An Orientation Behavior of Microfibrillated Cellulose Crystallites

Byongfa CHUN and Keizo OKAMURA

ミクロフィブリレーテッドセルロース クリスタリットの配向挙動

全　　炳　和・岡　村　圭　造

Résumé

Microfibrillated cellulose (MFC) is a new form of expanded high-volume cellulose obtained by a homogenization process. When a cellulose sheet was formed from MFC, no uniplanar orientation of cellulose I crystallites was observed. However, if MFC was mercerized, the resulting cellulose II sheet clearly showed a uniplanar orientation parallel to (101) crystallite plane. Besides, the higher polarity of solvent was used, the higher orientation took place. This phenomenon is interpreted as follows. The surface activity of cellulose crystallites parallel to (101) plane is higher than those of other planes, and on drying the crystallites orient preferentially parallel to (101) plane. Cellulose I of MFC did not show any preferential orientation simply because the surface activity of (101) plane would not be different from those of other planes.

要　　旨

ミクロフィブリレーテッドセルロース (MFC) は均質化プロセスによって得られる，新しいタイプの容積の大きいセルロースである。この MFC からシートを形成すると，セルロース I のクリスタリットの単面配向はみられなかった。しかしながら，MFC をマーセル化すると，マーセル化により生じたセルロース II のシートは明らかに (101) 結晶面に平行な単面配向を示した。さらに，シート形成の際に，より極性の大きい溶媒を使用すれば，より高度な配向性がみられた。この現象は以下の様に解釈できる。すなわち，セルロースクリスタリットの(101)面に平行な表面活性は，他の面よりも大きく，従って乾燥に際してクリスタットは(101)面に平行に選択的に配向する。セルロース I の MFC が選択的配向を示さないのは，単に(101)面の表面活性が，他の面の表面活性とあまり変らないことによるのであろう。

1.　Introduction

It has been widely recognized that (101) crystal plane of cellulose crystallites tends to orient uniplanarily parallel to the film surface whenever the cellulose crystallites are formed as a film.

This phenomenon has been found, for example, in the cell wall of *Valonia*[1,2], other green algae[3,4] and even regenerated cellulose film[5]. This selective uniplanar orientation was found in the microfibrillar particles of ramie and cotton fibers which were formed by hydrolysis with sulfuric acid[6].

The purpose of the present work is to study an orientation behavior of "microfibrillated cellulose (MFC)" crystallites which were claimed to expose smaller fibrils and microfibrils by repeated high pressure homogenization process[7]. The orientation behavior of MFC was studied on MFC *per se* and on mercerized MFC.

2. Experimental

2.1. MFC samples

A commercially available MFC for food thickening was used in this study. The cellulose raw material is a softwood pulp derived from sulfite pulping process. The MFC has the appearance and properties of a gel, and the solid content was 2.29 wt%. After diluting with distilled water, MFC was observed with a transmission microscope without further treatment.

2.2. Hydrolysis

With the intension of further defibration of MFC, 87 g of MFC gel (2.29 wt%) was mixed with 113 ml of 5.0 N aqueous H_2SO_4 solution. The acid concentration became 2.8 N, and the mixture was hydrolyzed at boiling temperature for either 3 or 6 hours. When 87 g of MFC was mixed with 113 ml of 10.0 N H_2SO_4 solution, the concentration became 5.7 N, and the mixture was hydrolyzed at 50°C for either 60 or 144 hours. After hydrolysis the sulfuric acid was removed by dialyzing against distilled water.

2.3. Mercerization

For mercerization of MFC, 119 g of MFC gel (2.29 wt%) was mixed with 305 g of 37.5% aqueous NaOH solution. The alkali concentration became 25 wt%. After leaving overnight at room temperature, the mixture was poured into 5 liter of distilled water. The flocculated solid of the mercerized MFC was collected by sedimentation, and washed thoroughly with distilled water. The mercerized MFC was washed further with a dilute aqueous acetic acid solution to completely remove remaining alkali in fibrils, and thoroughly washed with distilled water.

