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Quantification of Crystallinity Change in Celluloses during Refining

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ABSTRACT

X-ray diffraction technique was used to quantify change of cellulose crystallinity during refining. XRD data confirmed that fiber wall delamination was caused by the structural conversion of celluloses which occurred in a liquid medium during refining. The quantified crystallinity of celluloses in pulp fibers was closely associated with the change of fiber wall delamination, which was defined by measurement of fiber wall thickness. In particular, it was well recognized that low intensity beating showed a better response in the change of crystallinity than high intensity one. The decrease of cellulose crystallinity during refining considerably enhanced the improvement of interfiber bonding ability of a dried sheet.

1. Introduction

Refining greatly contributes to improvement of fiber conformability including fiber flexibility and collapsibility. This is due to the fact that refining causes pulp fibers to be externally and internally fibrillated. During internal fibrillation, crystalline region of cellulose is converted to amorphous region, which leads to water absorption to internal structure of fibers. Such morphological change in fiber walls is visualized by microscopic techniques but quantification of crystallinity change in cellulose during refining is not readily done. The first attempt to characterize cellulose crystallinity was made by the observation of a distinct but diffuse X-ray scattering by cellulose fibers in the early 1920s.[1,2] FTIR and NMR have also been used to calculate cellulose crystallinity.[3,4] Since then, it has been made clear that the crystallizing ability of polymer materials is determined by the chemical constitution and conformation, the regularity of the molecular structure, the molecular flexibility and the presence of active groups able to form secondary interlinkages such as hydrogen bonds between neighbouring molecules.

Using the Raman spectroscopy, Atalla[5] showed that refining contributed to the structural modification of cellulose I to cellulose II. Mannan confirmed by X-ray diffractometer that mercerized jute fibers produced more amorphous content than cellulose I to cellulose II conversion.[6] These facts imply that modification of pulp fibers under hydration, mecerization and regeneration of cellulose generates a remarkably different X-ray diffraction pattern. Thus X-ray diffraction technique can be used to establish stan-

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dards for assessing a change of crystallinity during mechanical and chemical treatment on pulp fibers.

The increase in fiber flexibility during refining leads to improvement of interfiber bonding. This is caused by the conversion of crystalline region to amorphous region. Here crystalline degree of cellulose fibers modified during refining can be accessed by X-ray diffraction analysis. As refining proceeds, the relatively amorphous regions will be increased leading to allowance of easy penetration of water. It means that, when celluloses are considered as several ordered levels of orientation, a rather randomly ordered region is developed with refining. On this paper, such physico-chemical variation of celluloses was studied with X-ray diffractometer. Jayme *et al.*[1] suggested the integral method based on the ratio of the areas of crystalline to the total scattered intensity from XRD curve. In general, a classical method has been widely used to calculate crystallinity, *i.e.*, the ratio of the areas of crystalline to the one of amorphous areas under the XRD peak.

Finally, this work aimed to quantify change of cellulose crystallinity with XRD changed before and after refining and to study its role in interfiber bonding.

2. Materials and Methods

2.1 Beating

Canadian Howesound softwood bleached kraft pulp was beaten by the Valley beater following TAPPI T 248 standard method. The pulp fibers were beaten with the standard loads, 2.5 kg for low intensity and 5.6 kg for high intensity for the required wetness, 20, 40 and 70° SR, respectively. Handsheets for physical and optical testing were prepared and tested according to TAPPI T 248, T 494 and T 414 at a basis weight of 60 gm^{-2}.

2.2 Quantification of cellulose crystallinity

To quantify crystalline degree of celluloses used Bruker AXS Analytical X-ray system (GADDS, Germany) at the National Instru-mentation Centre for Environmental Management of Seoul National University in Korea (see Fig. 1).

