

Synthesis of composite polymer particles with carbon nanotubes and evaluation of their mechanical properties

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Abstract

In the present study, a method for synthesizing composite polymer particles with multi-wall carbon nanotubes (MWCNTs) was developed, and the particles' mechanical properties were evaluated. First, the surfaces of MWCNTs were modified by acids to increase their hydrophilicity, resulting in surface-active MWCNTs. Then, a Pickering emulsion was formed using liquid benzyl methacrylate monomer and the surface-active MWCNTs. The surface charge of the surface-active MWCNTs greatly influenced the surface coverage and size of the composite particles. Furthermore, when untreated MWCNTs were added to the monomer phase, surface coverage of the resulting particles was enhanced because MWCNTs on the surface of the particles interacted with MWCNTs incorporated inside the particles, thus preventing the surface-active MWCNTs on the surface from being released into the bulk. As a result, the mechanical properties of the composite polymer particles were successfully improved because the incorporated MWCNTs worked well as fillers.

Keywords: carbon nanotube, composite particle, polymerization, mechanical property

1. Introduction

Carbon nanotubes (CNTs) [1] have been widely studied in many fields because of their excellent mechanical, thermal and electrical properties [2-4]. To exploit these advantages and develop novel materials, many studies on the synthesis of the composite materials using CNTs have been carried out [5-7]. In particular, soft matter materials with CNTs [8-12] are very attractive, highly functional materials because they are easily designed and manufactured. To achieve these composite materials, techniques to surface-modify CNTs have been developed to disperse them in the desired medium, such as adding functional groups to nanotube surface [13-16], because the dispersion of CNTs in the polymer matrix is one of the most important factors for the performance of the composite materials [17].

In previous studies, soft materials, such as polymeric particles, have been successfully covered with CNTs [18-21]. However, incorporating CNTs inside the particles has been difficult, probably because for the most part, these composite materials have not been fabricated through in situ polymerization of monomers. Hence, the mechanical properties of the materials did not sufficiently benefit from the properties of CNTs. To enhance the mechanical properties, we attempted to fabricate a composite of surface-active CNTs and monomer droplet in an aqueous phase, similar to a Pickering emulsion [22, 23]. Then, the monomers were polymerized and solidified by oil-soluble initiators to prepare polymer particles with CNTs. If the carbon nanotubes were dispersed inside the monomer droplets, the particles incorporated the CNTs within themselves. Finally, compaction tests of the fabricated composite particles were carried out to evaluate their mechanical properties.

2. Experimental

2.1. Materials

In the present study, 0.50 wt% of multi-wall CNTs (MWCNTs, VGCF-H, SHOWA DENKO K.K.) were surface-modified using 75 vol% of sulfuric acid (Kishida Chemical Co.,Ltd.) and 25 vol % nitric acid (NACALAI TESQUE) at 70 °C with stirring of 400 rpm in a screw bottle of 5 mL (HSH-10VA, AS ONE) for up to 6 hours [9]. The MWCNT dispersion was then filtered using a membrane with 100 nm pores (VCTP01300, Millipore) was carried out to obtain surface-active MWCNTs.

The water used in the polymerization was purified using a purification system (WG250, Yamato Scientific), and nitrogen gas was then bubbled into the water to remove any dissolved oxygen. Benzyl methacrylate (BMA, Tokyo Chemical Industry) with a density of 1.04 g/cm³ was used as received as the monomer for the polymerization. As the radical initiator 2,2'-azobisdiisobutyronitrile (AIBN, Sigma Aldrich Co. LLC.), which is a common oil-soluble initiator, was used without further purification [24-26]. Their chemical structures are shown in **Fig. 1**.

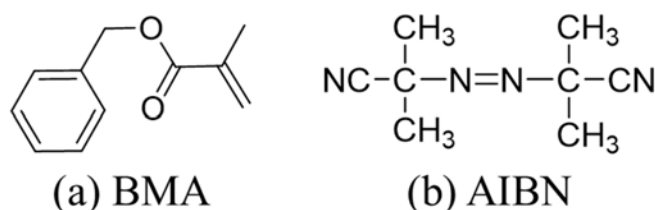


Fig. 1. Chemical structures of the (a) BMA monomer and (b) AIBN initiator.