The mercerized MFC was homogenized in a laboratory-scale homogenizer, since, when mercerized, the MFC lost its dispersibility. After homogenization the mercerized MFC restored the original dispersibility.

2.4 Sheet formation

The untreated and hydrolyzed MFC suspension was poured onto a parafilm placed on a watch glass and dried in a desiccator over phosphorous pentaoxide. The water in the mercerized MFC was replaced with methyl alcohol, ethyl alcohol and finally with benzene. The mercerized MFC suspended in benzene was similarly poured on a glass plate and vacuum dried. In either case, a sheet-like MFC was obtained.

2.5 X-ray diffraction

X-ray diffraction was recorded on a Fuji Rx X-ray film in a flat-film camera with a vacuum

device. A Shimadzu compax X-ray generator was used with nickel filtered CuKα radiation generated at 40 kV, 20 mA.

2.6 Transmission electron microscopy

All the samples were negatively stained with 2% uranyl acetate, and were supported on a thin film of uranyl acetate suspended across a hole in a triafol microgrid. The specimens were observed under a JEM-100C transmission electron microscope operated at 100 kV.

3. Results and Discussion

3.1 Transmission electron microscopy

Figure 1 (a)–(c) are the transmission electron micrographs of untreated MFC. There is seen wide range of width distribution from the wide fibril of 1 μm width (as seen in Fig. 1 (a))
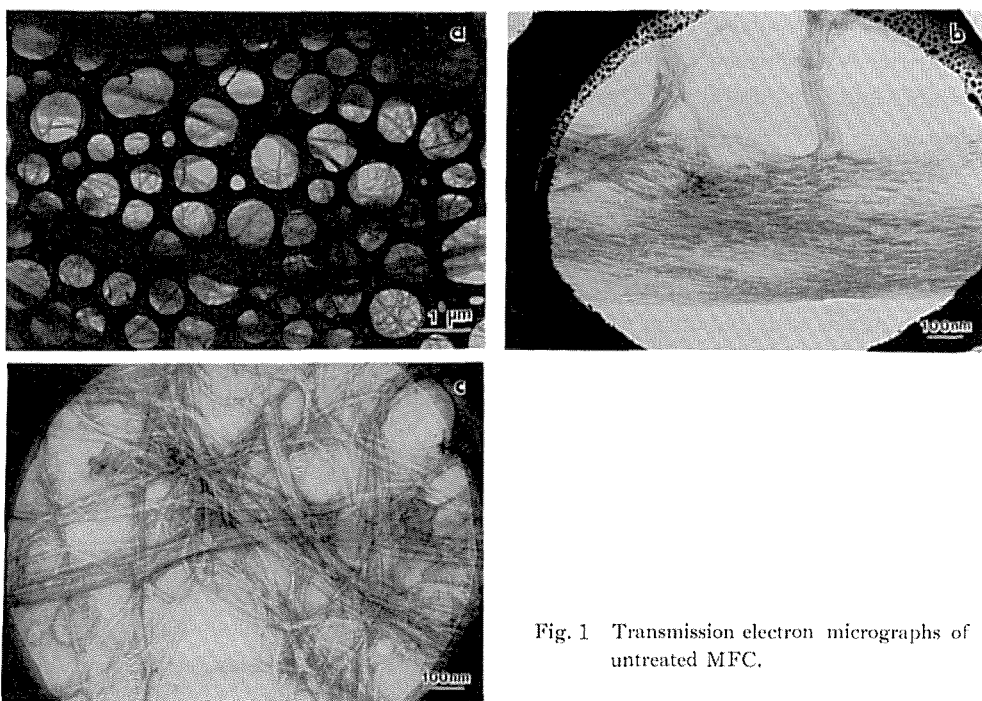
Fig. 1 Transmission electron micrographs of untreated MFC.
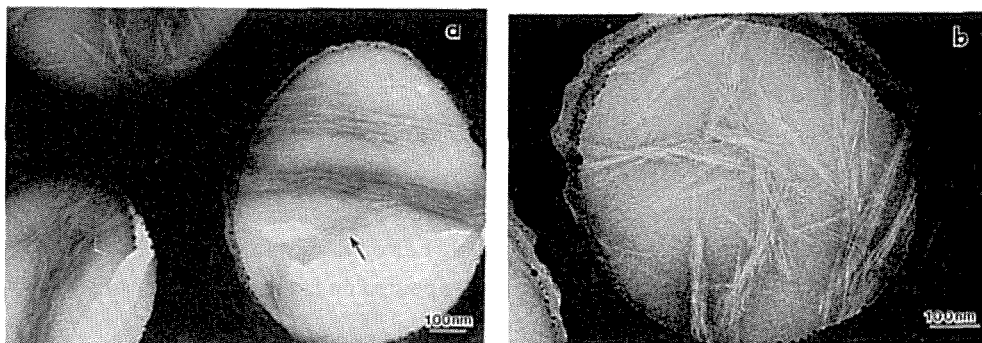
Fig. 2 Transmission electron micrographs of H₂SO₄ hydrolyzed MFC: (a) 5.7 N H₂SO₄, 50°C, 60 hr., The arrow indicates shortened fibril. (b) 5.7 N H₂SO₄, 50°C, 144 hr.
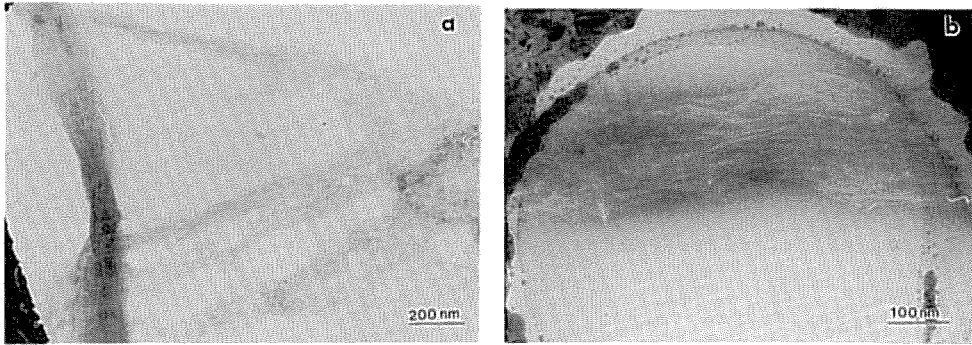
Fig. 5   X-ray diagrams of MFC sheet.   The X-ray beam was radiated parallel to sheet surface, and the fiber axis horizontal: (a) MFC (cellulose I), (b) mercerized MFC (cellulose II).