The paper sheet (0.01~0.02 g, 10×10 mm) with a constant thickness was placed at the sample holder of GADDS system. The XRD peaks were analysed to calculate crystallinity value by EVA, GADDS operating software. The base point to define crystalline or amorphous regions was 2θ=18°, which was a purely amorphous one, and since there, the tangential line was drawn to a starting and ending point of cellulose crystal regions (see Fig. 2). The areas, C1 and C2, formed between the XRD curve and the tangential lines was regarded as the crystalline area and the amorphous area of celluloses, A, was defined as the one above the line connected to two contact points. Finally, to quantify crystalline degree of celluloses used the following equation:

Fig. 1. Bruker GADDS system configuration.

$$\text{Relative Crystallinity} = (C1+C2)/A \quad (1)$$

where,
C1 and C2=crystalline area
A=amorphous area.

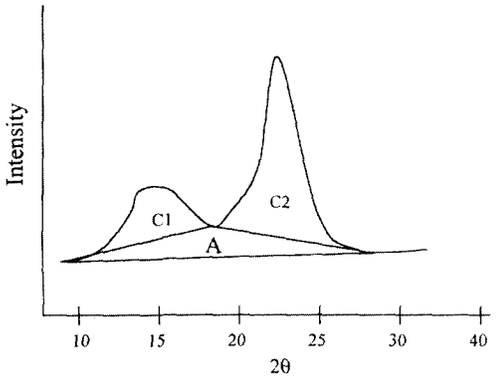


Fig. 2. Method for determination of X-ray crystallinity : A=amorphous area, C1+ C2=crystalline area.

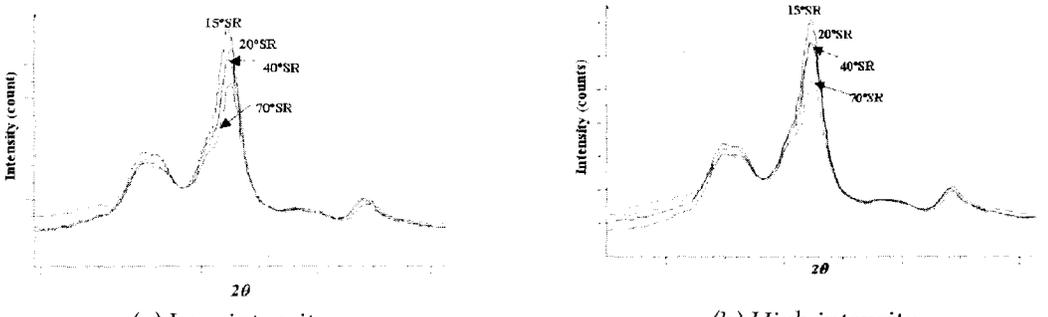
3. Results and Discussion

3.1 XRD peak of cellulose fibers

XRD curve patterns of celluloses changed before and after refining are displayed in Fig. 3. With mechanical treatments on fiber walls, the peak intensity showing cellulose crystallinity gradually decreased, irrespective of low or high refining loads. However, in order to quantify cellulose crystallinity through the XRD curves, the influence by the peak backgrounds should be removed using the equation 1.

Fig. 4, thus, shows the curves of the relative crystallinity at which the peak backgrounds were discarded by the equation. It clearly shows that the continuos impacts imparted on the pulp fibers between the refiner bars affected the reduction in the crystallinity of celluloses. Due the close relation of the mechanical impacts to internal fibrillation, the decrease in the cellulose crystallinity suggests the increase in the amorphous region allowing plain absorption of water into fiber walls. That is, this means that internal fibrillation of the pulp fibers contributed transformation of parallel chain structures (cellulose I) into anti-parallel chain ones (cellulose Ⅱ). Although most native woods seem to have a significant fraction of cellulose Ⅱ, it could be well understood that the structural conversion from cellulose I to cellulose Ⅱ occurred during refining.

In relation to refining intensity, high inten-



(a) Low intensity (b) High intensity

Fig. 3. Typical XRD curves of cellulose in pulp fibers refined under low and high intensity.

