Influence of PMSA-Based Polymer on the Settling Velocity of CNT in Aqueous Media

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The preparation of a stable suspension dispersing carbon nanotube (CNT) in aqueous media using polystyrene maleic acid (PSMA)-based polymer as surfactant was attempted to be subsequently used in the fabrication of high-performance ceramic matrix composites. Settling velocity under centrifugation analysis was experimentally evaluated as one of the stability criteria of the dispersion and pulsed nuclear magnetic resonance was used to evaluate the adsorbed molecules. The settling velocity decreased considerably with the PSMA concentration up to the saturation at around 7 mass%, then further decreased gradually with PSMA. The former was thought to be based on the dissociation of CNT agglomerate and the latter would be attributed to the surfactant-induced network structure formed in the aqueous media.


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1. Introduction

Numerous studies have been conducted on carbon nanotubes (CNTs), a cylindrical material constructed with graphene-sheet.1-3) Peng et al. reported that CNTs have an extremely high pulling strength (100 GPa) and elastic modulus (1000 GPa), one to two orders higher than that of conventional materials.4) Thus, CNTs are increasingly being used in fiber-reinforced applications5-9) and have been added to ceramic composites to enhance their resilience to fracture. The fabrication process for ceramic composites requires a well-dispersed precursor slurry to promote microstructure homogeneity.10) However, the dispersion stability of the precursor in an aqueous solution depends on various mutually related physical and chemical factors.11)

Many techniques have been used to evaluate the dispersion stability of particles in the precursor manufacturing processes of ceramics. These techniques commonly include an evaluation of the macroscopic characteristics and sedimentation rate, as well as rheology and molded body packing density measurements. Particle-size distribution analysis and zeta-potential measurements involve electrostatic interactions with the particle surface; however, these techniques are limited mostly to dilute solutions. Thus, precursor evaluation using these methods does not always provide a realistic dissociation from the bulk characteristics of the material.

Pulsed-NMR can also be used to analyze the dynamic behavior of adsorbed molecules in an aqueous solution by measuring the relaxation time (T2). This method has the potential to clarify the molecular motions of particles adsorbed to various surfaces.12-14) Accordingly, this method can be applied to homogeneous or nonhomogeneous particle dispersion solutions.

The centrifugation method shows the overall change in concentration under an enormous accelerating centrifuging force via a light detection system.15) This analysis is applicable to highly concentrated systems, similar to the actual concentration of the precursor slurry used for ceramic composites.16,17)

In this study, settling velocity under centrifugation analysis was experimentally evaluated as one of the stability criteria of the dispersion and pulsed-NMR was used to evaluate the adsorbed molecules. The relationship between the adsorption quantity of surfactant on the CNT surface and the restraint state of water was clarified.

2. Experimental Procedure

2.1 Materials

Multi-walled carbon nanotubes (MWCNTs, MWNT-7K, Hodogaya Chemical Co., Ltd., Kanagawa, Japan) used in this study were produced using the vapor growth carbon-fiber method. The CNTs were 40–90 nm in diameter and 12 µm in length on average. A calcination temperature of 2200°C resulted in a carbon purity of >99.5%.

A polystyrene maleic acid (PSMA)-based polymer (GD55R, Senka Corporation, Osaka, Japan; m/w: 4000) was used as the surfactant. The carbonyl structure of maleic acid orients to the aqueous solution side when adsorbed on the CNT surface.18-22)

2.2 CNT-dispersed aqueous solution

CNTs were dispersed throughout the aqueous solution in the following way. The prescribed amount of the GD55R surfactant was added to 150 mL of distilled water and mixed together. The concentration of GD55R varied from 0.7% to 14%. CNTs (1.5 g) were added to the mixture. The solution was then stirred at 60 rpm for 10 h.
2.3 Quantitative analysis of the adsorbed surfactant
The adsorbed surfactant was measured as follows. The CNT-dispersed aqueous solution containing the non-adsorbed surfactant was pipetted to test tubes by 10 mL. The solution was filtered using a membrane made of hydrophilic polytetrafluoroethylene (PTFE) with 0.2 µm mesh. The filtrate was dried under decompression, and the residual surfactant left behind in the vessel was weighed. The amount of adsorbed surfactant was calculated by subtracting the non-adsorbed surfactant from the total.

2.4 Pulsed-NMR characterization of the CNT-dispersed solution
Pulsed-NMR can distinguish the restraint state of the two phases of the water molecule by measuring the change in its relaxation time (T2). In this study, we examined the relationship between the restraint state of water and the amount of surfactant adsorption on the CNT surface.

NMR relaxation times, T2, were measured using an Acorn Area™ system (Xigo Nanotools Inc., Bethlehem, PA, USA). NMR measurements were carried out at room temperature (293 ± 1 K). The resonance frequency used was 13 MHz. The 1H spin–spin relaxation time, T2, was determined by the spin-echo strength of the Carr–Purcell–Meiboom–Gill (CPGM) sequence.

