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Water-dispersible carbon nanotube prepared by non-destructive functionalization technique of admicellar polymerization

Montira Seneewong-Na-Ayutthaya, Thirawudh Pongprayoon *

[a] Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand
[b] Center of Eco-Materials and Cleaner Technology, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand

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ABSTRACT

Water-dispersible carbon nanotube (CNT) was prepared by admicellar polymerization — a non-destructive functionalization technique. Polyacrylic acid (PAA) and polyvinyl acetate (PVAc) were synthesized on the CNT surface for improving water dispersion. The optimum amount of monomer for polymer film formation was investigated by the colloidal stability in water testing, turbidity measurement and laser particle size analysis. Percentage of polymer film formation was also analyzed by thermal degradation. FT-IR and TGA were used to characterize the polymer film on the CNT surface. SEM and TEM were used to observe its morphology. The structure damage after modification was analyzed by FT-Raman. It was found that CNT modified by a coating with PAA and PVAc via admicellar polymerization was highly dispersed in water. The optimum surfactant:monomer ratio for preparation of water-dispersible CNT was 1:10 for both polymers. Percent film coated on CNT was 10 wt.% and 12 wt.% for PAA and PVAc, respectively. The results from FTIR, TGA, SEM and TEM confirmed that CNT was successfully coated by PAA and PVAc. Lastly, FT-Raman was used to prove that admicellar polymerization is a method of non-destructive functionalization.

1. Introduction

Carbon nanotube (CNT) exhibits excellent mechanical, electrical and magnetic properties as well as nanoscale diameter and high aspect ratio. Many research works were carried out to improve its properties in composite materials to enhance surface adhesion and dispersion in a matrix. Normally CNT is insoluble in water, but most of its applications need good water dispersion property as in cement work, biosensor and drug delivery [1–4]. There were interests in using CNT as reinforcing materials due to its high mechanical strength, elasticity and corrosion resistance [5,6,7]. Although CNT shows great potential in many applications, they can hardly be dispersed in water due to nanotube–nanotube or van der Waals interaction and tend to aggregate [8]. Therefore, it is highly desirable to improve water-dispersion property by functionalization of CNT surface to increase its hydrophilicity.

Functionalization is a chemical modification technique of material surface that can be divided into covalent and non-covalent functionalizations [1,9–11]. Covalent functionalization for improving water dispersion of CNT that was examined in the previous works includes oxidation reaction with concentrated nitric acid and sulfuric acid [2,12,13] and polymer grafting of poly(acrylamide) [14]. Non-covalent functionalization for improving water dispersion includes surfactant adsorption using anionic and non-ionic surfactants [15], polymer wrapping with polyvinyl pyrrolidone and polystyrene sulfonate [16] and biopolymer wrapping with chitosan [8]. Most of the reviewed literatures on CNT modification for water dispersion improvement used covalent functionalization with oxidation using concentrated acid and polymer grafting. The disadvantage of concentrated acid oxidation is that it may destroy the structure and surface of CNT. Non-covalent functionalization is based mainly on physical adsorption of surfactant or polymer which is less destructive to the structure and surface of CNT than covalent functionalization [17–19]. Admicellar polymerization is a non-covalent functionalization involving the bilayer surfactant adsorption on substrate surface. The bilayer surfactant on the surface, called “admicelle”, is used as a medium in which a nanoscale polymeric film is formed. Admicellar polymerization was first introduced by Wu et al. in 1987 [20]. The process generally consists of four steps: admicelle formation, monomer adsolubilization, polymer formation and surfactant removal [21,22]. The first report of using admicellar polymerization to modify CNT surface was published by Poochai and Pongprayoon for enhancing the dispersion of CNT in a polyacrylonitrile matrix [23]. Admicellar polymerization was utilized to modify different materials using various polymers for a wide range of applications, such as polystyrene thin-film coating on cotton [22], polymethyl methacrylate on aluminum pigments [24], precipitated silica with polystyrene [25] and improving antimicrobial resistance of clay polymer nanocomposites [26]. For improving the hydrophilicity of materials by polymer coating, PAA and PVAc were used to modify sand particle surface [27].

* Corresponding author.
E-mail addresses: tpongprayoon@yahoo.com, thirawudh.p@eng.kmutnb.ac.th (T. Pongprayoon).

