3D model of short-range order of one-hour milled cellulose

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Abstract. The main purpose of this work was to investigate the structure of short-range order of microcrystalline cellulose (MCC) milled for one hour. Usually mechanical milling produces amorphous segments of crystalline cellulose. Investigation of short-range order was conducted by Debay’s method to get X-ray diffraction (XRD) pattern when the coordinates of atoms in a cluster are known. The samples were studied by XRD. Crystallinity degree was measured using Segal’s method. Cellulose Iα and Iβ were used as the initial structures to form clusters. The profile factor ($R_p$) was used, as the evaluation factor. The results showed that the cluster based on cellulose Iβ insufficiently characterized the short-range order of crystalline-amorphous cellulose ($R_p$<18%). Consequently, we examined a unit cell consisting of one cellobiose fragment. The final modeling cluster had the size of 35Å×22Å×29Å. The cluster consisted of 3 layers oriented randomly in relation to one another. The result of comparison of theoretical and experimental XRD patterns revealed that $R_p$ was 11.4%. Therefore, the structure of short-range order of one-hour milled cellulose can be characterized by disordered cellulose chains with the length of 21 Å.

1. Introduction

Cellulose is a linear polymer with crystalline and amorphous regions alternating along the axis of microfibril [1]. Cellulose chains are located randomly in amorphous regions so interaction during reaction takes place more easily than in crystalline regions. Most of reactions takes place on plane of crystallites and in amorphous domains without affecting the intracrystalline regions [2].

The long-range order of crystalline in a microfibril results from intermolecular interaction such as van der Waals’s force and hydrogen bonds. A physical or chemical influence may destroy intermolecular forces in crystallites of cellulose. For example, the higher the time of mechanical milling, the higher increase of amorphous degree in cellulose fibers. XRD pattern of crystalline amorphous cellulose has amorphous galo and peaks belonging to crystalline regions. Amorphous galo defines the presence of the short-range order in the structure of cellulose. The method of randomly disordered layers (Debay’s method) gives information about the structure of short-range order [3]. Therefore, the aim of this paper is to use Debay’s method to investigate the influence of mechanical milling on the structure of the short-range order for one-hour milled MCC.

2. Experimental details

5 ml of MCC was introduced into an agate bowl and the milling was performed in a planetary ball mill (Pulverisette 7 premium line, Fritsch, Germany) using agate balls (5 mm diameter) during one hour. A rotation speed of 750 rpm was used.
XRD measurements of the MCC and one-hour milled cellulose were carried out using a DRON-4.0 automated diffractometer with MoKα radiation. Scattering intensities were measured over an angular range of 2° to 70° with a step size of 0.1° and an angular range of 70° to 145° with a step size of 0.2° in the reflection and transmission geometry. Debay’s method used to obtain the distribution curves of scattering intensity from randomly disordered clusters. Debay’s formula is given as [3]:

\[ I(s) = \frac{1}{N_f} \left[ \sum_{i=1}^{N} f_i^2 + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{2} \left(f_i f_j^* + f_i^* f_j\right) \frac{\sin(s r_{ij})}{s r_{ij}} \exp \left(-0.5 \sigma_{ij}^2 s^2 \right) \right] \tag{1}\]

where \( I(s) \) – scattering intensity; \( N_f \) – the number of formula units per cluster; \( N \) – the number of atoms in the cluster system; \( f_i^2 \) – the atomic scattering factor for \( i \) atom; \( s \) – diffraction vector; \( r_{ij} \) – the distance between \( i \) and \( j \) atoms, \( \sigma_{ij} \) – dispersion of \( r_{ij} \). The method is described in more detail in [3]. Crystalline degree is measured by Segal’s method [4]. Segal’s method is empirical and evaluates the ratio of the difference between the maxima intensity of reflection with (200) index (\( I_{200} \)) and the intensity of amorphous galo (\( I_{am} \)) to \( I_{200} \). Crystalline degree is calculated as follows:

\[ CD(\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \tag{2}\]

The fitting quality of the experimental data have been assessed by the profile factor defined as follows:

\[ R_p(\%) = \frac{\sum_j |I_j - I_j^*|}{\sum_j I_j} \times 100 \tag{3}\]

where \( I_j \) is the experimental point and \( I_j^* \) is the calculated point and the summation includes all points of data.

3. Results and Discussion

The XRD pattern for the sample MCC and one-hour milled cellulose in the reflection geometry is shown in figure 1. The XRD pattern of MCC has been analyzed using Rietveld method. The obtained results show that MCC had the structure of cellulose Iβ with antiparallel orientation of cellulose chains in monoclinic symmetry. The refined cell parameters were \( a=7.84\pm0.02 \text{ Å}, b=8.13\pm0.03 \text{ Å}, c=10.34\pm0.02 \text{ Å}, \alpha=\beta=90^\circ, \gamma=96.2\pm0.2^\circ \). Crystalline degree of MCC was 80±5%.

