

X-Ray Study of Thermal Expansion and Transition of Crystalline Cellulose

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ABSTRACT: For the cellulose crystals I and II, the spacings and intensities of some typical X-ray reflections were measured over a range of temperature from room temperature to 200°C. The spacing vs. temperature curve for each reflection exhibited a distinct break at about 150°C for Cell I and at about 100°C for Cell II. The thermal expansion coefficients estimated from this curve for the (10 $\bar{1}$) reflection of Cell I were $5.1 \times 10^{-5} \text{ K}^{-1}$ below 150°C and $1.6 \times 10^{-4} \text{ K}^{-1}$ above 150°C. The intensity vs. temperature curve for each reflection also exhibited a break at the same temperature as that for the break of the corresponding spacing vs. temperature curve. The reason for the appearance of these breaks is not yet clear.

KEY WORDS X-Ray / Spacing / Intensity / Cellulose I / Cellulose II / Transition /

In our previous papers,^{1,2} the fine structure of a cellulose crystal was investigated and a long spacing crystal structure was found. In the following study, attention is directed to thermal effects on the X-ray diffraction angle and intensity in two cellulose crystals.

EXPERIMENTAL

The lattices of the two crystal structures examined were of the types usually referred to as Cellulose I and Cellulose II. The samples used for Cell I were cotton and hemp yarns which showed clear equatorial reflections and a softwood hemlock-spruce which showed clear meridional reflections. The samples used for Cell II were a viscose rayon and mercerized cotton and hemp yarns.

X-Ray diffraction experiments on a given sample were performed at a number of temperatures from room temperature to 200°C, using a diffractometer equipped with a high temperature attachment. The entire diffraction profile was measured after the sample was maintained at the desired temperature for 1 h, and the profile at a specified Bragg angle as a function of temperature was determined by raising or lowering the temperature at a rate of 1.25

K min⁻¹. In the latter, the diffractometer was scanned repeatedly over the range of $\pm 2^\circ$ about the specified Bragg angle at a rate of 1° min⁻¹. The X-ray source was the nickel-filtered Cu-K α radiation from a generator driven with 40 kV and 20 mA. A slit of 1° was used for the divergence of radiation and a slit of 0.15 mm for the reception of diffracted rays.

The sample yarns were uniformly wound on a metal plate of 25 mm long, 15 mm high, and 0.5 mm wide, while the sample plates of hemlock-spruce were cut into pieces of 24 mm long, 15 mm high, and 1.4 mm wide.

RESULTS AND DISCUSSION

Figure 1A illustrates the equatorial diffractograms of cotton (Cell I) and Figure 1B the meridional diffractograms of hemlock-spruce (Cell I), both at some selected temperatures. The following features can be seen from these diffractograms: the peak angle of the (101), (10 $\bar{1}$), and (002) reflections decrease monotonically as the temperature is raised, while the peak angle of the (040) reflection first increases and then turns to decrease. For the (040) reflection the peak angle changed reversibly with a

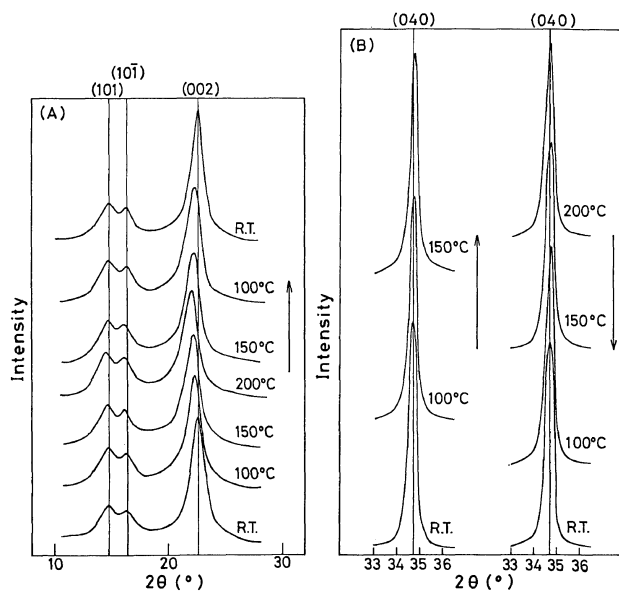


Figure 1. X-Ray diffractograms at various fixed temperatures. A, equatorial patterns of cotton (Cell I); B, meridional patterns of hemlock-spruce (Cell I).