2.2. Polymerization and synthesis of composites

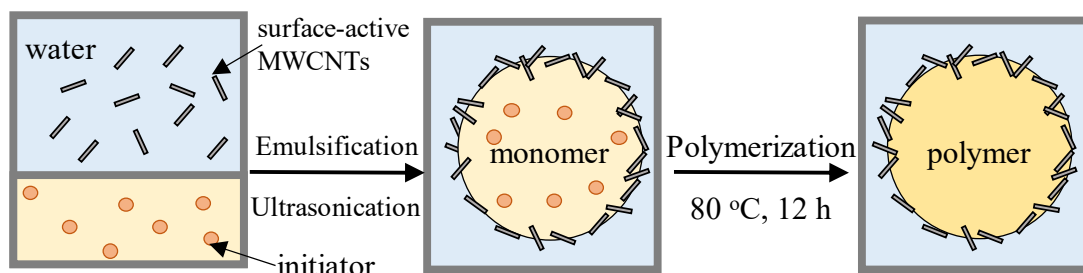
BMA monomers were polymerized by AIBN to synthesize the composite materials with MWCNTs under the conditions in **Table 1**.

Table 1 Experimental conditions of the polymerization

Water [g]	15.0
Monomer [mmol/L]	64.0
Initiator [mmol/L]	2.03
Temperature [°C]	80.0
Weight ratio of surface-active MWCNTs to monomer [wt%]	0.10
Weight ratio of untreated MWCNTs to monomer [wt%]	0.10-1.00

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 hours. The polymerization experiments were carried out as follows. The surface-active MWCNT aqueous dispersion and the monomer/initiator mixture were poured into the reactor. The denser monomer phase immediately fell to the bottom of the reactor. The reactor was immersed in a bath sonicator operating at 38 kHz (US-5KS, SND) for 10 minutes to prepare the emulsion with surface-active MWCNTs [27]. The reactor was then heated to 80 °C using an electric hot heater. **Fig. 2** schematically shows the syntheses of the composite materials. The composite particles fabricated in the present study were classified into the following two types: (a) polymer particles with surface-active MWCNTs only on the surface and (b) polymer particles with MWCNTs both inside and on the surface.

(a) MWCNTs on surface of polymer particle



(b) MWCNTs on surface and inside of polymer particle

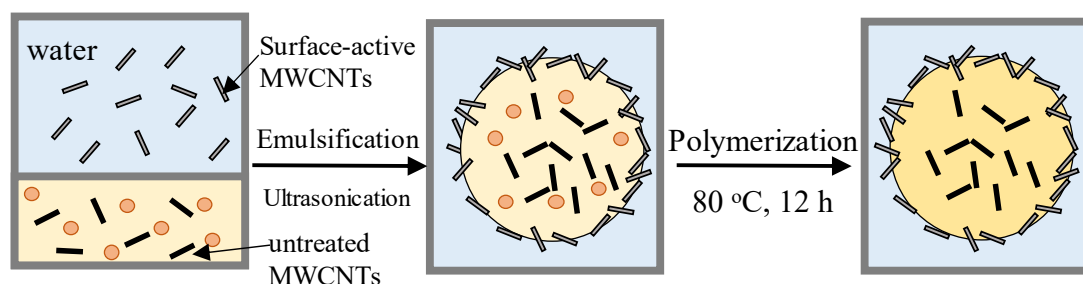


Fig. 2. Schematic diagrams of the syntheses of the composite polymer particles, which were classified into two types: (a) MWCNTs on the particle surface, (b) MWCNTs inside and on the surface of the polymer particle.

2.3. Evaluation of the surface and mechanical properties of the composite particles

The zeta potential of the surface-active MWCNTs before and after the acid treatment for various times was measured in acetone using a ZETASIZER Nano-ZS in acetone (Wako Pure Chemical Industries). The morphologies of the synthesized composite materials were observed by scanning electron microscopy (SEM, S-3000N, Hitachi High Technologies). SEM samples were prepared as follows: a small amount of solution was sampled from the bottle; then, a drop 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 surface coverage θ was defined as the ratio of the area of the particle surface covered by the MWCNTs to the total surface area of the composite particle. The particle size

and surface coverage were calculated from the SEM images. An image analyzing software (Azokun, Asahi Kasei Engineering Corporation) was applied to the SEM images of small surface areas of the particle, which meant the effect of curvature was negligible, to analyze the MWCNTs on the particle surface.