more clearly observed in Fig. 3 (b).   From these photographs, it was found that the mercerized MFC showed the fragmented cellulose crystallites of which morphology is different from that of the untreated MFC.
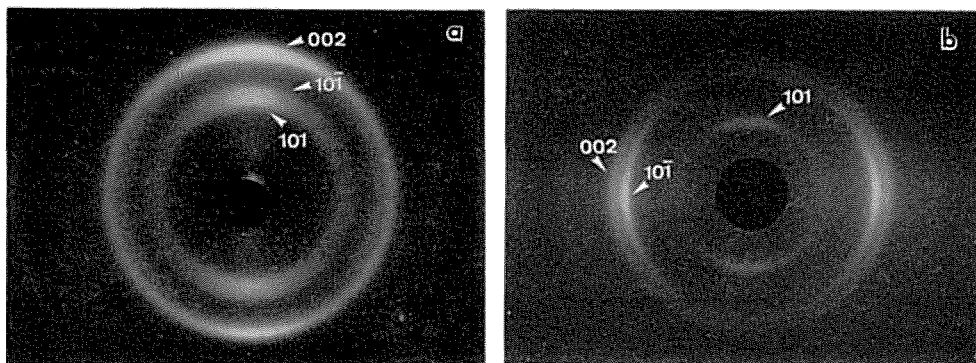
3.2   X-ray diffraction

