# Dispersion of Carbon Nanofibers Modified with Polymer Colloids to Enhance Mechanical Properties of PVA Nanocomposite Film

Author Names. Naoya Toyoda, Tetsuya Yamamoto*

Author Address. Department of Materials Design Innovation Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

Corresponding Author. Phone: +81-52-789-3378

E-mail: yamamoto.tetsuya@material.nagoya-u.ac.jp

## Abstract

Polymer colloids were used to modify the surface of carbon nanofibers (CNFs), to enhance the mechanical properties of polyvinyl alcohol (PVA) resin/CNF nanocomposite materials prepared by the solution casting method. However, the CNFs showed uneven dispersal within, and adhesion to, PVA resin.

In the present study, the colloidal technique using polymer particles was applied to achieve more uniform dispersion of CNFs in PVA resin. This results in the polymeric particles functioning as spacers, thereby inhibiting CNF clustering; and in hydrogen bonding between PVA and polymer particles, thereby increasing surface adhesion between CNF and PVA. Polymer colloids prepared by the emulsion polymerization of styrene and *N*-vinylacetamide showed particularly notable enhancements of dispersion and surface adhesion in the composites. Consequently, PVA composite film containing uniformly distributed CNFs showed significantly enhanced tensile strength and modulus even at CNF mass fraction of 5.0 wt%.

**Keywords:** Polymer colloid, Nanocomposite film, Carbon nanofiber, Dispersion

## 1. Introduction

Carbon nanotubes (CNTs) are one of the most promising nanomaterials for use as high-functional filler in nanocomposite materials using a matrix resin as a base material, due to their unique electrical, thermal, and mechanical properties [1]. Several studies have examined the mechanical properties of CNT composite materials using matrix resin [2-4]. Single- and multi-walled CNTs, as well as vapor-grown carbon nanofibers (CNFs) are promising materials for reinforcing various polymer matrixes. Among these matrixes, polyvinyl alcohol (PVA) is a hydrophilic polymer that has wide applications and provides benefits of low cost, good safety, and easy handling. CNFs have excellent mechanical properties, such as exceptionally high axial strength and an axial Young's modulus of the order of several hundred GPa [5-7]. However, to date, the mechanical strengths of CNF composite materials have been lower than expected according to this complex law. To obtain CNF composite polymer materials with high mechanical properties, it is necessary to achieve uniform dispersal of CNFs within the resin and ideal surface adhesion between these components. In actual CNF polymer composite materials, CNFs were not uniformly dispersed in the matrix resin. Furthermore, CNFs did not carry a tensile force but instead were pulled out of the resin at the time of fracture due to poor adhesion to the resin [8]. To resolve these problems, many studies have presented methods for modifying the CNF surface using surfactants [9-12], polymers [13-15], and metallic complexes [16, 17].

Our recent study used polymer colloids to modify the surface of carbon materials, thereby enhancing the mechanical properties of carbon/polymeric composites [18-20]. Our methods involved the adsorption of polymer particles onto the surface of carbon materials by electrostatic interaction or electrodeposition, to improve their dispersion in resin and their adhesion to the polymer. In this study, CNTs modified with polymer colloids were dissolved in PVA solution, and a composite film was obtained from the solution by the casting method [21, 22]. The mechanical properties of the composite film were measured by a tensile test-rig to evaluate the effectiveness of the proposed surface modification technique using polymer colloids through emulsion polymeriztaion.

## 2. Experimental

### *2.1 Materials*

CNFs, vapor-grown carbon fiber (VGCF-H, Showa Denko K.K.) with average fiber length of 9 μm and diameter of 150 nm, were used as fillers in the composite films. The PVA (Wako Pure Chemical Industry) matrix resin was 98% hydrolyzed with degree of polymerization from 1500 to 1800. Polymer colloids were prepared by emulsion polymerization using the following materials. The water used in the emulsion was purified using a purification system (WG250, Yamato Scientific), and nitrogen gas was then bubbled through the water to remove any dissolved oxygen. Styrene monomers (Tokyo Chemical Industry) were washed four times with 10% sodium hydroxide solution to remove polymerization inhibitors, and then purified by distillation under reduced pressure [23]. PVA or *N*-vinylacetamide (NVA, Showa Denko K.K.) was used to stabilize the monomer emulsion and synthesized particles. The chemical structures of PVA and PNVA are shown in **Fig. 1**. 2,2′-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, Sigma Aldrich Co. LLC) was used as a radical initiator for the present emulsion polymerization without further purification. VA-044 enabled the particles synthesized by polymerization to be positively charged.