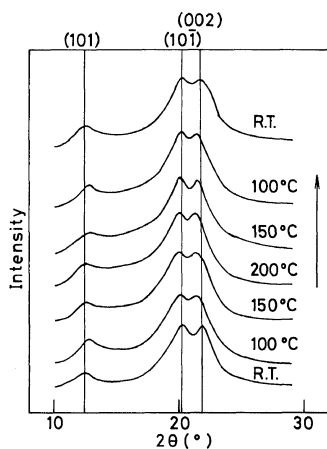


Figure 2. X-Ray diffractograms of viscose rayon (Cell II).

cyclic change in temperature, as shown in Figure 1B.

The X-ray diffractograms of Cell II were obtained only for equatorial reflections, since the fiber axes of the specimens used could not be placed vertically to the surface of the specimen holder. Figure 2 illustrates the diffractograms of a viscose rayon (Cell II). It is seen that the peak angles of the $(10\bar{1})$ and (002) decrease monotonically and that of the (101) re-

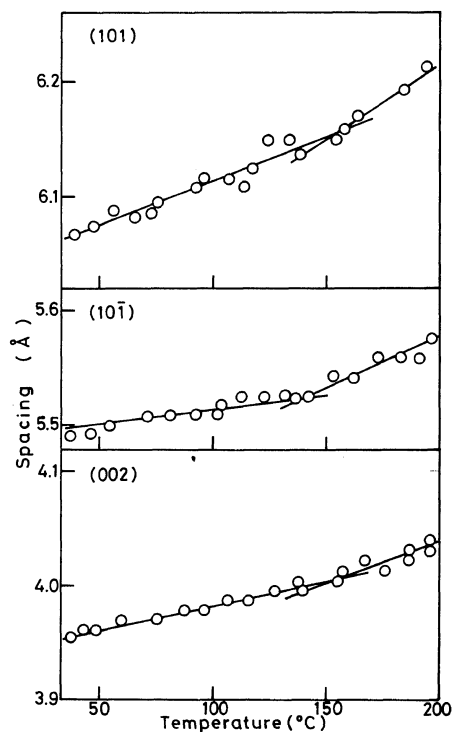


Figure 3. Spacings of the (101) , $(10\bar{1})$, and (002) reflections of cotton (Cell I) plotted as a function of temperature.

flection first increases and then decreases slightly, as the temperature is raised.

The peak angles were converted to *d*-spacings using the Bragg relation. Figure 3 shows the (101), (10 $\bar{1}$), and (002) spacings of cotton (Cell I) as a function of temperature. For each reflection, the data points can be fitted by two straight lines of different slopes which intersect at a temperature of about 150°C. The thermal expansion coefficients determined from these lines below 150°C ranged from 5.1×10^{-5} to $1.3 \times 10^{-4} \text{ K}^{-1}$, with the one in the (10 $\bar{1}$) direction being the smallest. The corresponding values above 150°C were from 1.6×10^{-4} to $2.3 \times 10^{-4} \text{ K}^{-1}$, which are conspicuously larger than the values below 150°C. A discontinuity in slope was found in the relative rigidity vs. temperature curve for a cotton linter at 140°C by a torsional braid analysis.³ It was also found⁴ from the measurement of infrared spectra of Cell I and Cell II that the relative absorbance of the OH stretching of intermolecular hydrogen bonds was weaker at 150°C than at room temperature. Our finding of the discontinuous change in the thermal expansion coefficient of Cell I at 150°C is consistent with these reported results, and thus may be attributed to some sharp change in the strength of intermolecular hydrogen bonds in the vicinity of 150°C.