To investigate the mechanical properties of the synthesized composite particles, the compressive modulus K_{10} was calculated from the following equation using the results from a micro-compression tester (MCT-W500, Shimadzu), where d , ΔL , and P are the particle diameter, compressive deformation, and load at 10 % deformation, respectively. This machine was operated at loading velocity at 8.30 mN/s and a force of 4000 mN.

$$K_{10} = \frac{3}{\sqrt{2}} \times \Delta L^{-\frac{3}{2}} \times \left(\frac{d}{2}\right)^{\frac{1}{2}} \times P \quad (1)$$

3. Results and discussion

3.1. Surface modification of MWCNTs by acid treatment

The surfaces of the MWCNTs were modified with acids. The zeta potential of the MWCNTs was measured in acetone as a function of the treatment time, and the results are shown in **Fig. 3**. The surface potential increased with the increasing treatment time. After 100 min of treatment, the suspensions appeared black, which suggested that the MWCNT dispersion was stable in water. This implies that the surface of MWCNTs was covered with hydrophilic functional groups, such as carboxyl acid [9], which are negatively charged.

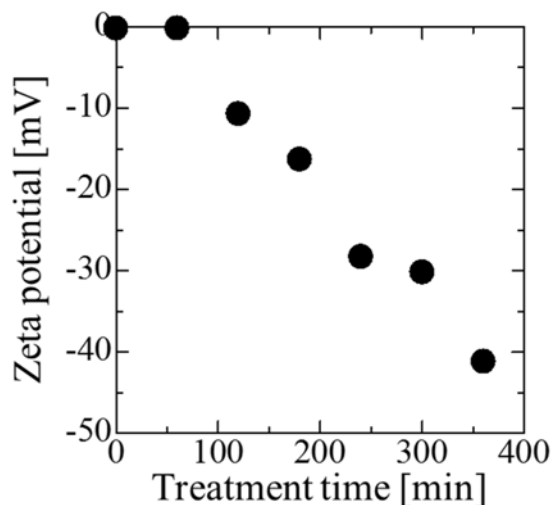


Fig. 3. Effect of the surface modification treatment time on the zeta potential of MWCNTs measured in acetone.

3.2. Controlling the particle size and surface coverage

The surface potential of the surface-active MWCNTs was controlled by the treatment time. As shown in **Fig. 2a**, surface-active MWCNTs stabilized the emulsion prepared by ultrasonication in the aqueous phase. This type of emulsion is called a Pickering emulsion [23], wherein surface-active colloidal particles stabilize the emulsion. In addition, the emulsions were solidified by oil-soluble initiators dissolved in the monomer phase during the heating process to make composite particles. **Fig. 4a** shows the particle morphologies of the composite particles synthesized using the surface-active MWCNTs with zeta potential of -10.7 mV. It was clear that the surfaces were covered with the MWCNTs as shown in **Fig. 4b**. Furthermore, to observe a cross section of the composite particles synthesized in the presence of the surface-active MWCNTs with a zeta potential of -10.7 mV, the particles were buried in the resins using a photopolymer (D-800, JEOL), and the specimen was cut using a microtome (EM UC7, Leica Microsystems) to observe the cross sections with an optical

microscope (MS-804, MORITEX Corporation), as shown in **Fig. 4c**. The MWCNTs were not densely distributed inside of the composite particles. Instead, they remained near the surface and helped to stabilize the aqueous dispersion.

The particle size and surface coverage were plotted as a function of the surface potential of the surface-active MWCNTs, as shown in **Fig. 5**. The surface coverage increased as the surface potential decreased because the electrostatic repulsive forces between the surface-active MWCNTs on the surface of the composite and in the bulk aqueous phase became weaker. Similarly, the particle size was increased because of the lower electrostatic repulsive forces between the MWCNTs on the composites.

Thus, the zeta potential of the MWCNTs was controlled by the surface modification, thereby controlling the size and surface coverage of the composite particles. The relationship between the surface charge and particle size was very similar to our previous results [24, 26, 28-31].

