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Characterization of Dispersion Condition of Colloidal Particles in Anisotropic Shape by Means of Dynamic Light Scattering and Ultrasonic Induced Birefringence Methods

動的光散乱法と超音波誘起複屈折法による異方性コロイド粒子の分散状態の評価

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1. Introduction

It is important thar to charaterize size and shape, dispersion condition of collodal particles in the colloid technology. The dynamic light scattering (DLS) method has been used to obtain the stokes radius of particles is estimated from translational diffusion constant.[1,2] However, no information of the shape of particles cannot be obtained from the DLS methods. On the other hand, ultrasonically induced birefringence (UIB) method enable us to obtain information of anisotorpy of the paricle though the reorientational relaxation time. The aim of this study is to characterize the dispersion condision of collidal particle in anisotropic shape using the both DLS and UIB methods. In this sudy, we carried out both measurements in rodlike titanium oxide (TiO_2) paticles in aqueous solutions. We investigate temporal change in dipersion condition of TiO_2 paticles under high power sonication using the DLS and UIB methods.

2. Experimental

Titanium oxide (TiO_2) powder in rod like shape (Sample code: FTL-100) was provided by Ishihara Techno Corporation. Sodium hexametaphosphate $(NaPO_3)_6$, which was used as dispersing agent, is purchased from Nacalai Tesque, inc. It was used without purification. Concentration of aqueous solution of the $(NaPO_3)_6$ was 2 wt%. Volume fraction of TiO_2 was about 2.5×10^{-7}. According to the catalogue provided from the manufacturer, mean length of the TiO_2 rod is 1.68 μm and mean diameter is 0.13 μm.

DLS measurements were carried out using DLS-7000DL (Otsuka Electronics Co. Ltd.). We have used Ar^+ laser (488 nm) as a light source. The scattering angle was 90°.

The UIB measurements were carried out laboratory made apparatus. The details are given in the literatures.[3,4] We carried out averaging of data to improve S/N ratio. Since the on-off cycle of ultrasound was longer than 20 seconds, the averaging was affected from drift of base line and amplitude fluctuation in long term. In order to minimize the harmful effects in the averaging procedure, the base line value was subtracted from the data and the subtracted data were normalized before averaging the data.

Sonication to sample solution was carried out using a ultrasonic homogenizer (Branson Sonifier S-450A) operating 20kHz. Sonication power is estimated using the calorimetry technique. The power was estimated by the calorimetry method. It was about 25 W.

The DLS and UIB measurements were carried out 25.0°C and sonication was carried out about 25°C.

3. Results and Discussion

Fig. 1 shows logarithm of the normalized first order autocorrelation functions $g_1(t)/\ g_1(0)$ vs. time at various sonication times, 0 min, 5 min, 10 min, and 20 min. All the curves cannot be expressed in the single exponential decay. At least two different decay process exists. We carry out the non-linear least square fit and obtained the decay time. For the data of sonocation time being 0 and 5 min., we use the sum of two exponential decay curves as a fitting function and obtain two decay time $\tau_{t,f}$ and $\tau_{t,s}$, which are assigned to the

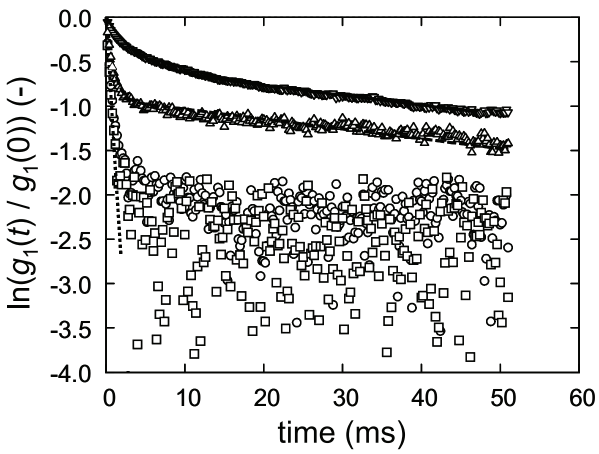

Fig.1 Plot of logarithm of the normalized first order autocorrelation functions vs. time of rodlike TiO_2 colloid dispersion at various sonication times. (▽ 0 min, △ 5min, ○ 10 min, □ 20 min).

