

The Effect of Moisture Present in Polymers on their X-Ray Diffraction Patterns

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Synopsis

The influence of imbibed water in cellulose, polypropylene, and polyester on their x-ray diffraction patterns has been studied. It was found that both hygroscopic and nonhygroscopic polymers behave similarly, in that the resolution of the peaks in their x-ray diffraction patterns increases. This is because the addition of water enhances the x-ray absorption coefficient of the polymers which are poor absorbers of x-rays in their dry state. It is concluded that there is no x-ray evidence at present which indicates that water has an influence on the cellulose lattice.

INTRODUCTION

Cellulose is an exceedingly hygroscopic substance. The literature on the absorption of water vapor by cellulose fibers and their swelling in water is extensive.¹⁻³ The sorption phenomenon is regarded by many workers as a function of the amorphous regions in the fiber. In contrast to this, some workers hold that the moisture is sorbed only on the available surface of the crystalline fibrils where most of the free hydroxyl groups are located.⁴ In the case of cellulose II, some early workers thought that moisture was included in the crystalline lattice as well. But Kratky and Treiber⁵ have shown that water molecules are not included in the lattice.

Subsequently, many workers in the field have studied the influence of relative humidity on the molecular order in cellulose fibers by the x-ray diffraction method. Ant-Wuorinen and Visapää⁶ and Ray⁷ noted a decrease in the molecular order with increasing water sorption, and this was interpreted to be in conformity with the observed decrease in density of the moist fibers.⁸ Chedin⁹ and Creely and Tripp,¹⁰ on the other hand, found that there is an increase in the lateral order with increasing sorption. These authors thought that a decrease in order upon drying is due to the induced stresses in the cellulose structure.¹⁰ They also pointed out that the differences in the findings of various workers may be due to the different methods of analyzing the data in each case. The contribution of water to the total scatter was found negligible by both Ray⁷ and Creely and Tripp.¹⁰

But in either case, whether there is an increase or decrease in the lattice order upon sorption of water, it is implied that water has an influence on the cellulose lattice and that there is a definite possibility of water disrupting the original lattice. The present study is, therefore, aimed at resolving this problem by studying not only the hygroscopic cellulose fibers under various humidity conditions but also some nonhygroscopic polymers for which there is no evidence of swelling by water.

EXPERIMENTAL

Materials

The following samples were studied during this investigation: (a) native Sudan cotton; (b) Sudan cotton repeatedly swollen in aqueous alkali solutions; (c) ramie fibers likewise repeatedly swollen in aqueous alkali solutions; (d) native cotton crosslinked with formaldehyde; and (e) commercial polypropylene and poly(ethylene terephthalate) staple fibers.

Methods

The x-ray diffraction patterns were recorded employing a Geiger counter and rate meter charts using Ni-filtered CuK_α radiation from a Philips PW1009 x-ray diffraction unit operated at 35 kV and 20 mA. For cellulose samples, diffraction patterns were also recorded photographically using a large Debye-Scherrer Camera with a fiber holder. The humidity within the camera was controlled by suitable means. For diffractometry, fibers were cut, sieved through a 300-mesh screen, and pressed to obtain rectangular pellets.

Cotton and ramie samples were studied in completely wet, 100% R.H., 50% R.H., and dry conditions. In one case, the ramie sample pellet was thoroughly wetted with water and then dried in a desiccator containing P_2O_5 by applying vacuum for durations of 30 min each. The diffraction scans were recorded at each stage after covering the sample with 2-mil-thick polythene film. After 10 hr, the drying periods under vacuum were increased to several hours, and the sample was dried for a total period of 130 hr.

The nonhygroscopic polypropylene and poly(ethylene terephthalate) samples were scanned in completely wet and room conditions.

Mercerized ramie and polypropylene pellets of varying masses (hence of varying thicknesses) were also studied.

Mercerized ramie samples were also mixed with 58% and 20% fine copper powder by weight, and the diffraction patterns of these pellets were recorded.