2.5 Characterization of CNT dispersion using analytical centrifugation
The sedimentation behavior of CNTs dispersed in an aqueous solution containing a surfactant was investigated using a LUMiSizer system (L.U.M. GmbH, Berlin, Germany). The cell containing the CNT aqueous solution was subjected to centrifugal force. The sedimentation behavior was measured in terms of the light transmission of the cell along the centrifugal axis. Three surfactant concentrations were examined for the CNT-dispersed aqueous solution: 3.5% (saturated front), 7%, and 11.7%. Their macroscopic viscosities were measured by a vibration type viscometer (VIVRO VISCOmeter, SV10A, AND, Tokyo, Japan).

Measurements were carried out under a centrifugal force that varied from 6–23000 G at 298 K. To evaluate the sedimentation behavior, the transmission profile was integrated from 114 to 124 mm, corresponding to the middle of the detection region (105–130 mm).

3. Results and Discussion
3.1 Pulsed-NMR characterization of the adsorbed surfactant on CNT
Figure 1 shows the experimentally determined relaxation time (T2) and the amount of adsorbed surfactant on the CNTs for various surfactant concentrations. The adsorbed surfactant on the CNTs increased with the surfactant concentration, and became saturated for surfactant concentrations that exceeded 4 mass% (versus CNT concentration). The saturated amount of surfactant adsorbed to the CNTs was ~0.018 g/g (CNT weight).

The relaxation time decreased linearly with increasing surfactant concentration. The decrease in T2 indicated that the increase in the surfactant affected the water molecules.

Accordingly, the change in T2 in pulsed-NMR readings should show the influence of the water restricted by surfactant adsorption on the CNTs. In contrast, upon reaching surfactant adsorption saturation, the T2 value tended to fluctuate; however, the details as to why this would occur have yet to be resolved.

3.2 Evaluation of sedimentation behavior
Figures 2(a), (b) and (c) show the sedimentation profiles of CNTs analyzed by centrifugation. In all samples, the transmission value increased over time. Especially for the C-1 sample at 3.5% surfactant concentration, a large increase in transmission was observed over the course of centrifugation (Fig. 2(a)); this increase appeared to accelerate over time. Thus, these results indicate that the CNTs in the aqueous solution did not settle uniformly. The non-saturated surfactant on the CNTs (C-1) contributes slightly to reduce the settling velocity of the CNT.

In contrast, for a surfactant concentration exceeding the saturated amount (samples C-2 at 7% and C-3 at 11.7%), a lower amount of sedimentation was observed than that for the C-1 sample (Figs. 2(b) and (c)). Further, the transmission value of the C-3 sample was lower than that of the C-2 sample. The time dependence of the integral transmission was used to evaluate the sedimentation behavior numerically.

Figure 3 shows the relationship between the integration transmission profiles and the centrifugation times; the slope of the curve describes the change in the integral transmission quantity per hour. Centrifugation was carried out at a rotation rate of 2000 rpm for ~1500 s. The rotation was then changed to 4000 rpm, and held at this rate until the centrifugation process was complete. The smaller slope indicates a lower settling velocity. Although the transmission quantity of C-2 (7 mass% surfactant concentration) was similar to C-3 (11.7 mass% surfactant concentration) at 2000 rpm, sample C-3 with a higher surfactant concentration exhibited a lower settling velocity than C-2.

When the surfactant adsorption on the CNT was not saturated, the surfactant acted to create wet conditions for the CNTs to induce the dissociation of the agglomerates. In contrast, above saturation conditions, the non-adsorbed
surfactant contributed to reduce the settling velocity. The role of surfactant was examined by measuring the viscosity of the aqueous solution in samples C-1, C-2 and C-3 before the centrifugation. The viscosity of the former was as large as 2.5 mPa/s, strongly suggesting the dissociation of the CNT agglomerates. At around the saturation condition C-2 it decreased to lower than 0.5 mPa/s. It slightly increased to 1.0 mPa/s in C-3, indicating a formation of a kind of network structure of CNT. In detail, the excessive surfactants exist as micelles in a water solution between CNTs with adsorbed surfactants, resulting in the network structure.23-25 In this case the settling velocity decreases while the viscosity increases.

4. Conclusions

We conducted an investigation of CNT sedimentation behavior in an aqueous solution with a PSMA-based polymer surfactant, using pulsed-NMR and centrifugation methods. The results of our study are summarized below.

(1) The amount of absorbed surfactant correlates with the relaxation time (T2). T2 decreased until the adsorption amount of the surfactant reached saturation (7 mass%). Despite favorably low settling velocity at 7 mass% surfactant concentration, the stabilization was not sufficient. Surfactant amounts exceeding 7 mass% further reduce the settling velocity of the CNT which would correlate with the increase in T2 with 11.7 mass% surfactant concentration.

(2) Reduction of settling velocity could not be accomplished only by surfactant adsorption to the CNT surface; thus, the effect could not be fully explained by the isothermal adsorption theory for particle dispersion. The presence of surfactant beyond the concentration contributed to decrease the settling velocity by forming a network structure.

(3) By combining pulsed-NMR and centrifugation analysis, we were able to evaluate the effect of surfactant adsorption quantity on CNT sedimentation behavior.

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REFERENCES

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