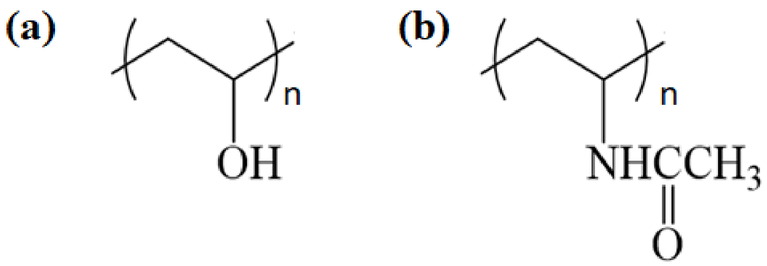


**Fig. 1.** Chemical structures of: (a) PVA; (b) PNVA.

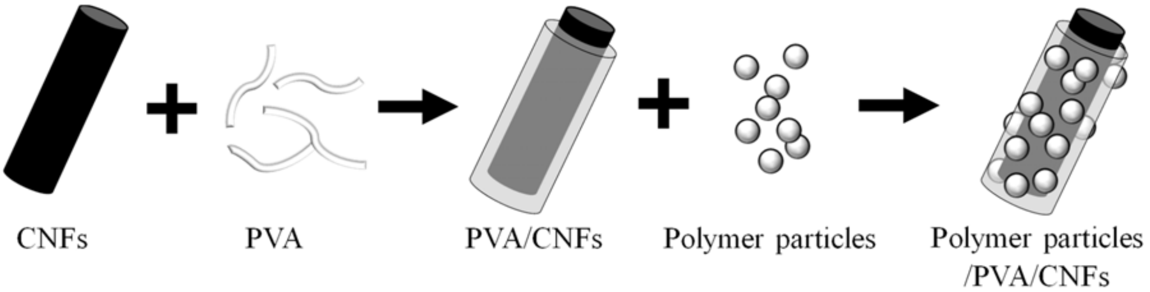
*2.2 Preparation of composite films*

For preparation of the polystyrene (PSt) colloid through the emulsion polymerization, 0.1 g of styrene monomer, 5 mg of VA-044, and 0.1 g of PVA or NVA were added to 15 mL of purified water, and the solutions were heated at 70 °C and stirred at 130 rpm for 6 h (EYELA, RCH-20L). The prepared PSt colloid was diluted 10 times with distilled water to make the CNFs modified. **Table 1** shows the zeta potentials and particle sizes of the synthesized PSt particles, measured by a ZETASIZER (Nano-ZS, MALVERN) and scanning electron microscope (FE-SEM; JSM-7500FA, JEOL), respectively [24]. pHs of the colloid solutions were measured to be from 4.88 to 5.85 by a pH meter (LAQUA F-72, HORIBA).

**Table 1** Characterization of the synthesized polymer particles.
Particle sizes were measured by FE-SEM.

| | PVA/PSt | PNVA/PSt |
|---|---|---|
| Zeta potential [mV] | 1.03 | 31.2 |
| Particle size [nm] | 72 | 69 |

Then, 1 g of PVA and 5~50 mg of CNFs were dissolved in 15 mL of distilled water. The mixture was ultrasonicated for 3 min and stirred at 90 °C for 3 h. Finally, the CNF surfaces were hydrophilized by PVA. Next, 9 mL of each PSt colloid with 10 times diluted was added to the PVA/CNFs solutions under stirring at 400 rpm for 3 h to promote the adsorption of the PSt particles onto the surfaces of the PVA/CNFs through electrostatic interactions. The morphologies of the CNFs modified with polymer particles were examined using a field emission scanning electron microscope (FE-SEM; JSM-7500FA, JEOL) and transmission electron microscopy (TEM, JEM-2100F/HK, JEOL). **Scheme 1** shows the adsorption of polymer particles onto CNFs. PVA/CNF composite film was prepared by the solution casting method. PSt/PVA/CNF solutions were poured onto a clean glass plate, and only water was evaporated on a hot plate (HPR-4030, AS ONE) at 70 °C for 6 h. The synthesized film was then dried at 80 °C for 24 h in a vacuum oven (AVO-200NS, ETTAS).