![Figure 1. XRD pattern of MCC (—) and one-hour milled cellulose (—).](image-url)
Figure 1 shows that MCC scattering intensity of peaks decreases sharply after one hour milling. One-hour milling led to 30% reduction of the crystalline index measured according to equation (2). Hence, mechanical milling resulted in the increase of the amorphous regions number in MCC, but one hour of milling was not enough to transform MCC into amorphous cellulose, as there are some weak peaks on the XRD pattern. Scattering from amorphous part of cellulose is maximal in case of using the transmission geometry [1]. Therefore XRD pattern of one-hour milled cellulose obtained in the transmission geometry was used for comparison with XRD pattern of models obtained by Debay’s method.

Next step was to construct clusters, get the distribution curve of scattering intensity of the sample (calculated by equation (1)) and do compare experimental and theoretical XRD patterns. A cluster was constructed by translating the unit cell of crystalline phase in three directions (a,b,c – the periods of unit cell). Cellulose Iβ, in which the unit cell consists of two cellulose chains rotated from each other by 180°, and cellulose Iα with one cellulose chain per unit cell was taken as the structure of different clusters. The values of the profile factor (calculated by equation (3)) for different sizes of clusters are shown in table 1.

Table 1. The profile factors for different sizes of clusters based on cellulose Iα and Iβ.

| A size of cluster | 1a×1b×1c | 2a×2b×2c | 3a×3b×3c | 3a×2b×2c |
|------------------|----------|----------|----------|----------|
| Cellulose Iβ     | Rp, %    | 19.7     | 24.0     | 37.1     | 29.3     |
| Cellulose Iα     | Rp, %    | 25.7     | 12.9     | 17.9     | 12.7     |

As can be seen from table 1, cellulose Iβ had the highest values of profile factor. It is due to the fact that there are two cellulose chains in unit cell that influence reflections of the diffraction pattern. The bigger the size of a cluster, the higher the intensity peaks. The cluster based on cellulose Iα allows us to reach significantly better results. So for the cluster of the size of 3a×2b×2c, the profile factor was minimal and equal to 12.7%. Consequently, the structure of short-range order crystalline-amorphous cellulose was characterized within the framework of the cellulose Iα model.

In order to improve fitting quality of experimental and theoretical XRD patterns, the initial cluster was divided into some layers. At the next step each layer was shifted in three directions (XYZ) and was rotated in plane of YZ taking into account the dispersion as to others layers. Operations of disorder are shown in figure 2b.

The initial cluster with the dimensions of 3a×2b×2c was divided into 3 layers with the size of 1a×2b×2c. Primary distance between layers along X was the period a of MCC unit cell. The rotation angle of second layer relative to the other ones was 180° to correspond the cellulose Iβ model of MCC.

As the consequence of modulating disorder parameters, it was found that the distances along X between the first and the second, and the third and the second layers were 7.34 Å and 7.80 Å, respectively. Rotation angle equaled -5° first layer as to the second one and 195° second layer as to the third layer. Shift of the first layer relative to the second and third layers along the direction of Y,Z was -0.5 Å and -1 Å, respectively. The comparison between experimental and theoretical XRD patterns is shown in figure 2a. The profile factor was Rp=11.4%.
Figure 2. (a) — the comparison between the distribution curves of scattering intensity for the sample (—) and theoretical XRD pattern for the disorder of cluster (—); (b) — the ways of disorder of layers from each other: 1 — the rotation operation; 2, 3, 4 — the shift operation along Y, Z, X.

Figure 2a shows that experimental XRD pattern of the one-hour milled cellulose can be described within the framework of a randomly disordered cluster model. The final cluster with the dimensions of 35 Å × 22 Å × 29 Å characterized the structure of short-range order. There were three layers consisting of disordered cellulose chains with the length of 21 Å in the cluster. The number of formula units in the cluster was 24. The cluster included 504 atoms.

4. Conclusion
Mechanical milling of MCC during one hour resulted in the cellulose amorphization as the amorphous domains prevailed on XRD patterns and crystalline degree reduced to 30%. The structure of short-range order of one-hour ground cellulose can be described by the cluster with the dimensions of 35 Å × 22 Å × 29 Å in which the three layers were shifted relative to each other on 7.34 Å and 7.80 Å, consequently. The rotate angles of the first layer as to the second one and the second layer as to the third layer were -5° and 195°. Thus, the structure of one-hour milled cellulose can be characterized by disordered cellulose chains with antiparallel orientation.

References
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