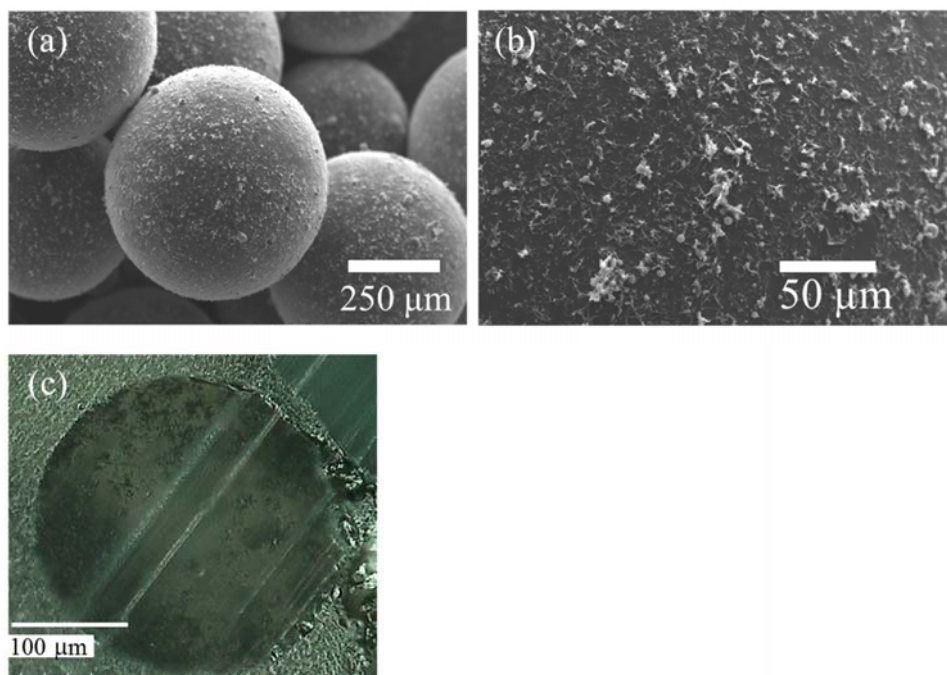


Fig. 4. Composite particle synthesized using MWCNT with the zeta potential of -10.7 mV: (a) particle morphologies observed by SEM; (b) zoomed up image of the surface area of (a); (c) cross-sectional view of the synthesized composite particles observed with an optical microscope.

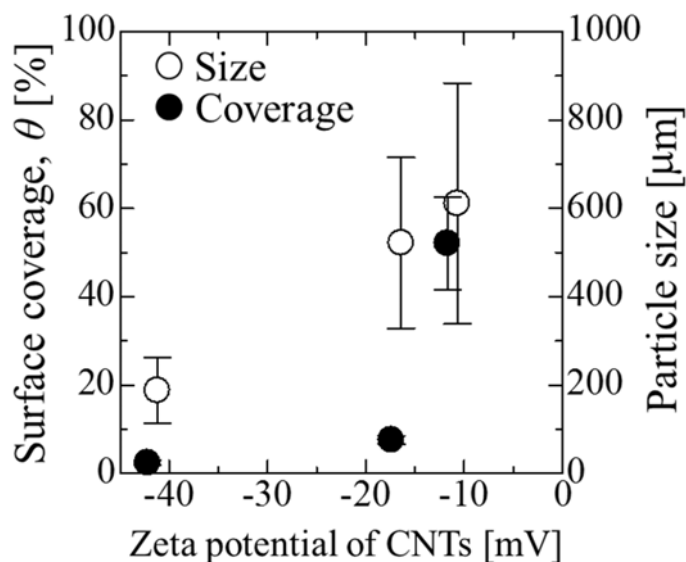


Fig. 5. Effect of the zeta potential of MWCNTs on the surface coverage and size of the synthesized composite particle.