**Scheme 1** Mechanism for adsorption of polymer particles onto CNFs.

### *2.3 Evaluation of CNF dispersion in the PVA solution and composite film*

The dispersion of CNFs in the PVA solution used to produce the composite film was evaluated by dynamic light scattering method using a ZETASIZER (Nano-ZS, MALVERN), and dispersion in the PVA composite film was evaluated quantitatively using an ultraviolet–visible spectrophotometer (UV-Vis, V-650, JASCO Corporation). Cutting at 5 places with a square of 2 cm from a composite film with a circle diameter of 10 cm to obtain the specimens, the specimens of the composite films were irradiated with light at a wavelength of 400 nm, and the transmittance was calculated as the ratio of transmitted light to incident light.

### *2.4 Tensile tests of the composite film*

The tensile strengths of the films were determined at room temperature using a small tensile testing machine (10073B, JAPAN HIGH TECH). The specimens (3 mm width, 30 mm gage length) were loaded at a crosshead speed of 17 μm/min. The mechanical properties were calculated from the following equations:

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

where $\sigma_d$ [MPa]: tensile strength, $F_{Max}$ [N]: maximum load, and $a$, $b$ [mm]: thickness and width of the specimen, respectively; and

$$Y = {\Delta\sigma \times 10^{-3}}/{\Delta\varepsilon} \qquad (2)$$

where $Y$ [GPa]: tensile modulus, $\Delta\sigma$ [MPa]: stress difference in a certain section, and $\Delta\varepsilon$ [-]: distortion difference of a certain section.

## 3. Results and Discussion

### *3.1 Adsorption of polymer particles onto CNFs*

At first, the surfaces of CNFs were coated with PVA through hydrophobic interactions between CNFs and the hydrophobic parts of the PVA. Thus, the surfaces of CNFs were hydrated and created hydration layers that showed low surface potential (-9.33 mV) but good dispersion stability due to their steric effects. Secondary, positively charged PSt particles by VA-044 and PVA or PNVA, as listed in **Table 1**, were adsorbed onto the surfaces of the CNFs by electrostatic interactions. Finally, the CNFs covered with PSt particles were dispersed in water by electrical double layers. Normally, electrostatic interactions were utilized to encourage polymer particles to adsorb onto the CNFs. However, the counter-charges for the adsorption decreased the dispersion stability of the CNFs in water on the basis of DLVO theory [25]. However, PVA helped maintain the dispersion stability of the CNFs in water by means of the hydration layers, even when positively charged PSt colloids were added to the system. The suspension colors remained black originated from the CNFs for longer, indicating their good dispersion stabilities. Thus, PVA coating achieved in-situ adsorption of polymer colloids onto CNFs. In the case of PNVA, the surface modification of CNFs was also achieved by the same mechanism in our resent study [18]. PSt particles, which were covered with PVA or PNVA, functioned as carriers of PVA or PNVA to CNFs. **Fig. 2** shows FE-SEM and TEM images of CNFs modified with polymer particles. It was clear that the CNFs were covered with the polymer colloids.

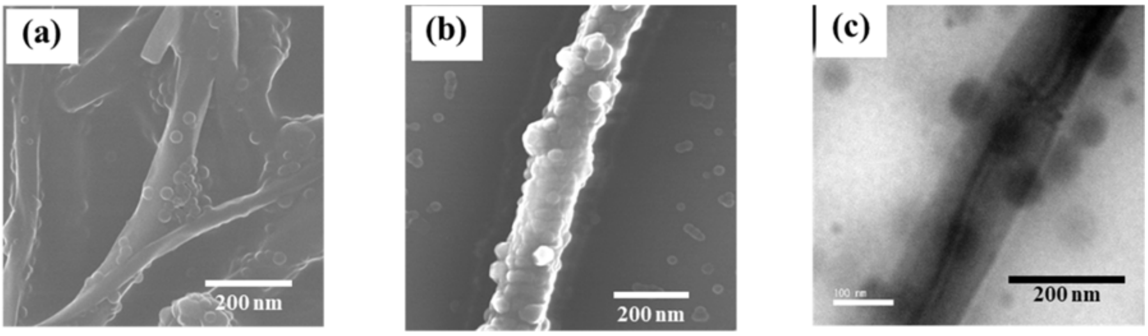


**Fig. 2.** Images of CNFs modified with the following polymer particles: (a) PVA/PSt by FE-SEM; (b) PNVA/PSt by FE-SEM; (c) PNVA/PSt by TEM.