Figure 4 illustrates a schematic representations of reciprocal lattice and X-ray diagrams when (101) uniplanar orientation exists within the cellulose crystallites.   When X-ray beam is radiated both perpendicular and parallel to the sheet surface (Fig. 4(a)), the resulting reciprocal pole direction only coincides with the tangential of a sphere of reflection in which X-ray beam is radiated parallel to sheet surface, and this is illustrated in Fig. 4 (a).   As the X-ray diagrams this uniplanar orientation should be as shown in Fig. 4 (b) and (c).   When X-ray beam is radiated perpendicular to the sheet surface, (101) plane would not be recorded on the X-ray film (Fig. 4 (b)).   And when X-ray beam is radiated parallel to sheet surface, the resulting X-ray diagram would be as shown in Fig. 4 (c): (101) diffraction spots appear on the vertical direction, and (10$\bar{1}$) spots on the horizontal direction.

Figure 5 (a) is the X-ray diagram of the acid hydrolyzed MFC (2.8 N H$_2$SO$_4$, 100°C, 6 hrs) in which X-ray beam was radiated parallel to the sheet surface.   The diagram suggests that there was no preferable orientation in the acid hydrolyzed MFC.

However, once MFC is mercerized, the uniplanar orientation parallel to (101) is clearly seen as shown in Figure 5 (b): two pairs of strong vertical (101) diffraction and horizontal (10$\bar{1}$) diffraction spots were observed with some 90° angle.   This uniplanar orientation was confirmed with an X-ray diagram when X-ray beam was radiated perpendicular to the sheet surface of the mercerized MFC.   When we compare the transmission electron micrographs of the untreated MFC (Fig. 1 (b)) and the mercerized MFC (Fig. 3 (b)), the appearance of fibril as well as bundle of fibrils is very similar, though the former is more rigid than the latter.   It is an amazing fact that the individual cellulose crystallite rotates and tends to align parallel to (101) plane on mercerization without accompanying a drastic morphological changes, since, after mercerization, MFC was not subjected to any homogenization process.   The densitometer traces of the diffractogram of mercerized MFC is shown in Fig. 6.   The (101) diffraction which appeared in the powder diagram (no orientation) is now missing in the diagram of the sheet.

The degree of (101) planarity was measured by estimating the intensity of meridional (101) plane (Fig. 5 (b)) with respect to azimuthal angle from the meridian (Figs. 7–9). In these figures the azimuthal intensity is plotted as the relative values of the largest meridional intensity. The more the cellulose crystallites orient uniplanarily, the narrower azimuthal intensity dis-
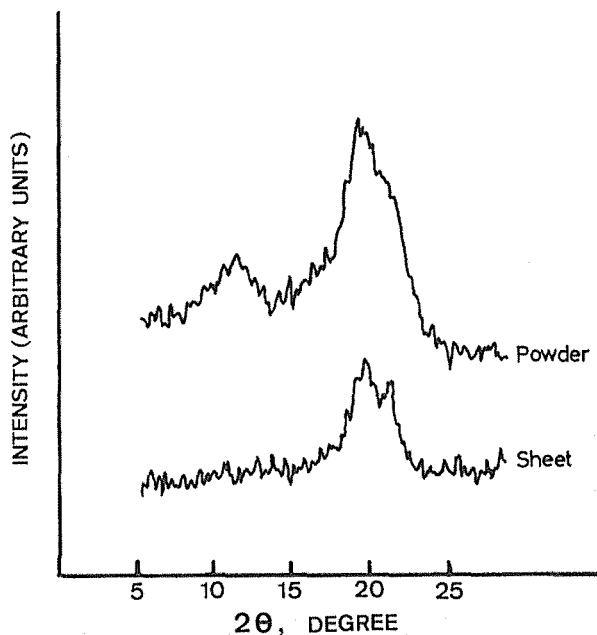

