

Dispersion of Nano-materials in Polymer Composite Materials

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Abstract Polymer composites materials are the subject of extensive studies because of their novel properties compared with their constituent materials. Dispersion stability of sub-micron sized particles in the medium is important from the point of colloidal views. In the present study, dispersion of nano-materials in the matrix polymer is one of the most important problems to enhance their mechanical properties. We tackled this problem to carry out surface modification of the nano-materials, such as carbon nano tubes (CNTs), using amphiphilic polymers, poly-*N*-vinylacetamide (PNVA), synthesized thorough radical polymerization. Hydrogen bond worked between PNVA onto the modified nano-materials and hydrophilic matrix, such as polyvinyl alcohol (PVA), to enhance surface adhesions and dispersions of the nano-materials in the matrix. As a result, the mechanical properties of their composites materials were strengthened. When CNTs were used in PVA, the transparency of the composite was also increased due to improvement of their dispersions. In addition, if the CNTs formed the networks in the composites, the highly conductive and transparent polymer composite films were fabricated.

1 Introduction

Carbon nanotubes (CNTs) have excellent mechanical, thermal, and electrical properties, and are used as highly functional fillers in nanocomposites based on polymer resins (Han and Fina, 2011). Some researchers have reported the mechanical properties of composites of CNTs and polymers (Thostenson *et al.*, 2001; Tong *et al.*, 2007). Although CNTs have excellent mechanical properties, CNT-polymer composites have poor mechanical properties than those expected on the basis of the conventional complex law. To improve the mechanical properties of CNT-polymer composites, it is important to ensure both uniform dispersion of CNTs in the matrix of the resin and adequate surface adhesion between the two materials. Enomoto *et al.* showed that CNTs in a CNT-resin composite fail to withstand the tensile force; instead, they were pulled out of the resin at the time of fracture, owing to their poor adhesion to the resin (Enomoto *et al.*, 2005). Many methods have developed for the surface modification of CNTs using surfactants and polymers to improve adhesion between the CNTs and polymers (Vaisman *et al.*, 2006). In a recent study, a polymer colloidal technique was used for the surface modification of carbon fibers to enhance the yield stress and elastic modulus of carbon/poly(methylmethacrylate) composites (Yamamoto *et al.*, 2017). The method used in this study involves the facilitation of the adsorption of polymer particles on the surface of carbon fibers using electrodeposition or electrostatic interactions, to enhance

adhesion between the CNTs and the polymer, poly(vinyl alcohol) (PVA), and their dispersion in the PVA matrix. PVA was chosen as the polymer in this study, because it one of the polymers that has the advantages of easy handling and high safety and it is used in numerous applications.

In the present study, CNTs modified with polymer colloids were dissolved in a PVA solution, and a polymer composite film was fabricated from the solution through a casting method. The tensile strength of the polymer composite was measured using a tensile testing machine to investigate the influence of the surface modification technique using polymer colloids presented here in on the mechanical properties of the composite.

2 Experimental

CNTs (VGCF-H, Showa Denko K.K.) with a diameter of 150 nm and average fiber length of 9 μm were used as fillers in polymer composite films. The PVA resin (FUJIFILM Wako Pure Chemical Industry) was 98% hydrolyzed with the degree of polymerization ranging from 1500 to 1800. Polystyrene colloids were synthesized through emulsion polymerization. Water used in the synthesis was purified using a purification system, and nitrogen gas was bubbled through the water to remove dissolved oxygen. The styrene monomer (Tokyo Chemical Industry) was washed with a sodium hydroxide solution to remove inhibitors, and then purified through distillation under reduced pressure. PVA or *N*-vinylacetamide monomer (NVA, Showa Denko K.K.)

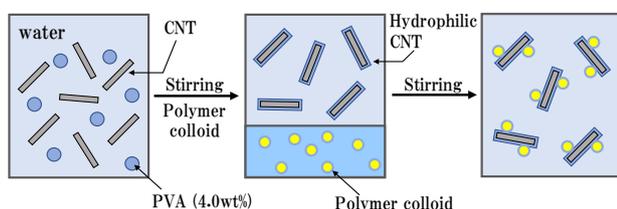
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were used as stabilizers of the synthesized emulsions and particles or CNTs. 2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, FUJIFILM Wako Pure Chemical Industry) was used as a radical initiator for the emulsion polymerization. Herein, VA-044 enabled the particles synthesized to be positively charged.

For carrying out the emulsion polymerization, 0.1 g of the styrene monomer, 0.1 g of PVA or NVA, and 5 mg of VA-044 were added to 15 mL of water. Then, the obtained solution was heated at 70 °C and stirred at 130 rpm for 360 min (EYELA, RCH-20L) (Toyoda *et al.*, 2019). The synthesized polystyrene (PSt) colloid was diluted 10 times with water before using for the surface modification of CNTs.

