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Structural Investigation on Aqueous Suspension of Microcrystalline Cellulose

M. Sugiyama, H. Iijima*, K. Hara**, A. Nakamura***[1], N. Hiramatsu***[2] and Y. Maeda****

Graduate School of Science, Kyushu University, Fukuoka, 812-8581 Japan
Fax: 81-92-642-2553, e-mail: sugi8scp@mbox.nc.kyushu-u.ac.jp
*Chemical Technology Department IV, Asahi Chemical Industry Co., Ltd., Nobeoka, Miyazaki 882-0847, Japan
Fax: 81-545-62-3189, e-mail: a7910878@ut.asahi-kasei.co.jp
**Graduate School of Engineering, Kyushu University, Fukuoka, 812-8581 Japan
Fax: 81-92-633-6958, e-mail: haratap@mbox.nc.kyushu-u.ac.jp
***Department of Applied Physics, Fukuoka University, Fukuoka, 814-0180, Japan
[1]Fax: 81-92-865-6030, e-mail: nakamura@ssat.fukuoka-u.ac.jp
[2]Fax: 81-92-865-6030, e-mail: hiramats@ssat.fukuoka-u.ac.jp
****Kansai Gaidai University, Hirakata, Osaka, 573-1001, Japan
Fax: 81-72-855-5534, e-mail: yumaeda@hkg.odn.ne.jp

D_2O aqueous suspensions of microcrystalline cellulose particles with the mean diameters of 3 and 0.5 μm were investigated by the small-angle neutron scattering and the ultra small-angle neutron scattering methods. It has been revealed that the fractal-like structure with the dimension of 2.2 in both microcrystalline cellulose particles was observed and maintained in the region from 6×10^{-3} up to 1.0×10^{1} μm. Since the maximum size, 1.0×10^{1} μm, is larger than that of both microcrystalline cellulose particles, the microcrystalline cellulose particles aggregate in the aqueous suspension keeping the fractal structure.
Key words : microcrystalline cellulose, SANS, USANS, fractal

1 INTRODUCTION

In recent years, a lot of attention has been devoted to natural materials since they are expected to be harmless to our environment. Under such a circumstance, many researchers have attempted to add a new functional character to them by means of controlling their structures, purifying the material and so on. A microcrystalline cellulose (MCC), which has been recently developed by Asahi Chemical Industry Co.,Ltd., is typical one of these materials. One of the remarkable features of this material is its "*smallness*" ; the average size of the MCC particle is controlled to be around 3 μm whereas the minimum size of the usual cellulose particle used to be around 10 μm.

Firstly the inner structure of the MCC particles is a subject of the investigation. It is well known that the cellulose usually consists of crystalline and amorphous regions because the degree of crystallinity cannot reach 100%. For example, the cotton composed of cellulose fibers has a fringed micelle structure ;[1] the crystalline domain (fringed micelle) is dispersed in the amorphous matrix. Its elasticity and water absorptive power are due to this complex structure. It was supposed that the MCC particle also has a fringed micelle structure since it is made by the hydrolysis of wood pulp. In our previous work, we revealed that the MCC particle has a fractal-like structure with the dimension of 2.2 in the scale range between 10 nm and 100 nm.[2] This result means that the fringed micelles exhibit a fractal structure in the MCC particle. However, the maximum and minimum sizes of the fractal structure have not been clarified yet.

Another interesting feature of MCC is the temperature dependence of the viscosity of its aqueous suspension. In the temperature range between 20°C and 80°C the viscosity of the aqueous suspension is almost constant whereas that of other food additives drastically becomes lower with increasing temperature.[3] This feature gives MCC an opportunity that MCC could be extensively used as a food additive. From the viewpoint of the fundamental science, it is also interesting to study

the relation between the structure and the viscosity in the aqueous suspension of the MCC particles.

Small-angle neutron scattering (SANS) and ultra small-angle neutron scattering (USANS) methods are powerful tools to observe the structure in the scales from 0.001 to 0.1 μm and from 0.1 to 10 μm, respectively. The advantage of a neutron beam as a probe is its high transmission for materials which do not contain special atoms, such as Li, B, Gd, Cd and so on. Therefore, we can easily observe the intra- and inter-particle structure of MCC in the aqueous suspension by the SANS and USANS methods. In addition, we can reduce the incoherent scattering from hydrogen atoms by replacing with deuterium atoms.