The (040) spacing of Cell I is plotted against temperature in Figure 4. This plot should represent thermal effects on the main-chain conformation. It is seen from the figure that, as the temperature increases to 150°C, the (040) spacing decreases linearly, and then it turns to increase linearly. The straight lines fitting the data points below and above 150°C give $-6.4 \times 10^{-4} \text{ K}^{-1}$ and $1.6 \times 10^{-4} \text{ K}^{-1}$ for the slopes. The reason for this temperature dependence of the (040) spacing is not yet clear.

Figure 5 shows the (101), (10 $\bar{1}$), and (002) spacings of Cell II as a function of temperature. The plot for the (101) reflection indicates the same behavior as the (040) spacing of Cell I. It has been reported⁴ that heat treatment of Cell II induces relaxation of the intermolecular hydrogen bonds, causing the crystal structure to change to an orthorhombic structure. Our data for the (101) spacing of Cell II do not contradict this reported result. Figure 5 indicates that the breaks in the spacing vs. temperature curves for Cell II occur at about 100°C, regardless of the reflections.

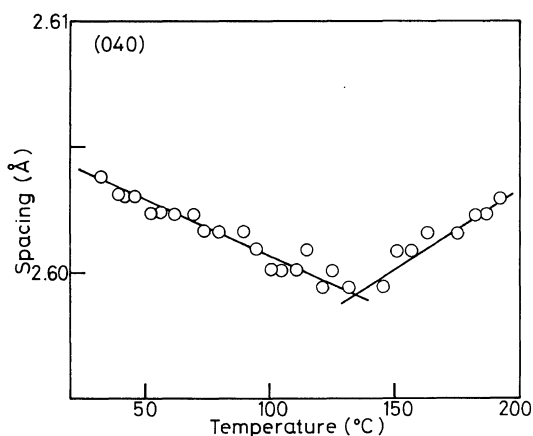


Figure 4. Spacing of the (040) of hemlock-spruce (Cell I) as a function of temperature.

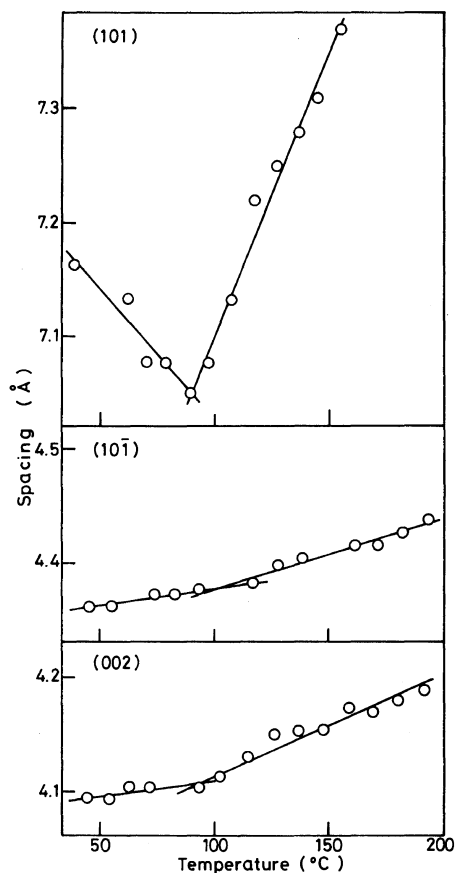


Figure 5. Spacings of the (101), (10 $\bar{1}$), and (002) reflections of viscose rayon (Cell II) as a function of temperature.

Table I. Thermal expansion coefficients of Cell I^c and Cell II^d

	(101)		(10 $\bar{1}$)		(002)		(040)	
	α_1^a	α_2^b	α_1	α_2	α_1	α_2	α_1	α_2
	K ⁻¹		K ⁻¹		K ⁻¹		K ⁻¹	
Cell I	1.3×10^{-4}	2.3×10^{-4}	5.1×10^{-5}	1.6×10^{-4}	1.1×10^{-4}	1.6×10^{-4}	-6.4×10^{-6}	1.6×10^{-5}
Cell II	-3.1×10^{-4}	6.8×10^{-4}	6.7×10^{-5}	1.6×10^{-4}	7.9×10^{-5}	1.9×10^{-4}		

^a α_1 , Thermal expansion coefficient below the transition point.

^b α_2 , Thermal expansion coefficient above the transition point.