Next, 5–50 mg of CNTs and 1 g of PVA were dispersed in 15 mL of distilled water. The mixture was ultrasonicated for 3 min and stirred at 90°C for 180 min. Finally, the surfaces of CNTs were hydrophilized by PVA. Next, 9 mL of the PSt colloid (diluted 10 times) was added to the PVA/CNT solution with stirring at 400 rpm for 180 min to promote the adsorption of the PSt particles on the surface of the PVA/CNT through electrostatic interactions. The adsorption of PSt colloids on CNTs is schematized in Scheme 1. PVA/CNT composite films were fabricated by solution casting. PSt/PVA/CNT solutions were poured on a glass plate and heated on a hot plate at 70°C for 360 min to evaporate water. The fabricated films were subsequently dried at 80°C for 1 day in a vacuum oven.

The morphologies of the CNTs modified with polymer colloids were observed by scanning electron microscopy (SEM; JSM-7500FA, JEOL). Dynamic light scattering was performed with a ZETASIZER to evaluate the dispersion of CNTs in the PVA solution used to fabricate the composite film. The transmittance of the composite film was determined using an ultraviolet–visible (UV-Vis) spectrophotometer (V-650, JASCO) to quantitatively evaluate the dispersion of CNTs in the PVA composite film. The samples were cut into rectangle-shaped specimens, which were then irradiated with light at the wavelength of 400 nm. The transmittance is defined as the ratio of the transmitted light to incident light.



Scheme 1. Schematic showing the adsorption of polymer colloids onto CNTs.

The tensile strengths of the films were measured using a tensile testing machine (10073B, Japan High Tech). The specimens (30 mm gauge length, 3 mm width) were loaded at a crosshead speed of 17 μm/min. The tensile strengths of the films were calculated using Equation (1):

$$\sigma_d = \frac{F_{Max} \times 10^6}{a \times b} \quad (1)$$

where σ_d [MPa] is the tensile strength, a and b [mm] are the width and thickness of the specimen, respectively, F_{Max} [N] is the maximum load.

3 Results and Discussion

3.1 Surface modification of CNTs by polymer colloids

The surface of CNTs was covered with PVA through hydrophobic interactions between CNTs and the hydrophobic parts of PVA. After modification, the CNTs showed hydrated and hydration layers formed around their surfaces. Therefore, their zeta potential was measured to be -9.3 mV and their dispersion stability was good because of the steric effects. PSt particles with positive charges induced by VA-044 and PNVA or PVA were adsorbed on the surface of the CNTs through electrostatic interactions. As a result, the CNTs coated with PSt colloids could be dispersed in water owing to the electrical repulsive forces between them.

In general, electrostatic interactions are used to promote the adsorption of polymer colloids on CNTs. Although the counter-charges developed through the adsorption lowered the dispersion stability of the CNTs in water, according to the Derjaguin-Landau-Verwey-Overbeek theory, PVA enabled the maintenance of the dispersion stability through the hydration layers. The sustenance of the black color of suspensions is attributed to the dispersion of CNTs for longer periods, indicating their good dispersion stability. Thus, the modification of the CNT surface with PVA facilitated *in situ* adsorption of polymer colloids on the CNTs. In a recent study, the surface modification of CNTs with PNVA was achieved by the same mechanism (Yamamoto *et al.*, 2017). The synthesized PSt particles, which were coated with PNVA or PVA, served as carriers of PNVA or PVA to be coated onto CNTs. Figure 1 shows the SEM images of the polymer colloids and CNTs modified with the polymer colloids. The images confirm that the CNTs are coated with the polymer colloids.

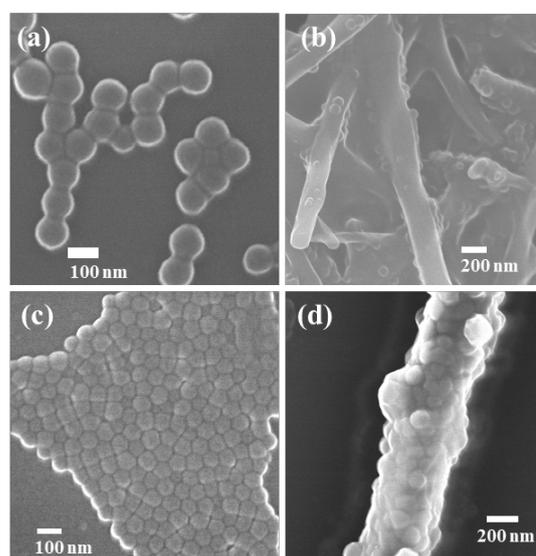


Figure 1. SEM images of (a) PVA/PSt colloid; (b) PVA/PSt/CNT; (c) PNVA/PSt colloid; (d) PNVA/PSt/CNT. ((d) Reprinted with permission from Ref. (Toyoda and Yamamoto, 2018). Copyright: (2018) Elsevier B.V.)