Measurement of Lateral Order

The method of measuring lateral order, or "crystallinity," has always posed difficulties to the workers in the field. The acceptance of a two-phase model would entail various assumptions and standards which will be

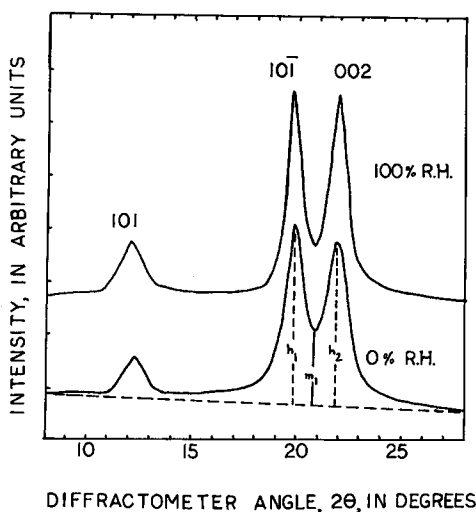


Fig. 1. Diffractometer tracings of repeatedly mercerized ramie samples conditioned at 0% and 100% humidity.

necessary in order to estimate the so-called crystalline and amorphous fractions. In actuality, the x-ray diagrams of the polymers truthfully depict the variations in the "molecular order" that are taking place in the system, but they do not reveal any information as to the manner in which these variations are taking place. Thus, a loss of order due to a reduction in the dimensions of the "crystallites" is indistinguishable from that due to increasing imperfection within the "crystallites." In a continuous network, the "total order" is reflected in the breadths of the x-ray interferences, be it short-range or long-range order. In order to differentiate the two, one would need at least three well-resolved orders of reflections from a given set of planes.¹¹ Unfortunately, in most polymer diffraction patterns, these are either not found or cannot be identified unequivocally as the unit cell cannot be conclusively determined. As the "total order" is reflected in the sharpness of the diffraction peaks, the most ideal solution is to measure the half-widths of the peaks. But in most cases, this also presents problems due to the overlapping of the peaks, and the separation of these involves some assumptions concerning the nature of the profiles of the peaks and the baseline, which may be quite arbitrary. However, the half-width can be measured in an indirect manner by determining the resolution of the peaks. In the present study, such a method is adopted.

For cellulose II diagrams, a baseline is drawn from $2\theta = 8^\circ$ to 28° , and the peak heights h_1 and h_2 of $10\bar{1}$ and 002 , respectively, and height m_1 of the minimum between these two peaks are measured (Fig. 1). Then, the resolution R is

$$R = \frac{2m_1}{h_1 + h_2}$$

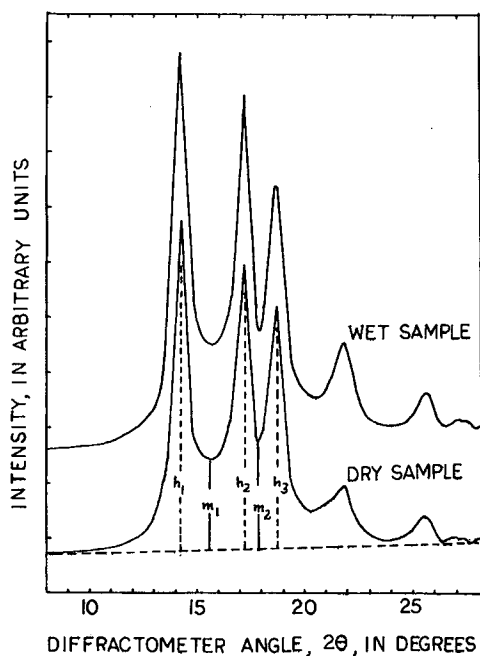


Fig. 2. Diffractometer tracings of the wet and dry polypropylene samples, illustrating the method of computing the resolution R of the diffraction pattern of the polymer.

In the case of polymers, where more than two peaks overlap as in polypropylene and poly(ethylene terephthalate), the baseline is similarly drawn, and all the peaks and the minima between them are measured (Fig. 2). Thus, for any polymer,

$$R = \frac{m_1 + 2m_2 \dots \dots \dots + m_{n-1}}{h_1 + h_2 \dots \dots \dots + h_n}$$

When the resolution is completely lost, R tends to be 1, and, conversely, R tends to be zero when the resolution is maximum. Thus, R is inversely related to the lateral order.