3.3. Incorporating MWCNTs inside the polymer particle

As shown schematically in **Fig. 2b**, composite particles were also prepared with MWCNTs without the surface modification, hereafter referred to as untreated MWCNTs, inside the particles. The surface morphologies were observed by SEM. To observe the untreated MWCNTs inside the composite particles, the particles were buried in resin to observe a cross section of a particle by the same method mentioned above. These results are shown in **Fig. 6**. Clearly, the surfaces of the synthesized particles were densely covered with the surface-active MWCNTs with a zeta potential of -41.2 mV. Furthermore, the untreated MWCNTs were uniformly and densely distributed inside the composite particles, as shown

in the cross-sectional image, which indicated that the untreated MWCNTs were uniformly dispersed in the monomer phase before the polymerization reaction. The influence of the mass fraction of the untreated MWCNTs in the monomer phase on the size and surface coverage of the composite particles was investigated, as shown in **Fig. 7**. The surface coverage increased to $\theta = 85.1\%$ with a MWCNT mass fraction of 1.0 wt%, but the particle size was nearly constant across all mass ratios. To explain these results, surface-active MWCNTs in the supernatant liquid were investigated using an UV-Vis spectrophotometer (V-650, Jasco Co.). The transmissivity of the supernatant liquid under each synthesized condition was measured at a wavelength of 600 nm (**Table 2**). The transmissivity of the suspension of surface-active MWCNTs with a zeta potential of -41.2 mV was very low because of their good dispersion stability. Using these MWCNTs to synthesize the composite particles, the transmissivity of the synthesized condition at $\theta = 2.44\%$ without the untreated MWCNTs was lower than that of the synthesized condition at $\theta = 85.1\%$ with the untreated MWCNTs, which indicated that the surface-active MWCNTs detached from the emulsion droplets or polymer particles and released into the bulk. They probably detached due to repulsive forces from the negatively charged polymer synthesized by BMA and AIBN [26]. In contrast, the untreated MWCNTs inside the particle prevented this detachment because they interacted with the surface-active MWCNTs on the surface by the hydrophobic effect, as shown in **Fig. 8**. Hence, the surface coverage increased with the increasing amount of untreated MWCNTs inside the particle. Because the particle size was determined by the surface charge of the MWCNTs used to prepare the emulsion, the change was not detected as it was in Figure 4, in spite of the increased surface coverage.

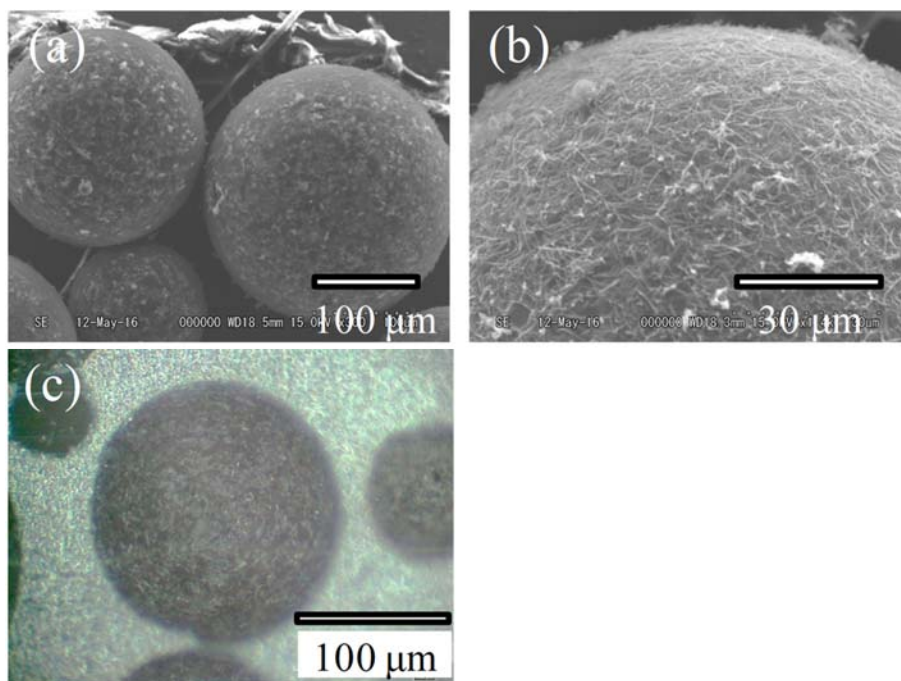


Fig. 6. (a and b) SEM images of the surface morphology of the synthesized composite particles and (c) optical microscope images of a cross section.