*3.2 Dispersion of CNFs in the PVA solution or PVA composite film.*

**Fig. 3** shows the apparent size distributions of CNFs with and without PNVA/PSt particles in the PVA solution using water estimated by a ZETASIZER. As a result, the CNFs modified with PNVA/PSt particles maintained good dispersion stability in the PVA solution because the sizes of the CNFs modified with PNVA/PSt particles were much smaller than those of the unmodified CNFs. Here, the particles played an important role as spacers or origins of the electrical repulsive forces between the particles to prevent the coagulations between the CNFs, because they were not dissolved but kept a solid state in the PVA solution.

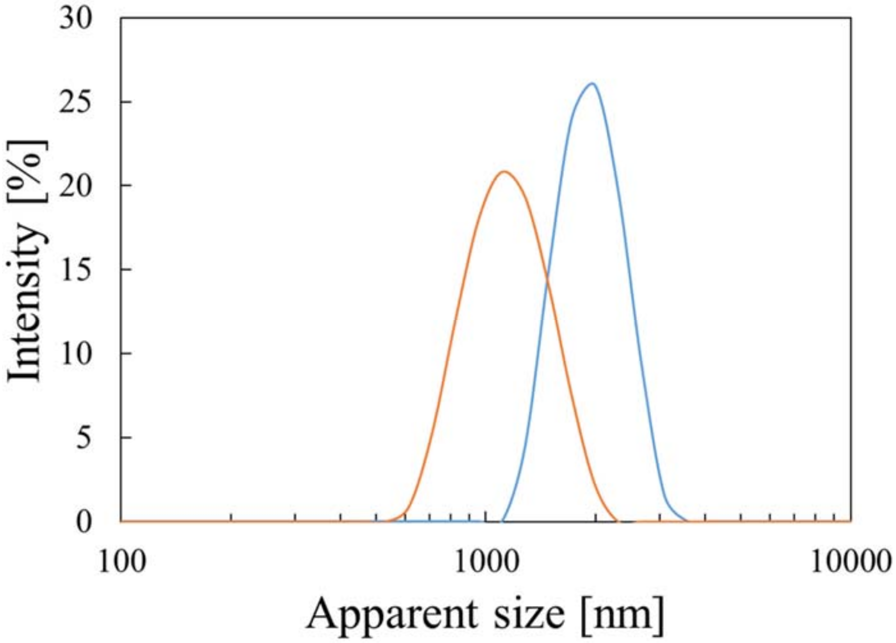


**Fig. 3.** Effect of surface modification with particles on apparent size distribution of the CNF in the PVA solution.

**Fig. 4** shows images of CNFs in the PVA composite film obtained by optical microscope (KH-8700, HiROX). CNFs with adsorbed polymer particles, whose weight ratio to PVA was measured to be 1.3 wt%, were well dispersed and diffused throughout the PVA resin, and few agglomerates were observed compared with untreated CNFs. This was because the adsorbed polymer particles functioned as spacers between the CNFs during the drying process at 70 °C, promoting their diffusion [19]. To quantitatively evaluate the dispersion of

CNFs in the PVA resin, the UV–Vis transmittance of the composite film was measured. The light did not penetrate the CNFs, since they are a perfectly black material. The transmittance of pure PVA film was found to be 100%. When CNFs were poorly dispersed in the resin, the amount of CNFs present varied according to the sampling location. Thus, transmittance was low for points containing many CNFs, and higher for those containing fewer CNFs. Therefore, samples with unevenly dispersed CNFs showed large variation in measured transmittance. Conversely, with uniform dispersion of CNFs within the resin, there is less variation in the CNF content between sampling points, and hence small variation in transmittance. **Fig. 5** shows the transmittance measurements for the PVA composite film. The variation in transmittance was 25% when using untreated CNFs (PVA/U-CNF), compared with 10.3% and 6.5% for CNFs modified with PVA-PSt (PVA-PSt/CNF) or PNVA-PSt (PNVA-PSt/CNF) particles, respectively. Surface modification by polymer colloid therefore enhanced the dispersion of CNFs within PVA resin. The CNFs covered with PSt particles were dispersed in water due to electrical double layers [18], and also in the PVA films prepared by casting the suspension.

