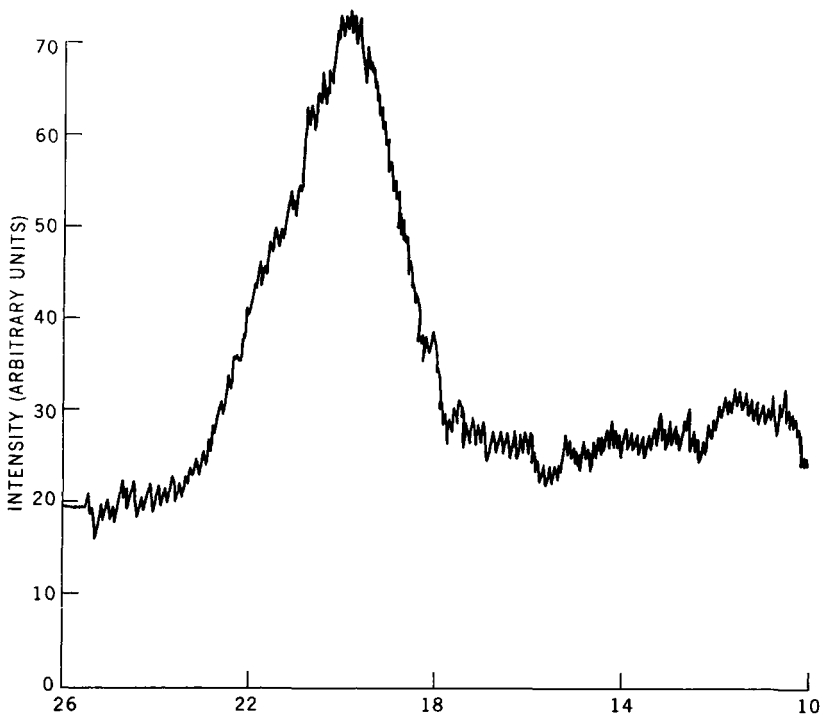
Fig. 6. X-Ray diffractogram of cellophane sample used in Figure 5, after rotating the surface (formed by the edge of a pile) containing the x-ray beam about an axis through 90°.
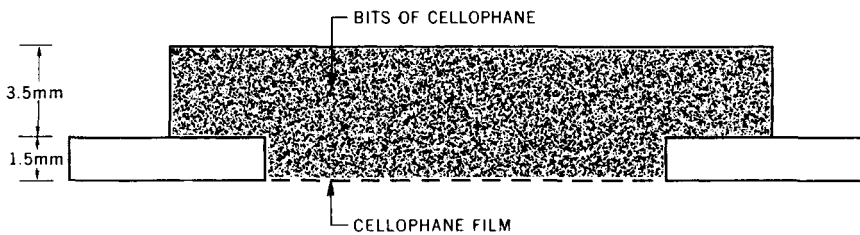

Fig. 7. Cross-section of aluminum sample holder containing small bits of cellophane.

Numerous x-ray diffraction methods have been reported in the literature to estimate the crystalline regions in cellulosic materials.[6-11] The radial intensity ratio, an estimation of the lateral order present in a cellulosic material calculated by Ingersoll,[12] would be unreliable if the samples are of different orientation, since large differences in orientation change the background corrections and interference intensities. Hermans and Wei-dinger[13] calculated the "crystalline–amorphous ratio" by estimating the "amorphous" portion from the height of the background curve obtained from ball-milled cellulose (assumed to be completely noncrystalline). Estimation of the "crystalline" cellulose was derived from the area between

the background curve and that of the diffraction intensity of the cellulosic material.