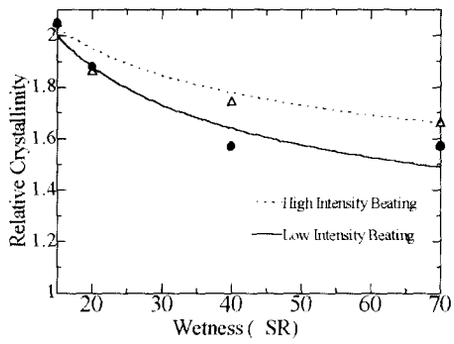


Fig. 4. Change of relative crystallinity of celluloses during refining.

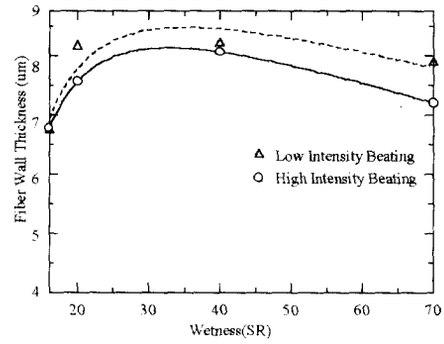


Fig. 5. Change of fiber wall thickness during refining: fiber wall thickness was measured with cross-sectional images obtained by CLSM and image analysis techniques (KS400).

sity refining showed better preservability of cellulose crystallinity than low intensity one. It means that high intensity refining had a greater propensity in shortening pulp fibers rather than in deriving internal fibrillation (see Table 1). As a result, lots of fiber walls under high intensity refining were kept less damaged compared to those under low intensity beating. This was confirmed by the CLSM and image analysis work,[7, 8] which proved that abrasion of pulp fibers between refiner bars developed lateral cleavage of fiber walls, leading to breakage of crystalline regions in celluloses. Thus the conversion from some crystalline regions to the amorphous ones in celluloses caused water to penetrate into fiber walls readily. Fig. 5 is a direct evidence showing the increase in fiber wall thickness of pulp fibers by uptaking water into amorphous areas.

Finally, it was physico-chemically concluded by XRD that fiber wall delamination was led by destruction of cellulose crystallinity during refining. Therefore it seems quite plausible to say that mechanical impacts on pulp fibers in water makes cellulose substances separated at the elementary fibrillar level.

Fig. 6 shows a relation of cellulose crystallinity with fiber wall thickness. It can be clearly seen that the decrease in crystallinity led to the increase in fiber wall thickness. However, despite the continous decrease in crystallinity, fiber wall thickness was dramatically decreased. If mechanical impacts are continuously imparted onto fiber walls

Table 1. Change of length-weighted mean fiber length during refining

Wetness (°SR)	Low intensity beating (mm)	High intensity beating (mm)
13	2.59	2.59
20	1.99	1.64
40	1.60	1.14
70	1.33	0.72

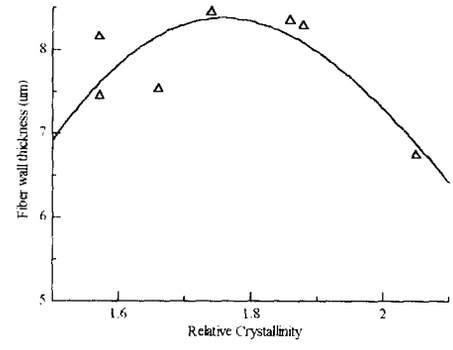


Fig. 6. Relationship of cellulose crystallinity with fiber wall thickness.

Fig. 7. CLSM images showing destruction of fiber walls after excessive refining.[5]

beyond tolerable limit of intrafiber bonding, parts of fiber walls become removed from parental fiber walls. This phenomenon was well observed by CLSM works,[7,8] as shown in Fig. 7. It explains why, in spite of the decrease in crystallinity, the fiber wall thickness was reduced after the critical value. Finally, it must be kept in mind that the decrease in cellulose crystallinity during refining does not always mean the increase in fiber wall thickness.

