

NOTE

Analysis of Lattice Distortions in Ramie Cellulose

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Received 27 January 1997; accepted 17 March 1997

Our earlier communications described X-ray measurements of various structural parameters of ramie, namely, crystallinity and disorder parameter using the Ruland and Vonk method,¹ lateral crystallite size and paracrystalline distortion parameter by the Fourier analysis technique,² and radial distribution function (RDF) analysis.³ The imperfect crystalline structure of cellulose gives a diffraction pattern with few broadened peaks and a high background. It is well known that distortions in a crystal lattice contribute to the broadening of the peaks and also to the diffuse scattering. In general, the distortions that occur in crystal lattices are classified⁴ as distortions of the first kind (or type I) and distortions of the second kind (or type II). In Type I distortions, the magnitude of the displacements of atoms, group of atoms, or molecules from their positions in an ideal lattice is independent of the location in the crystal and the long range order is preserved. If the distribution of the displacements from the ideal sites is assumed to be Gaussian, the net effect of type I distortions on the diffraction pattern is functionally indistinguishable from the effect of thermal vibrations. Type I distortions, including thermal motions, reduce the intensities of sharp Bragg peaks which are redistributed in reciprocal space as diffuse scattering. Such effects can be analyzed by a factor analogous to the Debye-Waller temperature factor. The disorder function D for the first kind of distortion can be written as⁴

$$D \simeq \exp(-k's^2) \quad (1)$$

where $s = 2 \sin \theta/\lambda$, 2θ is the diffraction angle, and λ is the wavelength in angstroms (Å). k' includes the effects of both thermal vibration (k_T) and lattice imperfections of the first kind (k_1); that is,

$$k' = k_T + k_1 \quad (2)$$

In type II distortions, the magnitude of the displacements of atoms, groups of atoms, or molecules from their ideal lattice sites increases with the distance from any arbitrarily chosen reference point and, in fact, as the square of the distance.⁴ Eventually the displacements are greater than the lattice spacings and there is no correlation with the lattice over large distances. Thus the long-range order is lost in the lattice. Distortions of the second kind result in both diminution of intensity and an increase in reflection breadth with increasing angle 2θ or reflection order. The term "paracrystalline" is applied to materials with type II distortions.

It is doubtful how much contribution should be attributed to lattice distortions for the intensity of the amorphous background in the X-ray scattering of cellulose. A careful analysis of the radial distribution curve

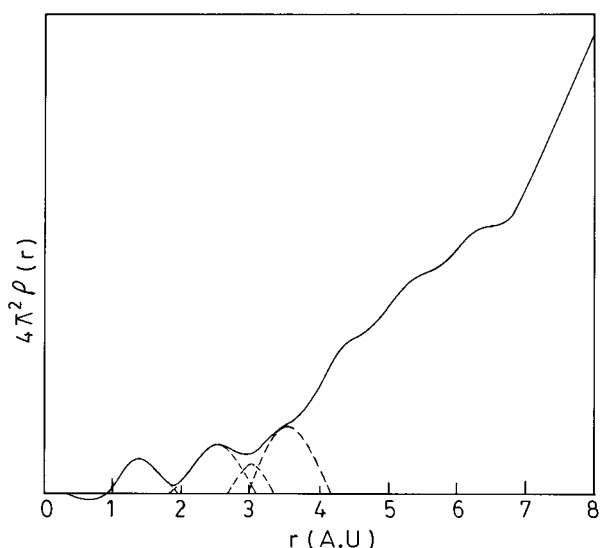


Figure 1 Radial distribution function curve of ramie.

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Journal of Applied Polymer Science, Vol. 66, 2045–2046 (1997)
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Table I Ruland Parameter (k) and First and Second Kinds of Distortions (k' and k_2) in Ramie

Ramie Fiber Sample	k (Experimental) (\AA^2)	k_2 (Experimental) (\AA^2)	$k' = k - k_2$ (\AA^2)	k' (RDF) (\AA^2)	k (Calculated) $= k_2 + k'$ (RDF) (\AA^2)
Untreated	6.3	0.7	5.6	4.7	5.4
Heat-treated (250°C, 1 h)	6.5	0.9	5.6	4.7	5.6
Mercerized					
18% NaOH at RT	6.7	1.2	5.5	4.7	6.0
30% NaOH at RT	6.8	1.4	5.4	4.7	6.1
12% NaOH at 0°C	7.2	1.5	5.7	4.7	6.2

RT, room temperature; RDF, radial distribution function.

might help determine to what extent thermal vibrations and distortions of the first kind are present. It is a fundamental difficulty that it is not possible to uniquely separate thermal scattering from diffuse scattering. In the RDF curve the overlapped peaks can be resolved by fitting a multiple Gaussian function (Fig. 1). As reported earlier,³ the mean square displacements of the atoms can be obtained from the half-intensity width of the resolved peak. A simplified theory of disorder, neglecting the interaction of higher neighbors, will be considered here. We can write³

$$k' = 8\pi\overline{\mu_s^2} \quad (3)$$

where $\overline{\mu_s^2}$ is the mean square displacement of atoms from their position of rest. Hence the value of k' can be calculated for the nearest neighbor atoms.

Ruland argued that all kinds of displacements of the atoms from their equilibrium positions can be lumped together in one Gaussian lattice-imperfection factor^{4,5}:

$$D = \exp(-ks^2) \quad (4)$$

where

$$k = k' + k_2 = k_T + k_1 + k_2 \quad (5)$$

k_2 is the distortion due to type II distortion (paracrystallinity). The value of k_2 can be estimated from the Hosemann parameter g_p , using the equation⁵

$$k_2 = 1.4\pi^2 g_p^2 d^2 \quad (6)$$

Thus, from the value of the Ruland isotropic lattice disorder parameter (k) and from equations (5) and (6), we can determine how the imperfections are apportioned between type I and type II. The results are given in Table I.

It has been observed² from the measured g_p values that this parameter is anisotropic, having different values for different reflecting planes. Hence an average value of g_p for the three equatorial reflections—namely, ($1\bar{1}0$), (110), and (020)—were taken for the estimation of k_2 . It is seen from Table I that there is good agreement between the calculated and experimental values of Ruland parameters within the limits of theoretical and experimental errors. The calculated values are observed to be slightly lower than the experimental values. This may be due to the averaging of k_2 values for the above three reflections and partly to the mean square displacement calculated for only the nearest neighbors. However, it is clear from the Table I that the lattice distortions of the first kind, including thermal vibrations, are the major source of distortion in cellulose. The result is in agreement with the inference of Hofmann and colleagues.⁶ It is interesting to observe that the values of k' do not change appreciably in heat-treated or in alkali-treated mercerized samples. However, there remains some uncertainty in this separation, as discussed above, which needs further development of the technique.

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