Segal and his colleagues[14] scanned the diffraction intensity from 12–24° which included the intensity peaks corresponding to the 101, 10$\bar{1}$, and 002 planes. "Crystallinity index" (C.I.) (in per cent) was calculated from the relation

$$C.I. = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \tag{1}$$

where I_{002} and I_{am} are the diffraction intensities from 002 planes at $2\theta = 22.6°$ and background scatter at 2θ about 18°. Note that in this and
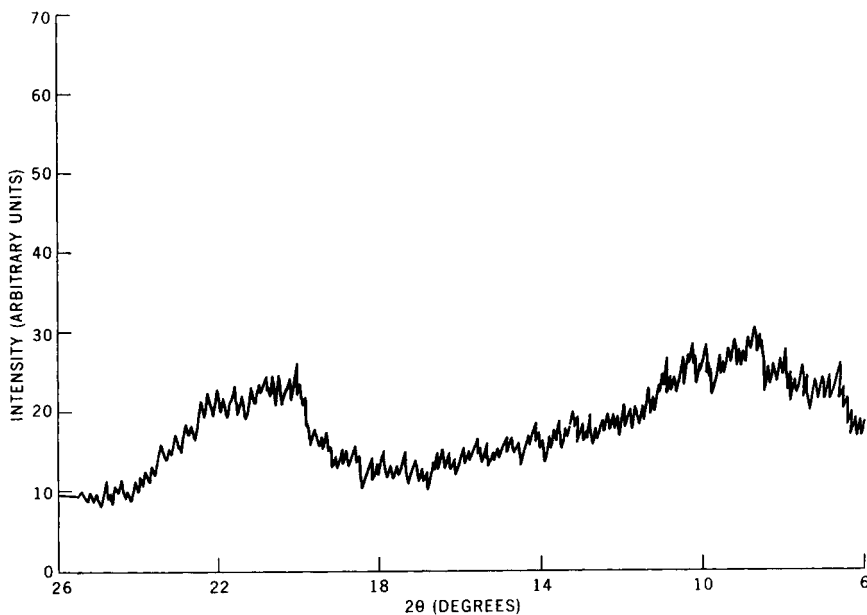

Fig. 8. X-Ray diffractogram of small bits of cellophane shown in Figure 7.

similar calculations the intensities observed in 101 and 10$\bar{1}$ planes are not taken into consideration despite the fact that they also indicate order in the system. Furthermore, in certain cellulosic materials, peaks with intensity of the same order of magnitude as those of the 101 and 10$\bar{1}$ have been observed near $2\theta = 30$ and 35° with a concomitant reduction in the intensity of the 002 peak.[15] Application of such formulas give only incomplete results. Calculation of "the index of order" proposed by Ant-Wuorinen and Visapää[16] also involves the intensity peaks corresponding to 002 planes. These authors stress that the crystallinity index is not considered to be a measure of the per cent crystalline content in a given cellulose sample. The values only depict "the general degree of order" prevailing in the samples.

Application of the basic theory of x-ray diffraction to estimate the crystalline content in any polymers also presents difficulties.   Consider the effects of the atomic arrangements on the x-ray diffraction intensity (from a plane) which are accounted for by the atomic structure factor denoted by F (hkl), where hkl are Miller indices.[17]   This factor, which appears in the intensity expression as F^2, is given by

$$F(hkl) = \Sigma f_{0,n} \exp 2\pi i(hx_n + ky_n + lz_n) \tag{2}$$

where $f_{0,n}$ is scattering factor of the nth atom, x_n, y_n, and z_n are the coordinates of the nth atom in the cell expressed as fractions of the cell edge lengths.   The modulus of $F(hkl)$ is known as the structure amplitude and is the ratio of the amplitude of the wave scattered in the order hkl by the atoms in one unit cell to the amplitude of the wave scattered by a single electron under the same conditions. $|F(hkl)|$ is thus a pure number.   The structure amplitudes calculated by means of eq. (2) cannot be directly compared with observed values since values of f_0 are calculated for atoms at rest.   Because of the thermal movements of atoms in a crystal, at any instant corresponding atoms are not separated by exact multiples of the cell dimensions.   Thus, two such atoms will not scatter exactly in phase in any particular order and the structure factor will be smaller than calculated. Accordingly, a correction deduced by Debye and Waller[17] is usually applied by which the scattering factor of each atom is reduced to

