



Rapid Communication

Synthesis and Electrical Properties of Composite Films Comprising Polymer Particles and Carbon Nanotubes



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ABSTRACT

In the present study, composite films were synthesized from composite polymer particles prepared with multi-wall carbon nanotubes (MWCNTs) by in situ polymerization. Because one of the advantages of MWCNTs compared to other preparation methods is high electrical conductivity, the electrical properties of the composite films were evaluated by the direct current two-terminal method. As a result, the composite film prepared by MWCNTs had conductive paths and showed higher conductivity even at lower mass fraction of MWCNTs compared with the previous works to keep transparency. This method was shown to decrease the mass fractions of MWCNTs and increase the transparency of the composite films.

Composite materials are the subject of extensive studies, because of their novel and excellent properties compared to their constituent materials. For example, carbon nanotubes (CNTs) [1] are used to develop polymer-based nanomaterials [2–4].

In this study, in situ polymerization was used to synthesize composite films comprising polymer particles and CNTs with high stiffness [4–8] to enhance the mechanical properties [9] of the resulting films, wherein the surfaces or inside of the polybenzyl methacrylate particles were covered or incorporated with CNTs. Because CNTs afford high electrical conductivity, many studies examined the synthesis of highly conductive composite polymer materials using CNTs [10–13]. However, the CNT mass fractions reported in the literature are usually high, which limits their commercialization. In this study, an attempt was made to synthesize conductive polymer composite films [14–16] with reduced CNT mass fractions using composite particles. That is, the membrane of the composite particles was melted to mold the composite polymer films. The electrical conductivity of the resulting composite films was measured and it was revealed that the surface coverage of the polymer particles by CNTs enhances the electrical conductivity. Therefore, the new synthesis method of composite polymer particles was developed using carbon tetrachloride as an organic solvent with a low boiling point, to prepare Pickering emulsions using the ultrasonic procedure. The organic solvent was allowed to evaporate to reduce the emulsion particles size and to enhance the surface coverage after the completion of polymerization in the emulsion.

In the present study, 0.50 wt% of multiwall CNTs (MWCNTs, VGCF-H, SHOWA DENKO K.K.) with fiber length of from 1 μm to 10 μm and average diameter of 150 nm was surface-modified by stirring in 75 vol

% of sulfuric acid (Kishida Chemical Co., Ltd.) and 25 vol% nitric acid (NACALAI TESQUE) at 70 °C and 400 rpm in a 5 mL bottle (HSH-10VA, AS ONE) for 2 h. The MWCNT dispersion was then filtered using a membrane with 100 nm pores (VCTP01300, Millipore) to obtain surface-active MWCNTs with the zeta potential of -10.7 mV [17].

The water used for polymerization was purified using a purification system (WG250, Yamato Scientific); nitrogen gas was then bubbled into the water to remove any dissolved oxygen. The following three monomer types were used in the polymerization. Styrene monomer (Tokyo Chemical Industry), which was washed four times with a 10% sodium hydroxide solution to remove the polymerization inhibitors and then purified by distillation under reduced pressures. Benzyl methacrylate (BMA, Tokyo Chemical Industry) and methyl methacrylate (MMA, Tokyo Chemical Industry), which were used as received for in situ polymerization. 2,2'-Azobisisobutyronitrile (AIBN, Sigma Aldrich Co. LLC.), a common oil-soluble radical initiator, was used without any further purification [18–20]. It was found that these chemicals can be dissolved in carbon tetrachloride (CCl_4 , Wako Pure Chemical Industries).

The above-mentioned monomers were polymerized by AIBN to synthesize composite materials with MWCNTs using the parameters listed in Table 1. The polymerization reaction was performed in a 30 mL round-bottom reactor. The temperature of the reactor was controlled by a heater (HSH-10VA, AS ONE), and the reaction time was set to 12 h.

To enhance the surface coverage, a new polymerization method was developed as follows. The aqueous dispersion of MWCNTs and the monomer/initiator mixture in CCl_4 were poured into the reactor. The

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Table 1
Experimental conditions for the polymerization.

Water [g]	15.0
Monomer and CCl ₄ [mmol/L]	128
Initiator [mmol/L]	2.03
Temperature [°C]	70.0
Weight ratio of surface-active MWCNTs to the total amount of oil phase [wt%]	0.10

denser oil phase immediately subsided to the bottom of the reactor. The reactor was then immersed into a bath sonicator operating at 38 kHz (US-5KS, SND) for 10 min to prepare Pickering emulsions with surface-active MWCNTs. The reactor was then heated to 70 °C using an electric heater for completion of the polymerization. In order to enhance the surface coverage of MWCNTs and for shrinking the composites, the temperature was increased to 80 °C to evaporate the CCl₄ solvent from the reactor. Fig. 1 shows a schematic picture of the synthesis steps. In the case of the MMA and MWCNTs with zeta potential of −10.2 mV using this method, the average particle size was 39.5 μm.