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Table I Decay time and Stokes diameter obtained by the DLS methods

Sonication Time (min.)	$\tau_{t,f}$ (ms)	$\tau_{t,s}$ (ms)	d_f (μm)	d_s (μm)
0	3.2	90	0.89	26
5	0.80	90	0.23	26
10	0.70	-	0.20	-
20	0.70	-	0.20	-

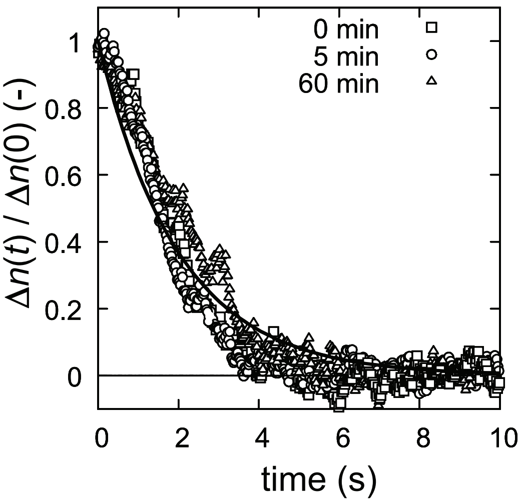

Fig. 2 Plot of the normalized ultrasonically induced birefringence vs. time of rodlike TiO_2 colloid dispersion at various sonication times.

fast and slow decay processes, respectively. For the data of sonocation time at 10 and 20 min., they are noisy when time is longer than 2 ms. The fitting are carried out at the time shorter than 2 ms using single exponential decay curve. From the decay time, we can determine the average Stokes diameters d using the following equations,

$$1/\tau_t = D_t q^2 , \quad D_t = k_B T/(3\pi\eta_0 d) \tag{1}$$

D_t is the translational diffusion constant, q is the wavenumber that is determined by the scattering angle, wavelength of the laser light, and the refractive index of the solution. Symbol k_B denotes the Boltzmann constant, T is the temperature and η_0 is the viscosity of the $(NaPO_3)_6$ solution.

Table I shows the $\tau_{t,f}$ and $\tau_{t,s}$ values, and the corresponding Stokes diameters, d_f and d_s, respectively. The Stokes diameter, d_f for the sample at sonication time of 0 min is 0.89 μm, which is near to that in the long diameter in the catalogue. This indicates that the $\tau_{t,f}$ value is related to the translational diffusion of particles without aggregation. The Stokes diameters obtained from $\tau_{t,s}$ for at sonication time of 0 and 5 min are 26 μm. The fact indicates that the slow decay process is related to the aggregates of TiO_2 particles. Comparing the curve of the sample at sonication time of 0 min to that at 5 min, we see that ratio of slow process decreases at 5 min. This indicates that the ultrasound breaks aggregates of TiO_2 particles. The stokes diameter for the fast decay process decreases with increasing sonication time but those of 10 and 20 min are almost the same.

Fig. 2 shows normalized of the transient trace of the UIB signal vs. time at various sonication times, 0 min, 5 min, and 60 min. All the curves are almost identical. The curve can be fitted single exponential decay curve, we can estimate the reorientational relaxation time τ_r and it is 2.0±0.4 s. Using the following relationship of τ_r for anisotropic particles in cylinder shape[5],

$$\tau_r = \pi\eta_0 L/(18 k_B T(\ln(L/b) - \gamma)) \tag{2}$$

we can estimate the length of the cylinder L. Here b is the diameter of cylinder and γ is a correction factor, which is 0.8 using the approximation.[5] We used the catalogue value of mean diameter of the sample as the b value. The estimated length L is 5.2 μm. It is larger than the mean length of the catalogue value 1.68 μm. However, from the SEM photograph provided by the manufacturer, we observed not small amount of rod like particles with length of about 5 μm. The UIB method is sensitive to the particle which has large anisotropy in shape. This might be a reason the UIB results may give larger length values than that in the catalogue. The fact that value of τ_r does not change after 60 min sonication indicates that the TiO_2 particles with the length of 5 μm still exist in solutions.

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References

1. B. J. Berne and R. Percora: *Dynamic Light Scattering (Dover Ed.)*, (Dover, New York, 2000).
2. T. Watanabe, Y. Ikeda, M. Hibino, T. Kudo, M. Hosoda, M. Miyayama and K. Sakai: Jpn. J. Appl. Phys. **41** (2002) 3157.
3. K. Yasuda, T. Matsuoka, S. Koda and H. Nomura: J. Phys. Chem. B. **101** (1996) 1138.
4. T. Matsuoka, K. Yasuda, K. Yamamoto, S. Koda, and H. Nomura: Colloids and Surfaces B **56** (2007) 72.
5. M. Doi and S. F. Edwards: *The Theory of Polymer Dyninmics*, (Oxford Univ. Press, New York, 1986).