# 3P2-13

## Studies on Stability of Carbon Black Suspensions Probed by Dynamic Ultrasound Scattering Techniques

## 動的超音波散乱法によるカーボンブラック懸濁液の分散安定性解析

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### 1. Introduction

Carbon black (CB) is widely used in inks, fuel cells and reinforced rubbers because of the low cost, high conductivity and large specific surface area for catalysis supports. In these applications, the stability of the particle in suspension is one of the most important factor to control the structure of the final product. However, the structure of CB in suspension was not studied well so far. Although Dynamic Light Scattering (DLS) techniques have advantages to probe the particle in liquid, there are some difficulties to measure CB suspensions by optical techniques. For example, due to large absorbance, the signal is extremely weak, and the size aggregation becomes beyond the detectable length scale of light scattering. Therefore, in this study, we utilize Dynamic ultraSound Scattering (DSS) techniques[1]-[4] and Ultrasonic Spectroscopy (US) to overcome the problems.

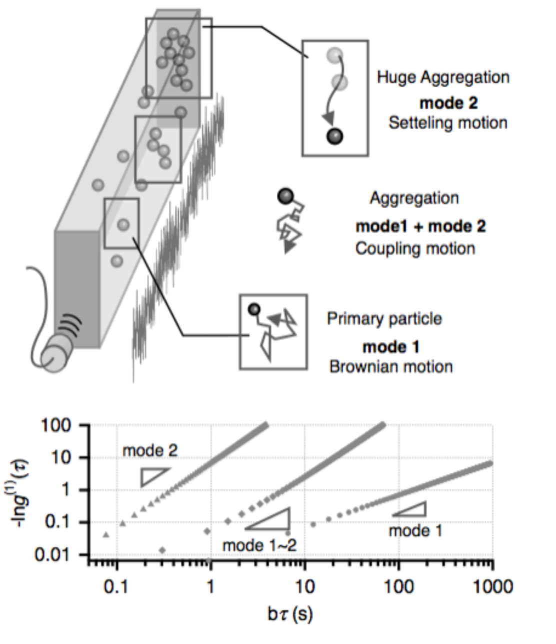


**Fig. 1** Scheme of various particle motions and the corresponding time-correlation functions.

The DSS techniques allow us to investigate the dynamics of nano- and micron-sized particles in suspension without disturbing the system. Particle motion could be obtained by the technique, such as diffusive motion for nanometer-sized particles and settling motion for micrometer-sized particles. **Fig. 1** shows a schematic diagram of the possible particle motions from nanometer to micrometer ranges. The purpose of this study is to extract the size distribution of CB particles including the primary nano-particles, secondary aggregation as well as their agglomerates. To achieve this purpose, CB particles are sonicated in the presence of heteropoly acid to obtained the small primary particle, then, the aggregation behavior was investigated in-situ.

### 2. Experiments and Results

50% compressed acetylene carbon black (CB) was purchased from Sterm Chemical (MA, USA). The CB particles with the volume fraction $\phi$ = 0.005, 0.015, 0.025, 0.05, 0.15, 0.25, 0.5% were dispersed in water in the presence of phosphotungstic acid (PWA). PWA is used as a stabilizer of CB particles in water as reported in the literature.[5] The resultant size distribution of nano-sized CB particle was found to be fairly narrow which is suitable for the further discussion. PWA was purchased from Wako chemical. The samples were sonicated (38 kHz) for 3 h, and filtered through a 200 nm membrane filter. After centrifugation, the CB particle was washed several times with dilute sulfuric acid and 1–propanol, followed by dispersing in pure water

**Fig. 2(a)** shows a time correlation function given by a DSS measurement. As shown in the figure, the correlation function decayed exponentially. The slope = 1 in the inset indicates the dynamics is dominated by the diffusive mode. Then, the correlation function was fitted with a model function to obtained the relaxation time and diffusion coefficient. The time correlation function is given by

$$g^{(1)}(\tau) = \exp(-Dq^2\tau) = \exp(-\Gamma\tau) \qquad (1)$$

for monodisperse diffusive nano-particles where $q$ is the magnitude of the scattering vector, $\tau$ is the time lag, $D$ is the diffusion coefficient. After a trivial calculation using the Stokes-Einstein formula, the particle size found to be $d$ = 62 nm for the CB suspension with $\phi$= 0.05%. Also **Fig. 2(b)** shows the decay rate vs $q$ plot. As indicated by the dotted line in the figure, the dynamics can be regarded as a diffusive motion. This is the minimum particle size of CB obtained in this study and now the aggregation behavior of the nano-CB particles is investigated.