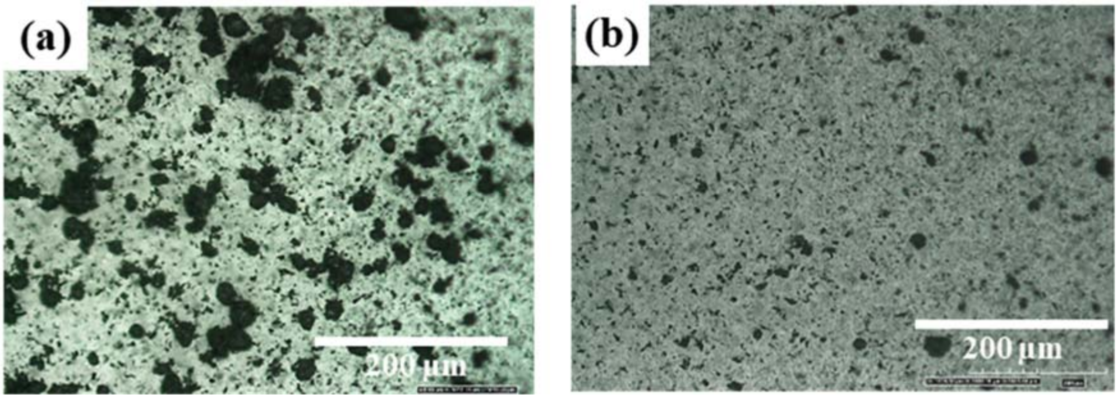


**Fig. 4.** Optical microscope images of composite films to evaluate dispersion of CNFs in PVA resin: (a) CNFs without modification; (b) CNFs modified with adsorbed polymer particles.

Normally, CNFs formed reagglomerations due to the π-π interaction and the van der Waals forces between CNFs during evaporation of the solvent from the CNF dispersion by heating. Hence, coagulations of CNFs were observed in the PVA resin, as shown in **Fig. 4a**. The proposed surface modification using electrostatic interaction between the polymer particles and the hydrophilic CNFs surface enabled uniform diffusion of CNFs throughout the PVA resin, as the adsorbed particles acted as a spacer between CNFs to prevent their reaggregation even during drying of the CNF dispersion in the casting method.

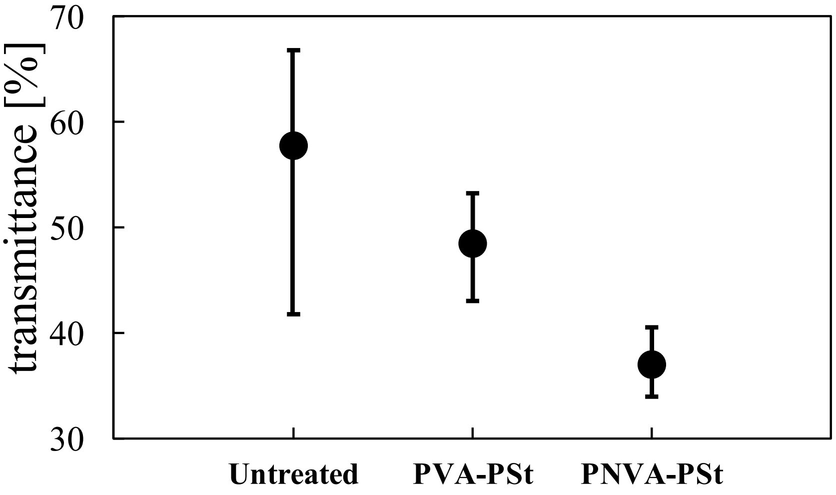


**Fig. 5.** Effect of particle type adsorbed onto CNFs, on the transmittance of PVA composite film.

### *3.3 Mechanical properties of the PVA composite films*

As shown in **Fig. 6a**, the addition of only PNVA-PSt particles or 2 wt% U-CNFs did not change the tensile strength of the PVA films markedly, when comparing PVA/ PNVA-PSt particles, PVA/U-CNF film, and PVA film without CNFs. This was because the amount of PNVA-PSt particles in the film was so small that their influence on tensile strength was negligible; and the CNFs were not uniformly dispersed in the resin but agglomerated, and did not carry a tensile force but instead pulled out of the resin at the time of fracture due to poor adhesion to the resin [8]. In contrast, both tensile strength in **Fig. 6a** and tensile modulus in **Fig. 6b** were significantly improved in composite film using CNFs/PVA-PSt or CNFs/PNVA-PSt. CNF dispersion in the PVA, and surface adhesion between CNFs and PVA were enhanced by surface modification using polymer particles (See Supporting Information) , so that the CNFs showed a significant effect when tensile stress was applied to the films.