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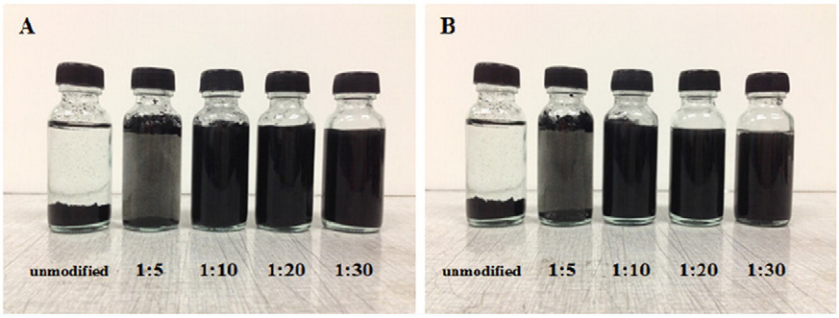

Fig. 1. Colloidal dispersion in water after 24 h of the modified CNT, (A) PAA-coated CNT and (B) PVAc-coated CNT.

PAA is a water-soluble polymer synthesized from acrylic acid (AA) and was applied in various fields such as in drug delivery system and as grafting material in diapers [28,29]. PVAc is also a water-dispersible polymer polymerized from vinyl acetate (VAc). PVAc has been used to fabricate nanofiber by electrospinning and to prepare glue and paint [30–32].

To improve water dispersibility of CNT without surface and structure destruction, admicellar polymerization was used in this study to synthesize water-soluble polymer film on CNT surface.

2. Experimental

2.1. Material and chemicals

Carbon nanotube (CNT) was purchased from Nano Generation (Thailand). It has a diameter of 27 nm, and length greater than 10 μm. The surfactant sodium dodecyl sulfate (SDS) was purchased from Merck (German). The monomers acrylic acid (AC) and vinyl acetate (VAc) were purchased from Sigma Aldrich (USA) and Sigma Aldrich (Germany), respectively. The initiator amonium persulsate (APS) was purchased from Ajax Finechem (Australia). All chemicals were used without further purification.

2.2. Admicellar polymerization

Water-dispersible CNT was prepared following the four steps of admicellar polymerization. Firstly, admicelle formation step was carried out in 5000 μM SDS solution in 50 mL vessel with buffer solution of pH 3.8 adjusted by acetic acid and sodium acetate. 1 g CNT was added into the SDS solution and then continuously mixed for 24 h at room temperature. Secondly, the monomer (AA or VAc) at the surfactant:monomer molar ratio of 1:5, 1:10, 1:20 and 1:30 was added into the mixture solution. The APS, using as an initiator, was added to the mixture based on mole of monomer. The mixture was continuously stirred for 24 h at room temperature for the monomer adsolubilization step. The third step or polymerization was carried out by heating the mixture to 90 °C and stirred continuously for 2 h. Lastly, the modified CNT was taken out and washed with distilled water several times to remove the outer-layer SDS. The CNT was then dried in the oven at 60 °C for 24 h.

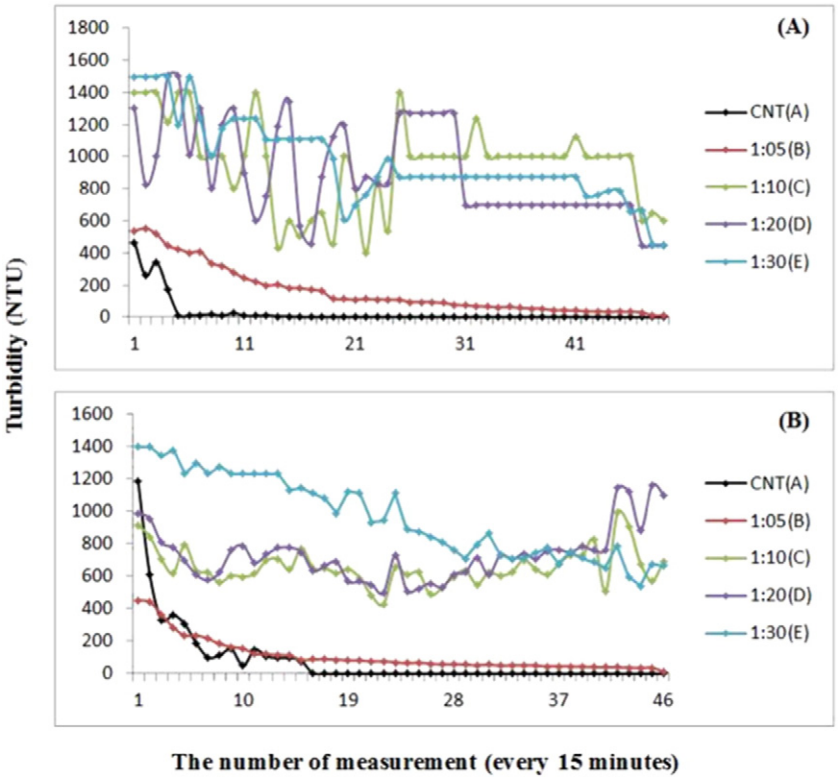

Fig. 2. Turbidity of (A) PAA-coated CNT and (B) PVAc-coated CNT.