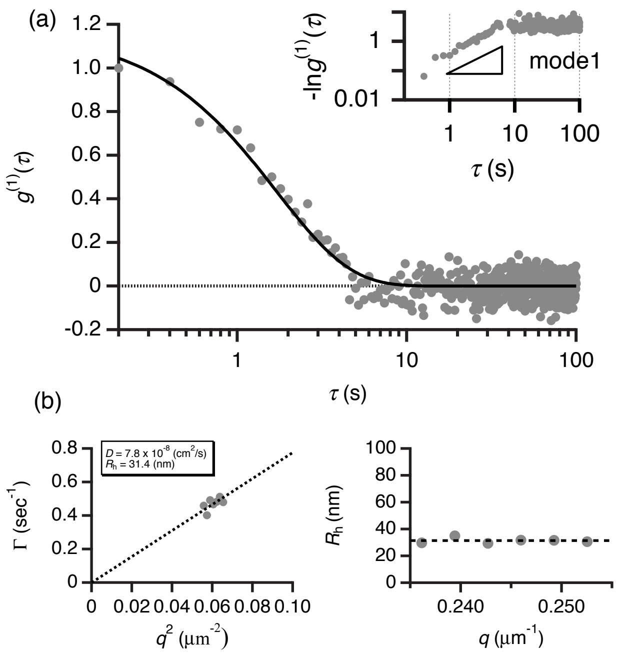


**Fig. 2** (a) Correlation function observed from CB suspension ( $\phi$ =0.05%) . Double logarithmic plot indicates the diffusive motion.

(b) Average hydrodynamics radius was obtained from $\Gamma$ vs $q^2$ plot (left), and $R_h$ as a function of $q$ was also demonstrated (right) .

Aggregation behavior of CB could depend on the initial concentration of the particles. Then, 1wt% of Nafion a polymer stabilizer, was mixed in the sample to suppress aggregation of CB. Although we tried to mix Nafion as quick as possible after sonication, the CB particle has started aggregating. In order to examine the stability of the sample, ultrasonic attenuation probed by US was demonstrated as a function of the concentration. As expected, the attenuation coefficient of suspension $\alpha_c$ normalized by that of PWA solution $\alpha_0$ increased with the CB concentration (**Fig. 3**.) where the solid and open squares indicate the result of CB/PWA suspensions with and without Nafion. Although both attenuation increased with the concentration, that without Nafion increased more drastically, suggesting that the sample is more or less unstable without the stabilizer. Note that the correlation functions obtained by DSS are almost equivalent between the samples with and without Nafion, suggesting the apparent hydrodynamic size of the aggregation is almost the same. Nevertheless, the attenuation of the aggregate without Nafion was larger than that with Nafion. This suggests the internal structure of CB aggregate was different. As shown in Fig 3, we concluded that the larger CB aggregation could be obtained without Nafion while that with Nafion may consist of small CB clusters coated by Nafion.

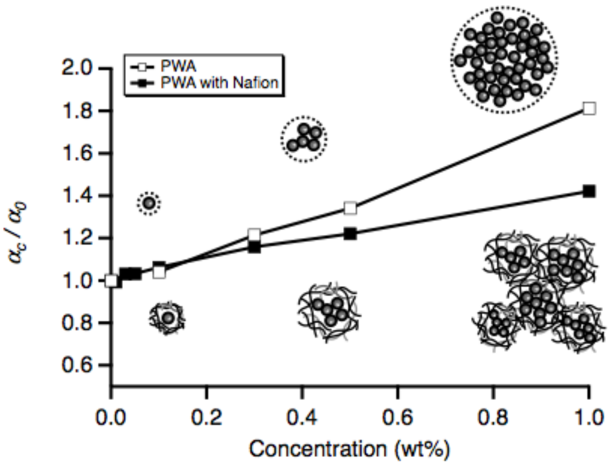


**Fig. 3** Attenuation coefficient behavior of CB suspension with or without Nafion.

## 3. Conclusion

Aggregation structure of carbon black particles was investigated by dynamic ultrasound scattering and ultrasonic spectroscopy techniques. Nafion was found to be an effective stabilizer to prepare more homogeneous suspension. It was also found that Nafion could have a role as a binder between small CB clusters.

## References

1. K.Igarashi, et. al., J. Appl. Phys, **115**(2014) 203506-1-8
2. M.Kohyama, et. al., Macromolecules **42(3)** (2009) 752-759
3. M.Kohyama, et. al., Polym. J **40**(2008) 398-399
4. K.Kobayashi, et. al., J. Appl. Phys, **122**(2017) 045106-1-8
5. P.Garrigue, et. al., Chem. Mater, **2014** 16 2984-2986