For cellulose I samples, only the half-widths of the 002 peaks are measured.

RESULTS

In conformity with the observations of the earlier workers, it is found that the reflections in the cellulose diagrams sharpen with increasing absorption of moisture.^{7,10} In the case of ramie sample which was dried intermittently in a vacuum desiccator, the resolution is maximum for the completely wet sample and decreases linearly with the gradual removal of water and finally attains a constant value after about 3 to 4 hr (cumulative) of drying (Fig. 3). Native, crosslinked, and mercerized cottons and ramie

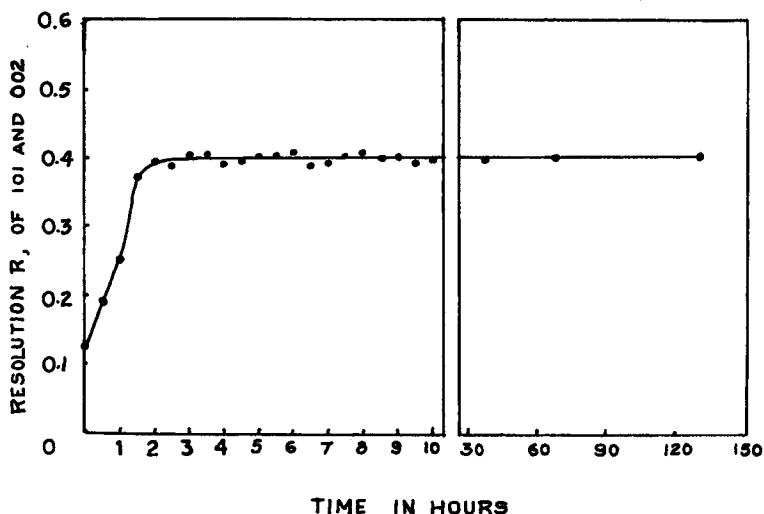


Fig. 3. Loss in the resolution of the $10\bar{1}$ and 002 peaks in the diffraction patterns of the repeatedly mercerized ramie sample dried in a vacuum desiccator at various intervals.

studied under various humidity conditions also follow the same trend (Tables I and II).

Even the polypropylene and poly(ethylene terephthalate) samples which were deliberately moistened with water show greater resolution of the peaks than their dry counterparts under room conditions (Fig. 2 and Table II). The resolution of the diffraction patterns increased with decreasing sample thickness for mercerized ramie and polypropylene samples (Table III).

The two ramie samples mixed with copper powder also show increasing resolution with increasing copper content (Table IV).

TABLE I
Half-Widths of the 002 Peaks in Degrees at Various Humidity Conditions

Sample	Completely wet ^a	100% R.H.	50% R.H.	Dry sample
Cotton untreated	1.3 (61.2%)	1.4	1.5	1.6
Cotton crosslinked	1.3 (66.0%)	1.5	1.65	1.7

^a Percentage of water in the sample is indicated in parentheses.

DISCUSSION

The results indicate that the imbibation of water in polymers, irrespective of whether they are hygroscopic or nonhygroscopic, improves the resolution of their x-ray diffraction patterns. In view of the low x-ray absorption coefficients of these organic polymers which contain only light elements, this is not surprising. The absorption coefficient of cellulose for CuK_α radiation

TABLE II
Resolution R of the Principal Peaks in Cotton, Ramie Polypropylene and Polyester Samples under Various Humidity Conditions

Sample	Completely wet ^a	100% R.H.	50% R.H.	Dry sample
Cotton repeatedly mercerized	0.15 (47.0%)	0.23	0.28	0.37
Ramie repeatedly mercerized	0.18 (56%)	0.25	0.32	0.41
Polypropylene	0.29 (27.3%)		0.36 ^b	
Poly(ethylene terephthalate)	0.58 (22.7%)		0.64 ^b	

^a Percentage of water in the sample is indicated in parentheses.