3.2 Effect of the surface modification of CNTs by polymer colloids on the dispersion of CNTs in a PVA solution or PVA composite film

Figure 2 shows the apparent cumulative size distributions of CNTs with and without PNVA/PSt colloids in a PVA solution determined with a ZETASIZER. When the CNTs were modified with PNVA/PSt colloids, their dispersion stabilities were found to be extremely good in the PVA solution because the sizes of the CNTs modified with PNVA/PSt colloids were much smaller than those of unmodified CNTs. The polymer colloids played an important role in facilitating electrostatic repulsive forces between the particles to prevent the coagulation of the CNTs or spacers. Consequently, they did not settle down but remained in the dispersed state in the PVA solution.

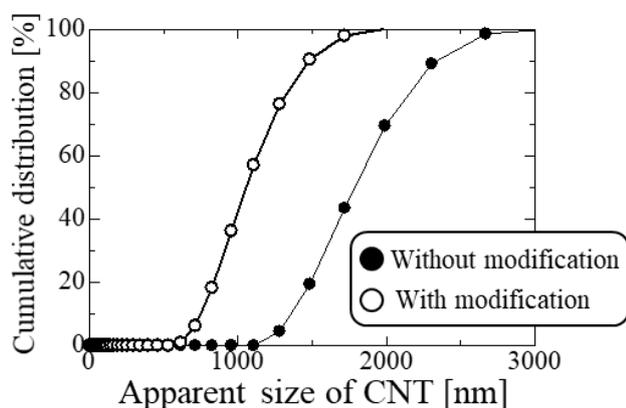


Figure 2. Influence of CNT surface modification with polymer colloids on the apparent cumulative size distribution of the CNTs in a PVA solution

Figure 3 shows the optical micrographs of the PVA composite film. CNTs modified with polymer colloids, the weight ratio of which with respect to PVA was determined to be 1.3 wt%, were well dispersed throughout the PVA resin because the adsorbed polymer colloids acted as spacers between the CNTs during the drying process at 70 °C, thus improving their diffusion. On the other hand, many agglomerates were observed due to the π - π stacking between CNTs when untreated CNTs were used, as shown in Figure 3a.

The UV-Vis transmittance of the PVA composite film was measured to quantitatively evaluate the dispersion of CNTs in the PVA resin. Figure 4 shows the influence of the polymer colloid adsorbed on CNTs on the transparency of PVA composite films. The transmittance of pure PVA film was found to be 100%. Because light does not penetrate the CNTs, transmittance of the PVA composite film depends on the sampling location when CNTs without modification are poorly and unevenly dispersed in the matrix of the resin. Therefore, samples

with poorly dispersed CNTs showed large variation in the measured transmittance. On the other hand, with the uniform dispersion of CNTs modified with polymer colloids in the matrix of the resin, as shown in Figure 3b, there is low variation in transmittance depending on sampling points. The variation in the transmittance was found to be greater than 20% in the cases of untreated CNTs (PVA/U-CNT) or PSt (PSt/CNT), which is higher compared to the transmittances of 10.3% and 6.5% of CNTs modified with PVA-PSt (PVA-PSt/CNT) or PNVA-PSt (PNVA-PSt/CNT) colloids, respectively. Hence, surface modification with PVA-PSt or PNVA-PSt improved the dispersion of CNTs within the PVA resin.

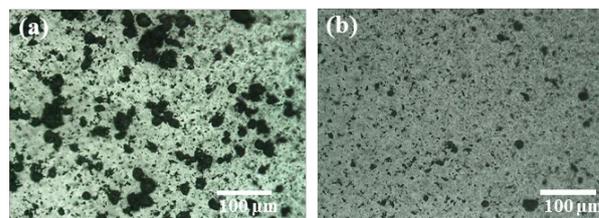


Figure 3. Observation of the dispersion state of CNTs in PVA composites by optical microscopy: (a) Composite with unmodified CNTs; (b) composite with surface-modified CNTs (the surface was modified with a polymer colloid). (Reprinted with permission from Ref. (Toyoda and Yamamoto, 2018). Copyright: (2018) Elsevier B.V.)