**Fig. 7** shows the influence of mass fraction of CNFs on mechanical properties of PVA/U-CNFs and PVA/CNFs/PNVA-PSt films. Tensile modulus increased with mass fraction of CNFs as a result of the high tensile modulus of CNFs. Surface modification with polymer particles enhanced surface adhesion, and then tensile modulus. In the case of PVA/U-CNFs, tensile strength did not change as the mass fraction of CNFs increased. A previous study reported no change in tensile strength even with the addition of CNFs to the resin, due to the small sizes of CNFs [26]. In the case of PVA/CNFs/PNVA-PSt, tensile strength increased as the mass fraction of CNFs increased up to 5 wt%. In a previous study, some CNF aggregations formed at CNF fractions >3 wt% [27]. With poor CNF dispersion within the resin, stress concentrated at points of CNF aggregations, leading to crack formation. In the present study, the effect of CNFs was significant even at 5 wt% by the present polymer colloidal technique. This was because both dispersion in the PVA and adhesion between CNFs and PVA were greatly improved by the treatment using polymer particles [20, 28, 29]. From the small variation in the mechanical properties of the PNVA-

PSt/CNF samples (see Fig. 7), it was clear that the CNFs were very uniformly dispersed within the PVA resin.

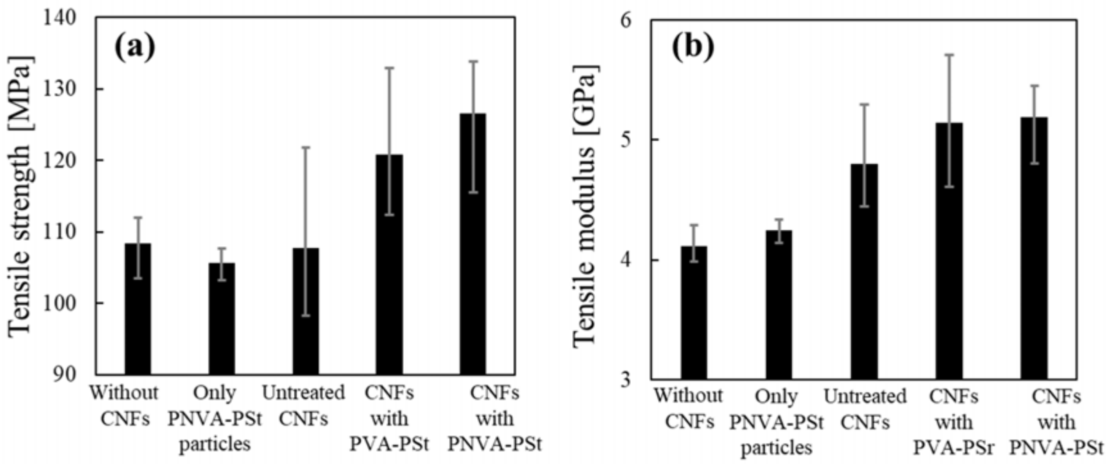


**Fig. 6.** Mechanical properties of PVA composite film containing 2 wt% CNFs with surface modification: (a) tensile strength; (b) tensile modulus.