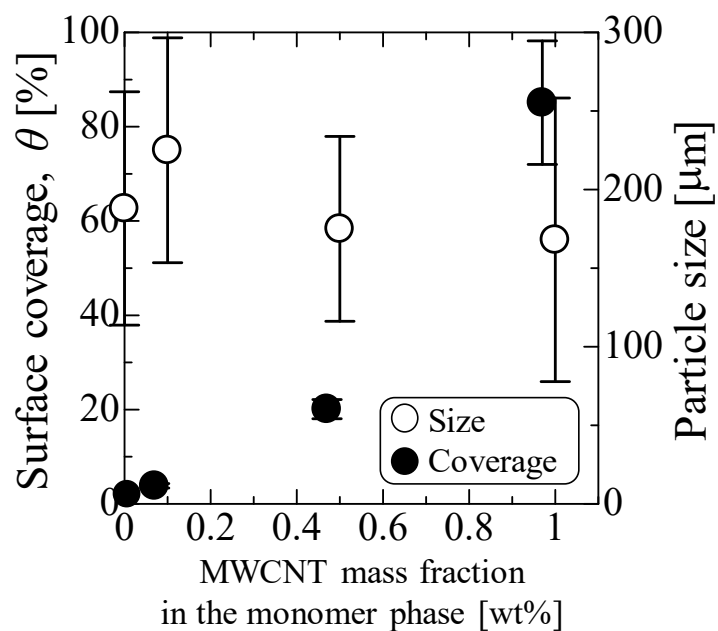


Fig. 7. Effect of the mass fraction of MWCNTs in the monomer phase on the surface coverage and size of the synthesized particles.

Table 2 Transmissivity of each supernatant liquid at a wavelength of 600 nm.

MWCNTs dispersed in water	MWCNTs on Surface ($\theta = 2.44\%$)	MWCNTs in Particle ($\theta = 85.1\%$)
8.3 %	41.7 %	63.5 %

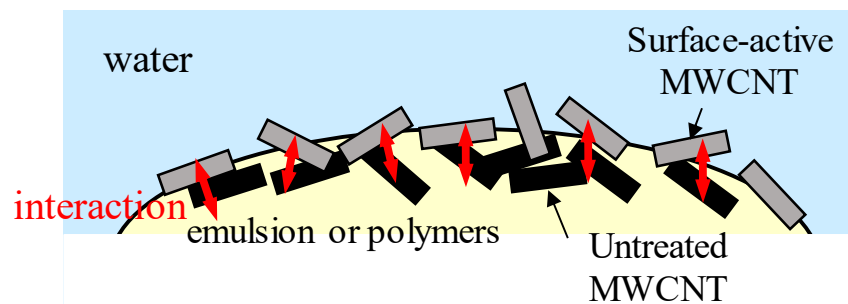


Fig. 8. Schematic illustration of the composite with high surface coverage using untreated MWCNTs in the monomer phase. The hydrophobic interactions between the surface-active and untreated MWCNTs worked to prevent the detachment of the surface-active MWCNTs from the surface.

3.4 Mechanical properties of the composite materials

To evaluate the mechanical properties of the synthesized composite particles, compaction tests were carried out using the micro compaction tester. The results are listed in **Table 3**. Only covering the composite surface with MWCNTs did not achieve large enhancement for mechanical properties. However, incorporating MWCNTs inside the composite particles and densely covering them significantly improved the mechanical properties, and MWCNTs worked well as fillers.

Table 3 Compressive modulus of each type of composite particle evaluated by compaction testing.

Sample	MWCNTs on Surface ($\theta = 2.44\%$)	MWCNTs on Surface ($\theta = 52.1\%$)	MWCNTs inside composite ($\theta = 85.1\%$)
Compressive modulus, K_{10} [kgf mm ²]	19-41	74-138	198-368

4. Conclusions

MWCNTs were surface-modified by acids to increase their hydrophilicity and stabilize their dispersion in water. The zeta potential was controlled by the treatment time. The surface-active MWCNTs in the aqueous phase enabled the formation of an aqueous Pickering emulsion. The surface charge of the modified MWCNTs greatly influenced the surface coverage and size of the composite particles. Upon heating, oil-soluble initiators in the monomer phase polymerized the emulsion droplets into solid composite polymer particles. When the monomer phase contained untreated MWCNTs, the surface coverage increased because interactions between MWCNTs inside and on the surface of the particles prevented the surface-active MWCNTs on the surface from being released into the bulk. As a result, the composite polymer particles were able to improve the mechanical properties because the MWCNTs worked well as fillers.

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