The morphologies of the synthesized composite particles were observed by scanning electron microscopy (SEM, S-3000N, Hitachi High Technologies). SEM samples were prepared as follows: a small amount of the solution was sampled from the bottle and then a droplet of the solution was placed on a freshly cleaved mica plate. The specimen was dried and then coated with a thin gold film by chemical vapor deposition (E-1010, Hitachi). The particle size and surface coverage were calculated from the SEM images. The surface coverage, θ , was defined as the ratio of the particle surface covered by the MWCNTs to the total surface area of the composite particle. Image analyzing software (Azokun, Asahi Kasei Engineering Corporation) was used to analyze the MWCNT surface coverage, and it was shown that the effect of the particle surface curvature was negligible.

After the synthesis of the composite films from composite particles,

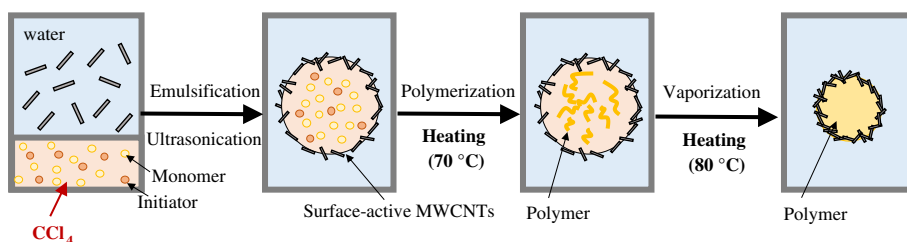


Fig. 1. Schematic of the synthesis steps of the polymeric composite particles with high surface coverage by MWCNTs.

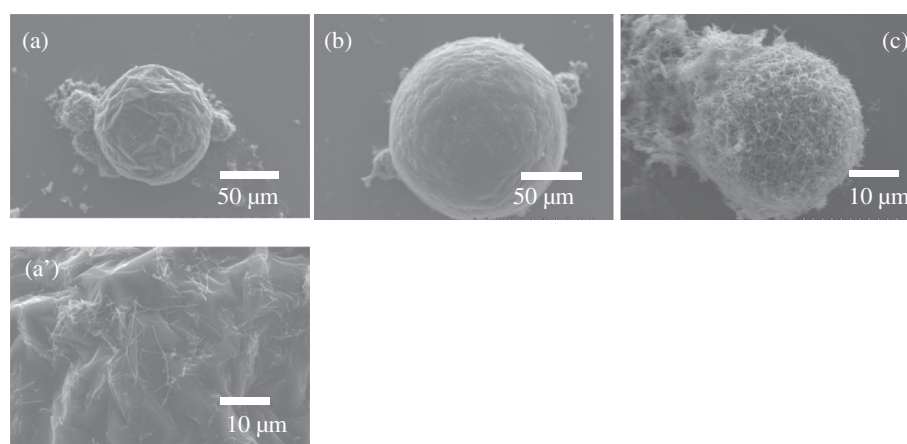


Fig. 2. SEM images of the composite particles using the following monomers. (a and a') Styrene, (b) BMA, (c) MMA. (a') Image (a) with higher magnification.

their electrical properties were studied. The conductivity, σ , was calculated according to Eq. (1), where R , S , and l were resistance, cross sectional area of the film, and length of the film, respectively. The resistance of the composite film was measured by the direct current two-terminal method using a direct-current power source (AD-8724D, A & D). The composite films were synthesized as follows. Initially, the composite particle solution was placed on a plate and dried at 80 °C for 12 h to fabricate the particle membrane. Then, the membrane was heated up to 150 °C for 10 min to mold it.

$$\sigma = \frac{l}{RS} \quad (1)$$

The composite particles were synthesized by a new method, as shown in Fig. 1, in which each monomer is polymerized by AIBN present in CCl₄ at a molar fraction of 0.5. Fig. 2 shows the SEM micrographs of the particle morphology. Because of the shrinkage of the particles caused by the evaporation of CCl₄, the surface roughness is high especially in case of styrene monomers. However, as shown in Fig. 2a', the composite particles were not fully covered in case of styrene and BMA. Because our previous studies revealed that the negative charges can be generated through the polymerization of aromatic vinyl monomers by AIBN [18–20], the negatively charged MWCNTs were subjected to repulsive forces from the polymers after the surface modification in order to move from the surface to the bulk. Additionally, MMA was polymerized by AIBN without any charges [20,21]; hence, the surface coverage was extremely high compared with that observed in other cases.

Fig. 3 shows the surface coverage and particle size distribution as a function of monomer molar fraction in the oil phase for styrene and MMA. As it can be seen, the particle size increased at a higher molar fraction of the monomer, because the ultrasonic power per monomer decreased [22]. This could be due to the higher water solubility of the MMA monomer than styrene. Consequently, the size of the Pickering emulsion, formed by ultrasonic method, is smaller in the oil phase. Due

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