3.2 Effect of cellulose crystallinity on interfiber bonding in a sheet

Thus refining has been used as a compulsory tool to endow flexibility and plasticity of fibers during stock preparation. When the decrease in cellulose crystallinity is considered as the increase in fiber conformability—flexibility and collapsibility, a dry strength of paper is increased by increasing the number of fiber-to-fiber bonds in a fiber network. Fig. 8 shows that the flexibility is an excellent contributor to improve bonding ability between neighbouring fibers. In relation to refining intensity, low intensity exerted much better response in development of interfiber bonding on the decrease in crystallinity than high one. As noted in quantification of fiber wall delamination using CLSM and image analysis work, this is closely associated with greater wall delamination of fibers by low intensity beating.

Although the successive reduction in cellulose crystallinity during refining is profitable to development of fiber conformability, the resistance force of fibers to tensile stress may be also reversely affected due to the decrease in fiber wall thickness. When paper is under tensile loads, fibers must absorb the tensile stress to resist against bonding failure. Otherwise, the interfiber bonding will be readily broken under stress. That is, the thinner the fiber walls, the weaker the ability to endure the tensile stress. As shown in Fig. 8, the ability of interfiber bonding decreased just after the maximum bonding as the cellulose crystallinity was continuously reduced. It should

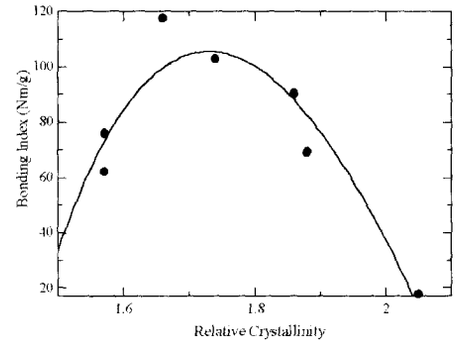


Fig. 8. Effect of cellulose crystallinity on fiber bonding index.

be remembered that, only when a shape of fiber wall is kept to an extent, the decrease in cellulose crystallinity could play a great role in fiber-to-fiber bonding.

4. Conclusions

It became clear that the cellulose fractions in pulp fibers which underwent structural conversion during refining was swollen at the molecular level in order for the transformation to take place. Such conversion was quantified by XRD and it disclosed that the decrease in cellulose crystallinity was closely related to the increase in fiber wall fibrillation. Also the reduction in crystallinity allowed better interfiber bonding due to the improvement of fiber conformability. With relation to refining intensity, low intensity refining showed better response on the decrease of crystallinity than high intensity. Finally, the conclusion stems from the fact that fiber wall delamination is a micro-structural conversion of celluloses.

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Literature Cited

1. Krassig, H. A., Cellulose: Structure, Accessibility and Reactivity, Gordon and Breach Science Publishers, 1993.
2. Sarko, A., "Recent X-ray Crystallographic Studies of Celluloses", Cellulose, Structure, Modification and Hydrolysis edited by Young, R. A & Rowel, R. M., John Wiley & Sons, 1986.
3. Marrinan, H. and Mann, J., J. Poly. Sci., 21:301 (1956).
4. Hirai, A. and Kitamaru, 186th National meeting, American Chemical Society, Washington, D. C., Sept, 1983.
5. Atalla, R. H., Energy Absorption by Swelling of Crystalline Regions during Refining, IPC International Symposium on fundamental concepts of refining, Sept. 16-18, 1980.
6. Manna, Kh. M., Polymer, 34(12):2485-2487 (1993).
7. Kim, C-H, Use of Microscopy Techniques to Study Refining Effects on Pulp Fibers, UMIST Ph.D. Thesis.
8. Park, J-M, Kim, C-H, Wadhams, K. R., Kim, S-H, Analysis of Fiber Wall Thickness to Study Mechanisms of Refining and Hornification by CLSM, Pre-Symposium of the 10th ISWPC held in Kwangju, Korea, May, 1999.