2 EXPERIMENTAL

2.1 Sample

Two aqueous suspension of the MCC particles with the average sizes of 3 μm (FP30) and 0.5 μm (FP05) were specially supplied by Asahi Chemical Industry Co., Ltd, Japan for this study. The size of the MCC particles in the aqueous suspension was measured with Laser Scattering Distribution Analyzer, LA-910 (HORIBA Ltd.). In order to reduce the incoherent scattering from the hydrogen atoms, the solvent was exchanged with D_2O. The exchange of H_2O for D_2O was carried out as follows. At first, the H_2O suspension was separated into the dilute and condensed MCC parts by centrifuge. Next, the condensed MCC part was dissolved in D_2O and the separation was repeated again. Then, the re-condensed MCC part was re-dissolved in D_2O. In our study, the concentration of both D_2O suspensions is 10 wt%.

2.2 SANS and USANS experiments

SANS experiments were carried out with KUR-SANS spectrometer installed at Kyoto University Reactor, Kumatori, Osaka, Japan and USANS experiments were performed with ULS spectrometer installed at JRR-3M in the Japan Atomic Energy Research Institute, Tokai, Japan. The ULS spectrometer is a Bonse-Hart type camera with two Si crystals for collimating the incident neutron beam. The observed scattering vector q was set to be in the ranges of 1×10^{-2} to 1.2×10^{-1} Å^{-1} by the KUR-SANS spectrometer and 6×10^{-5} to 3×10^{-3} Å^{-1} by the ULS spectrometers. All scattering intensities were observed at room temperature.

3 SANS AND USANS FROM A FRACTAL OBJECT

A small angle scattering intensity $I(\boldsymbol{q})$ is given by[4]

$$I(\boldsymbol{q}) = \left| \int d\boldsymbol{r}\rho(\boldsymbol{r}) \exp(i\boldsymbol{q}\cdot\boldsymbol{r}) \right|^2, \quad (1)$$

where $\rho(\boldsymbol{r})$ is a scattering length density, and $\boldsymbol{r}$ and $\boldsymbol{q}$ are position and scattering vectors, respectively. With $\boldsymbol{R} \equiv \boldsymbol{r}' - \boldsymbol{r}$, this equation is expressed by

$$I(\boldsymbol{q}) = \int d\boldsymbol{R}\{\int d\boldsymbol{r}\rho(\boldsymbol{r})\rho(\boldsymbol{R}+\boldsymbol{r})\}\exp(i\boldsymbol{q}\cdot\boldsymbol{R}). \quad (2)$$

Next, we define fluctuation of the scattering length density,

$$\delta\rho(\boldsymbol{r}) \equiv \rho(\boldsymbol{r}) - \bar{\rho}, \quad (3)$$

where $\bar{\rho}$ is the average of the scattering length density. The second integral term in Eq. 2 is given by

$$\int d\boldsymbol{r}\rho(\boldsymbol{r})\rho(\boldsymbol{R}+\boldsymbol{r}) = < \delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{R}+\boldsymbol{r}) > + \bar{\rho}^2, \quad (4)$$

where $<\ >$ indicates statistical average and then $< \delta\rho(\boldsymbol{r}) > = < \delta\rho(\boldsymbol{R}+\boldsymbol{r}) > = 0$. The first term in the right side of Eq. 4 is a correlation function $C(\boldsymbol{R})$ of the fluctuation of the scattering length density. Substituting Eq. 4 into Eq. 2 and using $C(\boldsymbol{R})$, we obtain

$$I(\boldsymbol{q}) = \int d\boldsymbol{R}C(\boldsymbol{R})\exp(i\boldsymbol{q}\cdot\boldsymbol{R}) + \bar{\rho}^2\delta(\boldsymbol{q}). \quad (5)$$

Since the last term in right side is zero except for $\boldsymbol{q} = 0$, we can ignore it. Therefore, we can obtain the scattering intensity in $q \neq 0$,

$$I(\boldsymbol{q}) = \int d\boldsymbol{R}C(\boldsymbol{R})\exp(i\boldsymbol{q}\cdot\boldsymbol{R}). \quad (6)$$

This equation means that the scattering intensity is Fourier transform of the correlation function of the fluctuation of the scattering length density.

Here, we assume the sample has no finite correlation length but a self-similar geometry, what is called fractal. The correlation function of the fractal is given by[5,6]

$$C(r) \sim r^{-\alpha}, \quad (7)$$

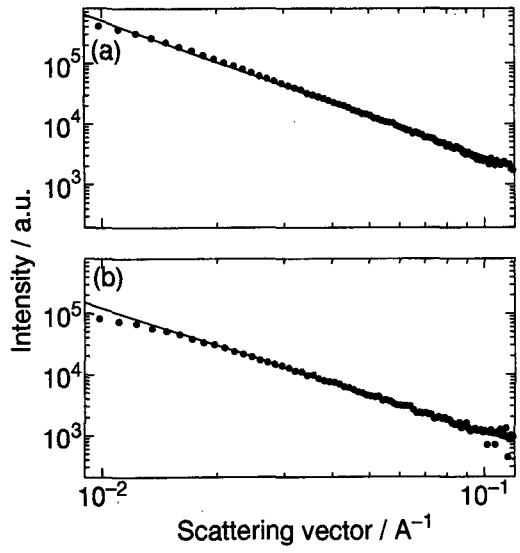

Fig. 1. SANS profiles of (a) FP30 (the average size 3 μm) and (b) FP05 (the average size 0.5 μm). The straight lines indicate the results of the least-square fit by Eq. 8.