$$f = f_0 \exp (-M) \tag{3}$$

where

$$M = \frac{8\Pi^2 \overline{U_s^2} \sin^2 \theta}{\lambda^2}$$

$$M = \frac{2\Pi^2 \overline{U_s^2}}{d^2} \tag{4}$$

$\overline{U_s^2}$ being the mean square displacement of the atoms from their mean positions in a direction perpendicular to the reflecting planes, and d is the interplanar spacing.   This is only an approximate treatment.   In fact, each atom should have its own value of M which itself may be dependent upon the orientation of the reflecting plane.   For much x-ray work, however, it is generally assumed that a mean value of M is appropriate.   Thus, the structure factor becomes

$$F(hkl) = \Sigma f_{0,n} \exp 2\pi i(hx_n + ky_n + lz_n) \exp (-M) \tag{5}$$

The intensity of the scattered radiation arising from a reflecting plane in a crystal lattice may be written[18] as

$$I(hkl) = AF(hkl) F^* (hkl) \tag{6}$$

where $F(hkl)$ is given by eq. (2), $F^*(hkl)$ is the complex conjugate of F, and A is a constant.

Interpretation of x-ray diffractograms of polymers using this last equation presents certain difficulties. For example, comparison between relative areas under the crystalline peaks and those under the noncrystalline regions has been employed as a method for the estimation of crystallinity. In this procedure it is assumed that the scattering from a unit of polymer is the same, irrespective of the lateral order, and this need not be necessarily valid. In fact, the total scattering depends upon the amount of material and the phase relationship of the scattered wave. It has been argued theoretically[19,20] that thermal vibrations of a crystal lattice may decrease the intensity of the crystalline peak while this need not be true for noncrystalline regions. A consequence of this could be that, on changing the temperature, the ratio of the areas under crystalline and noncrystalline x-ray patterns would change without a corresponding alteration in the true amount of the crystalline material. In eq. (6) it is seen that the intensity I decreases as the temperature increases because M increases. $F(hkl)$ may increase or decrease with temperature: the contributions of the atoms move in or out of phase as the density of the crystalline material changes with temperature. Thus, areas under the crystalline peak, or a comparison between the areas under the crystalline and noncrystalline regions, cannot be directly interpreted as representing the amount of crystalline material in the polymer.

The fact that neither the area nor the intensity can be used as a measure of crystallinity can be clearly seen from x-ray diffractograms of cellophane (Figs. 1, 2, 3, 5, 6, and 8) in which it has been found that in addition to the shift of the 101 peak toward 002 (which is usually observed[21] when fibers are mercerized to produce cellulose II), a reversal of intensity was also found in the cellophane diffraction pattern. If the area under the intensity peaks, or the height of the 101 peak, is taken as a measure of the amount of crystallinity, these cellophane samples (cellulose II) would have crystalline portions of about 70%! Whichever approach is used, an appreciable uncertainty in the x-ray method arises from one's inability to estimate with certainty that part underlying the peak which is attributable to the noncrystalline phase.

According to Statton,[22] in the various areas of polymer study there is perhaps no other area which has so much controversy as the interpretation of x-ray diffractograms. The main reason for this seems to be the fact that a considerable amount of variability is found in the diffraction patterns of different materials. "Difficulty comes when we make the mistake of assuming that our models are true pictures of the solid state of polymers."[22]

Recently, Viswanathan[23] reported that he has experimental evidence which "unequivocally establishes the fact that the role of degree of crystallinity *per se* has been hitherto overemphasized and that the degree of crystallinity is really identical not only for all cottons but also for mercerized and regenerated cellulose fibers, the absolute value of degree of crystallinity having no import whatsoever."

In view of all the factors just described, it appears that the x-ray method for estimating x-ray crystallinity is not applicable to cellophane.

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