Fig. 6 Densitometer trace of X-ray diffraction patterns of mercerized MFC powder and mercerized MFC sheet. The X-ray beam was radiated perpendicular to the sheet surface.
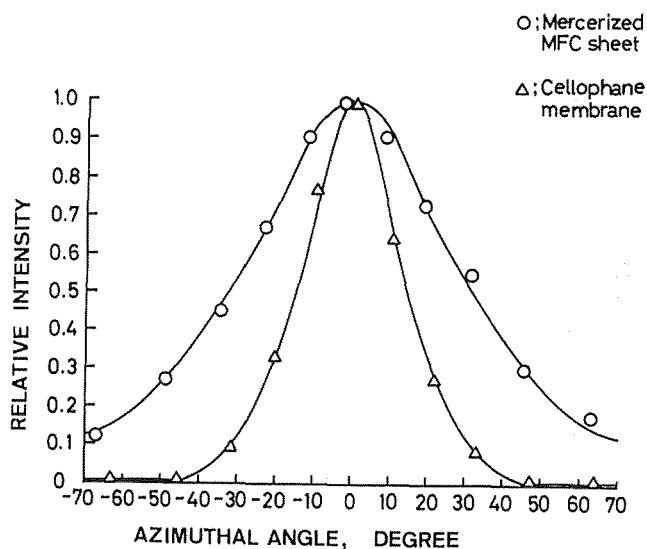

Fig. 7 Comparison of degree of planarity of MFC sheet and a commercial cellophane. The intensity is expressed as fraction relative to the highest value, and is plotted against azimuthal angle.

tribution is expected. In Fig. 7 the degree of planarity of mercerized MFC sheet, which is dried from water medium, is compared with a commercial cellophane. As expected the mercerized MFC showed wider distribution than a commercial cellophane: i.e. the half width of the former was about 63° while that of cellophane was 30°.

The degree of (101) planarity was also examined in terms of polarity of solvents. In Fig. 8 the degree of planarity of mercerized MFC was expressed as relative intensity with three different polar solvents from which the MFC sheet was formed. The higher polarity of the
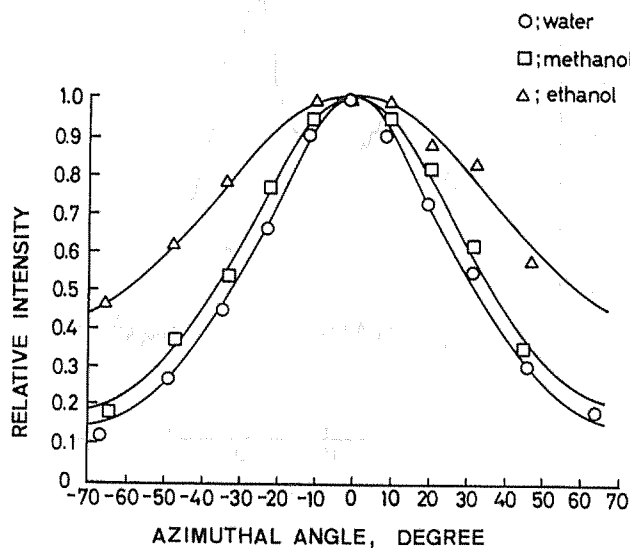
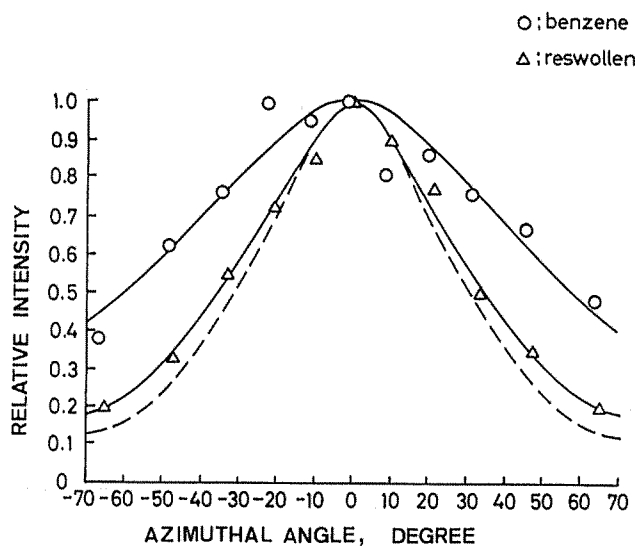Fig. 8 Dependency of degree of planarity of mercerized MFC on solvent replaced.