^b These nonhygroscopic polymers are almost dry at room condition itself.

TABLE III
Resolution of the Principal Peaks in the Diffraction Patterns of Ramie and Polypropylene at Various Thicknesses of the Sample (Indicated by Specimen Mass in Brackets)

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Ramie repeatedly mercerized	0.33 (0.3023 g)	0.32 (0.146 g)	0.31 (0.0728 g)	0.30 (0.0383 g)	0.28 ^a (0.019 g)
Polypropylene	0.43 (0.127 g)	0.40 (0.100 g)	0.38 (0.0654 g)	0.35 (0.0327 g)	0.28 ^a (0.0164 g)

^a In these cases, the polymer sample was evenly spread on a lead sheet placed in the sample holder and pressed with a glass slide as the specimen mass was too small to make a pellet in the usual manner.

TABLE IV
Resolution of the $10\bar{1}$ and 002 Peaks in the Diffraction Pattern of the Repeatedly Mercerized Ramie Sample Mixed with Pulverized Copper Metal Powder at Room Conditions

Copper content in ramie sample, wt-%	58	20	nil
Resolution R of the $10\bar{1}$ and 002 peaks	0.23	0.27	0.32

is ≈ 7.7 . This would mean that in symmetrical reflection geometry, the incident beam would penetrate the sample deeper and thereby causing the lower layers of the sample also to contribute to the diffracted beam (Fig. 4a). This results not only in the broadening of the diffracted beam but also in an asymmetry of the peak profile toward lower angle. Keating and Warren¹² have discussed the case of scattering by a specimen with a low absorption coefficient and have proposed a correction for the broadening and asymmetry of the peak.

With imbibation of water in the sample, however, the absorption coefficient of the specimen will increase (the absorption coefficient of water for CuK_α is ≈ 10.3). Therefore, not only the incident beam would suffer

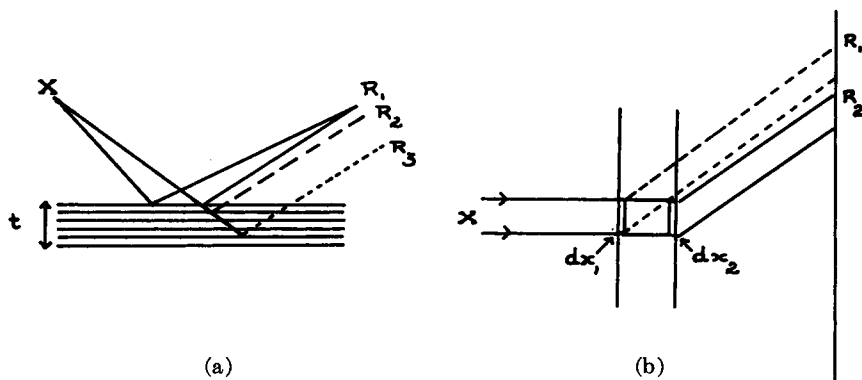


Fig. 4. Asymmetry of the diffraction peaks for a sample of low x-ray absorption coefficient: (a) in symmetrical reflection geometry; (b) in normal beam transmission geometry.

absorption in the sample but the weaker diffracted rays from the lower layers would suffer further absorption while traveling back through the upper layers of the specimen and thereby fail to contribute significantly to the total diffracted intensity. As such, only the top layers would contribute to the total diffracted intensity which results in sharper symmetrical peaks.

That the resolution of the x-ray pattern is dependent upon the amount of water contained in the sample is clearly demonstrated in Figure 3 and Tables I and II. Further, the repeatedly swollen cotton sample was thoroughly soaked in water for a day and scanned, after which the sample was further pressed and blotted to remove excess adhering water and scanned again. The resolution values for these samples are 0.12 and 0.20, respectively, which leaves no doubt that it is only the amount of imbibed water in the specimen which influences its x-ray diffraction pattern and not any variation in structure.¹³ The resolution attained by mixing various amount of copper with ramie also confirms the above view. The resolution in the diagram of crosslinked sample does not alter much under room and dry conditions, for the simple reason that the moisture sorption of the sample has been reduced by crosslinking.