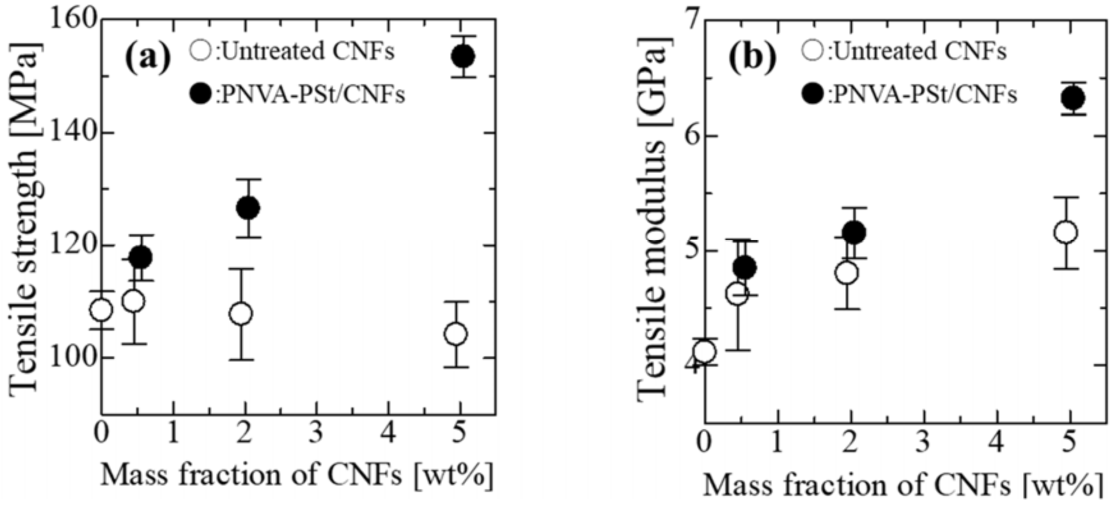


**Fig. 7.** Influence of CNF mass fraction on mechanical properties of PVA composite films: (a) tensile strength; (b) tensile modulus.

## 4. Conclusions

This study presents a method for modifying the surface of CNFs, via polymer colloid obtained through emulsion polymerization using PVA or NVA, which improved the mechanical properties of PVA composite films containing the modified CNFs. In-situ adsorption of polymer particles onto CNFs modified with PVA was conducted. The modified CNFs were dispersed uniformly throughout the PVA resin because the polymer particles adsorbed onto the CNFs functioned as spacers between CNFs, and because CNF surface adhesion to the PVA was significantly improved between PVA and PNVA. The addition of the CNFs modified with polymer colloids enhanced both the tensile strength and modulus of the composite PVA film. When this technique is applied to the fillers in other polymer composite materials, the mechanical properties of the composite materials would be expected to be strengthened.

## Supporting Information

Surface adhesion between carbon material and PVA film was evaluated by the fragmentation test, as shown in **Fig. S1**, and the mechanism is illustrated by **Fig. S2** in the supporting information.

## Acknowledgement

This study was supported financially in part by Hosokawa Powder Technology Foundation. The CNFs and NVA monomers were provided by SHOWA DENKO K.K. The measurements by ultraviolet–visible spectrophotometer were carried out at the instrumental analysis center, Nagoya University.

## References

[1] S. Iijima, Helical microtubules of graphitic carbon, Nature, 354 (1991) 56-58.
[2] E.T. Thostenson, Z.F. Ren, T.W. Chou, Advances in the science and technology of carbon nanotubes and their composites: a review, Compos Sci Technol, 61 (2001) 1899-1912.
[3] J.N. Coleman, M. Cadek, R. Blake, V. Nicolosi, K.P. Ryan, C. Belton, A. Fonseca, J.B. Nagy, Y.K. Gun'ko, W.J. Blau, High Performance Nanotube-Reinforced Plastics: Understanding the Mechanism of Strength Increase, Advanced Functional Materials, 14 (2004) 791-798.
[4] X. Tong, J. Zheng, Y. Lu, Z. Zhang, H. Cheng, Swelling and mechanical behaviors of carbon nanotube/poly(vinyl alcohol) hybrid hydrogels, Materials Letters, 61 (2007) 1704-1706.
[5] M.M.J. Treacy, T.W. Ebbesen, J.M. Gibson, Exceptionally high Young's modulus observed for individual carbon nanotubes, Nature, 381 (1996) 678-680.
[6] E.W. Wong, P.E. Sheehan, C.M. Lieber, Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes, Science, 277 (1997) 1971-1975.
[7] P. Poncharal, Electrostatic Deflections and Electromechanical Resonances of Carbon Nanotubes, Science, 283 (1999) 1513-1516.
[8] K. Enomoto, T. Yasuhara, N. Ohtake, Mechanical Properties of Injection-Molded Composites of Carbon Nanofibers in Polypropylene Matrix, New Diam Front C Tec, 15 (2005) 59-72.
[9] R. Rastogi, R. Kaushal, S.K. Tripathi, A.L. Sharma, I. Kaur, L.M. Bharadwaj, Comparative study of carbon nanotube dispersion using surfactants, J Colloid Interface Sci, 328 (2008) 421-428.
[10] L. Vaisman, H.D. Wagner, G. Marom, The role of surfactants in dispersion of carbon nanotubes, Adv Colloid Interface Sci, 128-130 (2006) 37-46.
[11] Y. Geng, M.Y. Liu, J. Li, X.M. Shi, J.K. Kim, Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites, Composites Part A: Applied Science and Manufacturing, 39 (2008) 1876-1883.
[12] B. Krause, M. Mende, P. Pötschke, G. Petzold, Dispersability and particle size distribution of CNTs in an aqueous surfactant dispersion as a function of ultrasonic treatment time, Carbon, 48 (2010) 2746-2754.
[13] S. Manivannan, I.O. Jeong, J.H. Ryu, C.S. Lee, K.S. Kim, J. Jang, K.C. Park, Dispersion of single-walled carbon nanotubes in aqueous and organic solvents through a polymer wrapping functionalization, Journal of Materials Science: Materials in Electronics, 20 (2008) 223-229.
[14] Y. Tsutsumi, T. Fujigaya, N. Nakashima, Polymer synthesis inside a nanospace of a surfactant–micelle on carbon nanotubes: creation of highly-stable individual nanotubes/ultrathin cross-linked polymer hybrids, RSC Advances, 4 (2014).