Fig. 9 Recovery of planarity of mercerized MFC. The planarity of MFC as mercerized (dashed line) loses some of planarity upon the replacement with benzene, but recovers its original planarity when benzene is replaced again by water.

solvent was used, the higher degree of planarity resulted: among the three polar solvents used, the order of planarity was water>methyl alcohol>ethyl alcohol. This is exactly the same order of dielectric constants of the solvents. Thus, the oreintation behavior of the mercerized MFC is greatly influenced by what solvent the MFC is replaced before the sheet formation.

Figure 9 shows the recovery of planarity of the mercerized MFC. When the mercerized MFC sheet was dried from water, the intensity profile of the sheet was as expressed as the dashed line. If water in the mercerized MFC was replaced with benzene and the sheet was dried from benzene, the intensity profile showed wider distribution. However, if the benzene replaced MFC sheet was again swollen with water, the intensity profile recovered its original distribution of the mercerized MFC.

The present work is summarized as the followings. When the cellulose sheet was formed with MFC *per se*, no preferential orientation was observed, while the mercerized MFC (cellulose II) clearly showed a uniplanar orientation parallel to (101) plane. The uniplanar orientation was observed in other polar solvents, such as methyl alcohol and ethyl alcohol, but not in non-polar solvent such as benzene. However, when the mercerized cellulose sheet which was dried from benzene was reswollen with water, the resulting sheet recovered the uniplanar orientation tendency. Thus the orientation behavior heavily depends upon the polarity of the solvents. These phenomena can be interpreted as follows: in cellulose II, the surface activity of (101) face of cellulose crystallites to the polar solvents is higher than those of other faces. Upon drying these active faces align each other, and degree of alignment is very much dependent upon the polarity of the solvent. In cellulose I (untreated MFC), such alignment effect is not noticed, and the surface activity of (101) face is in the same magnitude of the other faces.

Acknowledgement

4. References

1) Preston, R. D. and Astbury, W. T.: The structure of the wall of the green alga *Valonia ventricosa*. Proc. Roy. Soc. B**122**: 76, (1937)

2) Tanaka, F. and Okamura, K.: Measurement of pole figures and orientation functions for *Valonia* cellulose. J. Polym. Sci., Polym. Phys. Ed. **15**: 897–906, (1977)

3) Frei, E. and Preston, R. D.: Cell wall organization and wall growth in the filamentous green algae *Cladophora* and *Chaetomorpha*. Proc. Roy. Soc. London Ser. B**154**: 70–94, (1961)

4) Nieduszynski, A. and Atkins, E. D. T.: Preliminary investigation of algal cellulose. I. X-ray intensity data. Biochim. et Biophy. Acta **222**: 109–118, (1970)

5) Takahara, H., Nomura, S., Kawai, H., Yamaguchi, Y., Okazaki, K. and Fukushima, A.: Dimensional stability of regenerated cellulose film in relation to orientations of crystalline and noncrystalline phases. J. Polym. Sci. Part A-2 **6**: 197–221, (1968)

6) Mukherjee, S. M. and Woods, H. J.: X-ray and electron microscope studies of the degradation of cellulose by sulfuric acid. Biochem. et Biophy. Acta **10**: 499–511, (1953)

7) Herrick, F. W., Casebier, R. L., Hamilton, J. K. and Sandberg, K. R.: Microfibrillated cellulose- Morphology and accessibility. J. Appl. Polym. Sci., Appl. Polym. Symp. **37**: 797–813, (1983)