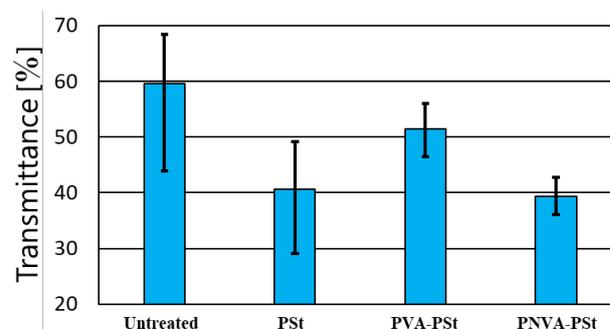


Figure 4. Influence of the polymer colloid adsorbed on CNTs on the transparency of the PVA composite film

The present surface modification using electrostatic interaction between the polymer colloids and the hydrophilic CNT surface enabled uniform diffusion of CNTs throughout the PVA resin, because the polymer colloids on CNTs played the important role of a spacer between CNTs to prevent their re-aggregation when the CNT dispersion was dried to fabricate the PVA composite film.

3.3 Effect of the surface modification of CNTs by polymer colloids on the tensile strength of PVA composite films

Figure 5a shows that the addition of only 2 wt% of untreated CNTs (U-CNTs) or PNVA-PSt colloids did not improve the tensile strength of the PVA films remarkably, as compared to the films of PVA/PNVA-PSt colloid, PVA/U-CNT, and PVA only. The effect of PNVA-PSt colloids on tensile strength of the film was found to be

negligible because their amount was very small and the dispersion of CNTs was not uniform in the PVA resin, owing to their agglomeration. Conversely, as shown in Figure 5a, enhanced tensile strength was observed for composite films based on CNTs/PVA-PSt or CNTs/PNVA-PSt. Because surface modification with polymer colloids improved the dispersion of CNT in the PVA matrix and surface adhesion between CNTs and PVA (Yamamoto *et al.*, 2017), the CNTs worked as nano-fillers in the composite, thus improving the tensile strength.

Figure 5b shows the influence of the mass fraction of CNTs on the tensile strength of PVA/U-CNTs and PVA/CNTs/PNVA-PSt films. Surface modification with polymer colloids improved the surface adhesion of CNTs. In the case of PVA/U-CNTs, tensile strength did not increase with the mass fraction of CNTs. No change, in a previous study on tensile strength, was observed with the addition of CNTs to the resin, because of the sizes of CNTs (Andrews and Weisenberger, 2004). In the case of PVA/CNT/PNVA-PSt, the tensile strength was enhanced as the mass fraction of CNTs was increased up to 5 wt%. Kobayashi *et al.*, in a previous report, showed some CNT aggregates formed at CNT fractions >3 wt% (Kobayashi *et al.*, 2007). In cases where CNT was poorly dispersed in the PVA resin, stress concentrated at points where CNTs aggregated, which led to crack formation. In this study, the significant influence of CNTs was observed even at 5 wt%, because of their surface modification using polymer colloids, which led to both good dispersion of CNTs in the PVA matrix and adhesion between CNTs and PVA. Because the variation in the tensile strength of PVA films with PNVA-PSt/CNT is small, we conclude that the dispersion of CNTs is very uniform in the PVA resin (Toyoda and Yamamoto, 2018).

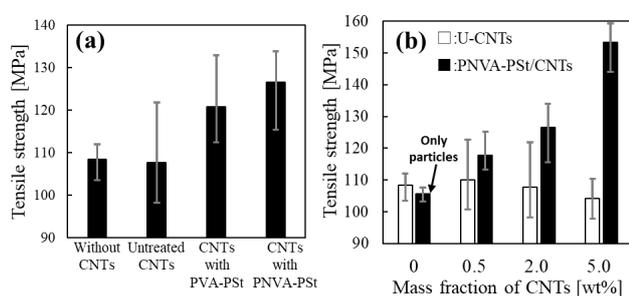


Figure 5. Influence of (a) polymer colloids adsorbed on the CNTs and (b) CNT content on the tensile strength of the PVA composite. (Reprinted with permission from Ref. (Toyoda and Yamamoto, 2018). Copyright: (2018) Elsevier B.V.)

4 Conclusions

A method was developed for the surface modification of CNTs using polymer colloids synthesized by the polymerization of styrene using PVA or NVA. This surface modification enhanced the tensile strength of PVA composite films with modified CNTs. CNTs were first modified with PVA to achieve *in situ* adsorption of polymer colloids on their surfaces. Because the polymer colloids adsorbed on the CNTs acted as spacers between

CNTs and the adhesion of CNTs to the PVA resin was enhanced owing to interaction between PVA and PNVA on the surface of CNTs, the modified CNTs were dispersed uniformly throughout the PVA film. The addition of CNTs modified with polymer colloids increased the tensile strength of the composite PVA film. Similarly, if other nanomaterials modified with polymer colloids are applied to other polymer resins, and the mechanical properties of the composite materials would be enhanced.

Acknowledgements

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