[15] A. Star, D.W. Steuerman, J.R. Heath, J.F. Stoddart, Starched carbon nanotubes, Angew Chem Int Ed Engl, 41 (2002) 2508-2512.
[16] K. Nobusawa, A. Ikeda, J. Kikuchi, S. Kawano, N. Fujita, S. Shinkai, Reversible solubilization and precipitation of carbon nanotubes through oxidation-reduction reactions of a solubilizing agent, Angewandte Chemie, 47 (2008) 4577-4580.
[17] K. Nobusawa, A. Ikeda, Y. Tanaka, M. Hashizume, J. Kikuchi, M. Shirakawa, T. Kitahara, N. Fujita, S. Shinkai, Angle-controlled arrangement of single-walled carbon nanotubes solubilised by 8-quinolinol metal chelate derivatives on mica, Chemical communications, (2008) 1801-1803.
[18] T. Yamamoto, N. Toyoda, In-situ Adsorption of Polymer Particles on Multi-wall Carbon Nanotubes Using Colloidal Techniques, Colloid and Interface Science Communications, 20 (2017) 1-4.
[19] T. Yamamoto, Y. Makino, K. Uematsu, Improved mechanical properties of PMMA composites: Dispersion, diffusion and surface adhesion of recycled carbon fiber fillers from CFRP with adsorbed particulate PMMA, Advanced Powder Technology, 28 (2017) 2774-2778.
[20] T. Yamamoto, K. Uematsu, T. Irisawa, Y. Tanabe, Controlling of the interfacial shear strength between thermoplastic resin and carbon fiber by adsorbing polymer particles on carbon fiber using electrophoresis., Compos Part a-Appl S, 88 (2016) 75-78.
[21] E. Otsuka, A. Suzuki, Swelling Properties of Physically Cross-linked PVA Gels Prepared by a Cast-drying Method, Prog Coll Pol Sci S, 136 (2009) 121-+.
[22] Y. Li, T. Yang, T. Yu, L. Zheng, K. Liao, Synergistic effect of hybrid carbon nantube–graphene oxide as a nanofiller in enhancing the mechanical properties of PVA composites, Journal of Materials Chemistry, 21 (2011).
[23] T. Yamamoto, K. Kawaguchi, Effect of electrolyte species on size of particle through soap-free emulsion polymerization of styrene using AIBN and electrolyte, Colloid Polym Sci, 293 (2015) 1003-1006.
[24] T. Yamamoto, Soap-free emulsion polymerization of aromatic vinyl monomer using AIBN, Colloid Polym Sci, 290 (2012) 1833-1835.
[25] E.J.W. Verwey, Theory of the Stability of Lyophobic Colloids, The Journal of Physical and Colloid Chemistry, 51 (1947) 631-636.
[26] R. Andrews, M.C. Weisenberger, Carbon nanotube polymer composites, Current Opinion in Solid State and Materials Science, 8 (2004) 31-37.
[27] H. Kobayashi, M. Shioya, T. Tanaka, T. Irisawa, Synchrotron radiation small-angle X-ray scattering study on fracture process of carbon nanotube/poly(ethylene terephthalate) composite films, Compos Sci Technol, 67 (2007) 3209-3218.

[28] T. Yamamoto, K. Uematsu, T. Irisawa, Y. Tanabe, Enhancement of surface adhesion between thermoplastic resin and carbon fiber using polymer colloids, J Adhesion, 93 (2017) 943-948.
[29] T. Yamamoto, K. Uematsu, T. Irisawa, Y. Tanabe, A Polymer Colloidal Technique for Enhancing Bending Properties of Carbon Fiber-Reinforced Thermoplastics using Nylon modifier, Composites Part A: Applied Science and Manufacturing, 112 (2018) 250-254.