^c Samples of Cell I used for diffraction measurements in the (101), (10 $\bar{1}$), and (002) directions and the (040) direction were cotton and hemlock-spruce, respectively.

^d Sample of Cell II was a viscose rayon.

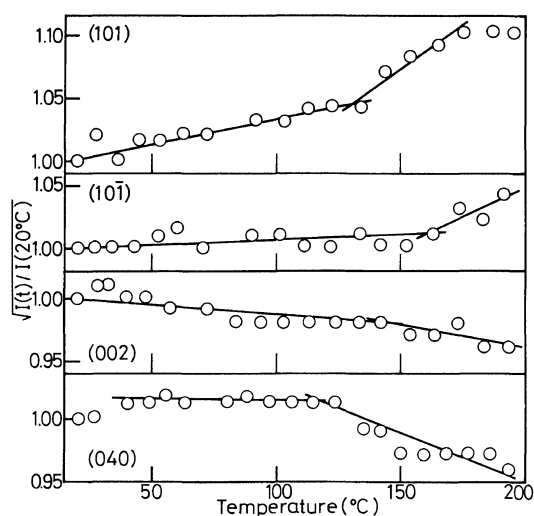


Figure 6. Square roots of the relative intensities of the (101), (10 $\bar{1}$), (002), and (040) reflections of Cell I (hemp and hemlock-spruce) as a function of temperature.

In summary, the slope of the spacing vs. temperature curve undergoes a discontinuous change at about 150°C for Cell I and at about 100°C for Cell II. These temperatures are called the transition points for the respective cellulose crystals. Table I summarizes the thermal expansion coefficients for each reflection below and above the transition point.

Figure 6 illustrates the relations between the square root of relative intensity and the temperature for the (101), (10 $\bar{1}$), and (002) reflections of hemp and for the (040) reflection of hemlock-spruce. The (101), (10 $\bar{1}$), and (002) reflections of cotton yielded

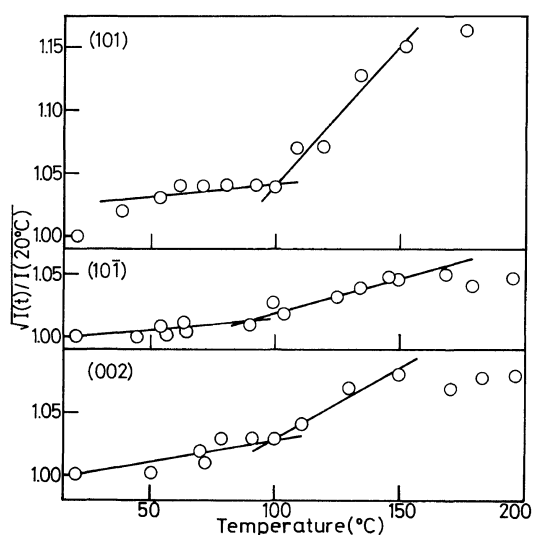


Figure 7. Square roots of the relative intensities of the (101), (10 $\bar{1}$), and (002) reflections of Cell II (viscose rayon) as a function of temperature.

results similar to those obtained with hemp. The intensities of the (101) and (10 $\bar{1}$) reflections increased with temperature, giving the temperature coefficients which change discontinuously in the vicinity of 150°C from lower to higher values. On the other hand, the intensities of the (10 $\bar{1}$) and (040) reflections remained nearly constant up to about 150°C and then decreased as the temperature increased.

The corresponding intensity vs. temperature curves for Cell II are shown in Figure 7. It is seen that the intensity of each reflection increases with

temperature and that the temperature coefficient undergoes a discontinuous change in the vicinity of 100°C. This coefficient above 100°C for the (101) reflection was significantly larger than those for the other reflections.

CONCLUSION

The present study shows that the temperature coefficients of the spacings and intensities of some typical reflections of X-ray for Cell I and Cell II undergo a discontinuous change at a temperature characteristic of each crystal structure, 150°C for Cell I and 100°C for Cell II. The reason for the existence of such "transition points" is not yet clear, but it is believed that the experimental data ob-

tained here deserve publication.

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