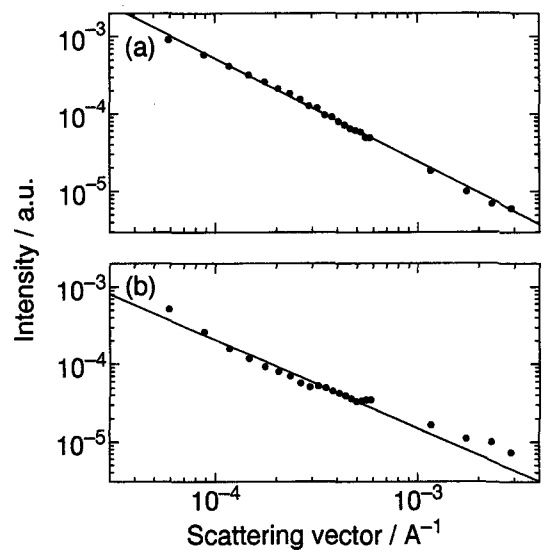

Fig. 2. USANS profiles of (a) FP30 (the average size 3 μm) and (b) FP05 (the average size 0.5 μm). The straight lines indicate the results of the least-square fit by Eq. 8.

where $\alpha = d - D$, and d and D are spatial and fractal dimensions, respectively. Substituting Eq. 7 into Eq. 6, we obtain

$$I(q) \sim q^{-D} \quad (d = 3). \tag{8}$$

When a scattering object has a fractal structure, the q dependence of the scattering intensity is depicted by a straight line in a double logarithmic plot. Accordingly, we can calculate the fractal dimension D from the inclination of the straight line.

4 RESULTS AND DISCUSSION

Let us begin with the inner structure of the MCC particles. The scattering intensities of FP30 and FP05 measured with KUR-SANS spectrometer are shown in Fig. 1 (a) and (b), respectively. The intense small-angle scatterings were observed from both samples. Since the scale observed in the SANS experiments corresponds to the range between 6 and 60 nm, which is smaller than the size of the MCC particles, the intense small-angle scattering means that the fluctuation of the scattering length density exists in both of the MCC particles. This fluctuation could be explained by the contrast in the scattering lengths between the crystalline and amorphous regions.

As indicated by the straight lines in Fig. 1 (a) and (b), these intense scatterings are well fit by Eq. 8. The inclinations of both the straight lines are almost same and are found to be 2.2, which agrees with our previous result obtained from an H_2O suspension of FP30.[2] Here, we can say that both of the MCC particles have same fractal structure with a dimension of 2.2 in this scale range. It implies that the MCC particle in FP05 could be a broken tip of the large MCC particle in FP30.

As shown in Fig. 1 (a) and (b), the observed scattering intensities satisfy Eq. 8 up to around 0.1 Å^{-1}. Therefore, the size of the unit cluster having the fractal structure is smaller than 6 nm.

In order to make clear the maximum size of the internal fractal structure and/or the external complex matrix structure composed of the MCC particles, we performed the USANS experiment. Figure 2 shows the USANS profiles of FP30 and FP05 in the double-logarithmic scale. The q dependence of both scattering intensities obeyed a power law with the index of -1.3. It has been known that an observed index added to one is a true index because of the smearing effect by the shape of the incident beam profile (length×width=2×1 cm^2) in the ULS spectrometer.[7] Therefore, the fractal dimension in this q-range is about 2.3 and almost same with the dimension observed in the SANS experiments.

As shown in Fig. 2 (a) and (b), the smallest

q value is found to be 6×10^{-5} Å^{-1} corresponding to around 10 μm in the real space. This is slightly larger than the average size of the MCC particle in FP30. Therefore, we might say that the aggregation occurs in the FP30 suspension. On the other hands, the situation becomes clearer in the FP05 suspension. For the MCC particle in FP05, the scale of 10 μm is 20 times larger than its size. Therefore, the MCC particles in FP05 aggregate each other setting up a fractal structure. It means that an attractive interaction exists between the MCC particles. The temperature dependence of the viscosity of the FP05 suspension is same as that of the FP30 suspension.[8] Accordingly, we suppose that the attractive interaction induces the particular feature of viscosity of the suspension of the MCC particles. More detailed experiments are now in progress.

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