That this is true for both hygroscopic and nonhygroscopic polymers indicates that water imbibation is equivalent to reducing the thickness of the sample, which results in the increased resolution of the pattern:

$$\text{thickness } t = \frac{3.2}{\mu} \frac{\rho}{\rho'} \sin \theta$$

where μ is the linear absorption coefficient and ρ and ρ' are the density of the solid material composing the powder and that of the powder, including interstices,¹⁴ respectively. Any variation in μ will naturally influence the

effective scattering mass, and μ is dependent on the amount of water sorbed by the sample. In this context, one can understand the variation in the relative intensities of 10 $\bar{1}$ and 002 in cellulose II diagrams with varying amounts of moisture.¹⁰ In dry samples, the peak broadening reduces the resolution, and as the asymmetry is toward lower angle, the broadening of the 002 peak will significantly contribute to the increase in the intensity of the 10 $\bar{1}$ peak. The increase in the so-called amorphous scattering at about $2\theta = 18^\circ$ is due to the asymmetric broadening of the 10 $\bar{1}$ peak¹⁰ toward a lower angle. Similarly, the increase in the background height at $2\theta = 18^\circ$ – 20° in cellulose I diagrams can be explained. *It is not sufficient to normalize the intensity data to a standard scattering mass by taking into account the absorption coefficient of only the cellulose sample, but the peak profiles need to be corrected for asymmetry in the case of dry samples, and the variation of μ with increasing moisture content also needs to be taken into account.* As both the methods of measuring crystallinity proposed by Segal et al.¹⁵ and Walkelin et al.¹⁶ are basically dependent upon measuring the sharpness of the x-ray diagram, any increase in resolution with increasing moisture sorption does not necessarily mean an increase in the lattice order.

On the other hand, in normal beam transmission geometry (Fig. 4b), the contribution to the recorded scattering by the elemental volume dx_1 will be greatly reduced if the absorption coefficient of the sample is increased owing to sorption of water, and only the elemental volume dx_2 will significantly contribute to the recorded intensity, which will result in a sharp diagram. However, the area under the intensity curve will be reduced for the moist sample as compared to that of the dry sample. For the dry sample, the broadening and the asymmetry of the peak in this case will, however, be toward the higher angle. Although the early workers have taken into account the scattering due to water^{7,10,16} (which may be negligible), the elimination of distortion of the profiles of the diffraction peaks from a sample of increased absorption coefficient (due to water) has not been considered. As such, the integrated area under the intensity curve cannot serve as an index of the lateral order either.

The decrease in the density of cellulose with water sorption has been quoted in support of the conclusion that the lattice order decreases with water sorption.⁸ It should be noted that the density of the conditioned sample so measured is not the density of cellulose alone, but the composite density of the cellulose–water system. The density of water being lower than that of cellulose, it is not surprising that the cellulose–water system has a lower density than dry cellulose at high regains. (In fact, it is also reported that the density of the cellulose–water system shows a maximum around 3–4% moisture regain.¹)

Therefore, there does not seem to be any x-ray evidence to support the conclusions that the sorption of water by cellulose influences the lattice order in any manner. One should take into account the increased absorption coefficient in hygroscopic polymers in order to study any variations in the lattice order.

It is also pertinent to mention here that in measurements to correct the peak widths of polymer samples due to instrumental broadening, it is customary to make measurements on a standard sample. In such cases, if the absorption coefficient of the two samples differ greatly, the correction so applied will be erroneous.

CONCLUSIONS

With increasing water imbibition in polymers, the x-ray diagram exhibits better resolution. This is due to the increased absorption coefficient of the polymer sample in which only the top layers contribute to diffraction. There is no x-ray evidence to show that the lattice order in cellulose is influenced in any manner on sorption of water. Observed sharpness and the reduction in the total intensity is only due to the presence of water, which increases the x-ray absorption coefficient of the sample. Care should be taken in the interpretation of diffraction patterns of hygroscopic polymers.

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