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Enhancing dispersion of carbon nanotube in polyacrylonitrile matrix using admicellar polymerization

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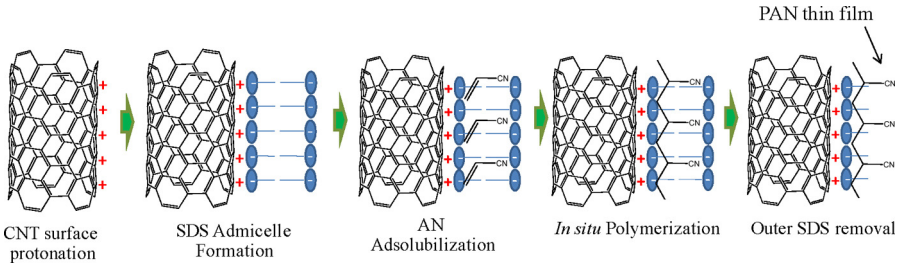
HIGHLIGHTS

- Carbon nanotube (CNT) surface was modified by admicellar polymerization with polyacrylonitrile (PAN) film coating.
- Zeta potential, FT-IR, FT-Raman, TGA, DSC, TEM, and SEM were used for characterization.
- The good dispersion of PAN-coated CNT in PAN matrix enhanced the mechanical strength of its composites.

GRAPHICAL ABSTRACT

Schematic of admicellar polymerization steps for preparing PAN-coated CNT.



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ABSTRACT

To enhance dispersion of carbon nanotube (CNT) in polyacrylonitrile (PAN) matrix for improving mechanical strength, electrical conductivity, and thermal properties of PAN-based carbon materials, the surface of CNT was modified by coating an ultrathin film of PAN using admicellar polymerization. Sodium dodecyl sulfate (SDS) and acrylonitrile (AN) were used as an absorbed surfactant soft-template and monomer, respectively, for two-dimensional polymerization on CNT surface. PAN-coated CNT was characterized by Zeta (ζ) potential, FT-IR, TGA, and TEM. The graphitic structure of modified CNT was obtained by FT-Raman. Cyclization temperature (T_c) and the enthalpy change (ΔH_c) of the PAN-coated CNT/PAN composite examined by DSC were found at 302 °C and 17.8 kJ/g, respectively. These are close to those of pure PAN indicating a good dispersion of PAN-coated CNT in PAN matrix. The results are in good agreement with SEM images. The mechanical properties of PAN composite were improved from using as-received CNT.

1. Introduction

Carbon nanotube (CNT) is of interest in the community of scientists, technologists and engineers due to their excellence in electrical conductivity, thermal properties and mechanical strength [1]. Many researchers have used CNT for improvement of the properties of composites with the development of surface adhesion dispersion of CNT in polymeric matrix. However, CNT always aggregate due to van der Waals forces that make it difficult to fabricate homogenous CNT/polymer composites [2]. To obtain the advantage of CNT as effective reinforcement and conductivity enhancement in composites, CNT must be localized and aligned completely in polymeric matrixes. The dispersion can be improved when covalent or non-covalent dispersion techniques are used to reduce van der Waals interactions by inducing interactions of functional groups between polymer matrix and CNT surface [3,4]. Grafting method has been reported with the use of carboxylic

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acid functionalized-CNT as an external initiating agent for nitrile cyclization for good dispersion inside PAN matrix [5]. Currently, in situ polymerization is being used for preparing various types of polymeric film such as polyaniline [6], polystyrene [7,8] and poly(methyl methacrylate) [7], on CNT surface. In these cases a homogeneous dispersion of CNT in polymer matrix is obtained due to the uniform polymeric coating on CNT surface.

Admicellar polymerization is one of the in situ polymerization techniques. This technique is done by forming a desired ultrathin polymeric film inside the bilayer of absorbed surfactant, called admicelle [9], on the substrate surface. The admicellar polymerization generally consists of four steps: admicelle formation, monomer adsolubilization, polymer formation, and surfactant removal. In general, admicelle can form very well on an ionic substrate surface with oppositely charged surfactant. Hence, in this work, the neutral CNT surface was modified by the surrounding H^+ in an acidic solution. The advantages of admicellar polymerization are low energy consumption, non-destructive substrate, friendly environment, and low cost. Admicellar polymerization has been successfully employed to create different types of polymeric thin films onto several substrates such as polystyrene on silica [10], alumina [11], and cotton [12,13], polypyrrole on mica [14], 2-hydroxy-4-acryloyloxybenzophenone on cotton [15], polyisoprene on silica [16,17], and polypropylene on calcium carbonate [18]. Most works were done on either the positively or negatively charged substrates such as silica, calcium carbonate, and the information on the use of admicellar polymerization to modify CNT surface is limited because the process generally does not work well with neutrally charged surface especially that of CNT. Hence, it is a good motivation for this work.

In general polyacrylonitrile (PAN) is the polymer used for the fabrication of carbon material due to its easy carbonization process. The advantages of PAN are high degree of molecular orientation, high melting point (T_m of 317–330 °C), and a high yield of the carbon material [19]. Producing high quality PAN-based carbon depends on the stabilization process which occurs through cyclization reaction transforming PAN to an infusible stable conjugated ladder polymer structure under air atmosphere and 200–300 °C temperature with low enthalpy of cyclization reaction [20].

In this work admicellar polymerization of acrylonitrle (AN) on carbon nanotube (CNT) surface was carried out using sodium dodecyl sulfate (SDS), an anionic surfactant, for admicelle formation. The dispersion of modified CNT particles inside PAN matrix was investigated through cyclization reaction and enthalpy change under N_2 atmosphere. The mechanical properties of PAN composites were improved using PAN-coated CNT.

2. Experimental

2.1. Chemicals

The CNT was received from the Department of Physics and Material Science, Chiang Mai University, Thailand. The CNT was synthesized by infusion chemical deposition of ethanol using nickel oxide as a catalyst. The average diameter, average length, and electrical resistivity of the CNT were approximately 27 nm, greater than 10 μm, and 5–8 × 10^{-1} Ω cm, respectively [21]. Polyacrylonitrile (PAN) with the average molecular weight of 150,000 g/mol and acrylonitrile (AN) were purchased from Sigma Aldrich (USA). Sodium dodecyl sulfate (SDS) was purchased from Merck (German), potassium persulfate (PPS) and N,N-dimethylformamide (DMF) were purchased from Ajax Finechem (Australia). All chemicals are analytical reagent grade prepared with ultrapure water (Milli Q water, resistivity of 18.2 MΩ cm^{-1}) and were used without further purification.

2.2. CNT pretreatment

The CNT was sonicated for 1 h and then stirred for 2 h with 3 M HCl. The mixture was then rinsed with deionized water by filtration through a 2.0 μm polytetrafluoroethylene (PTFE) membrane until it was neutralized. The filtered CNT powder was dried in an oven at 70 °C overnight.

2.3. Zeta potential measurement

To study the electrostatic charge of CNT in solution with varying pH, the pH of the solution was adjusted from 2 to 11 using HCl and NaOH solutions and measured by a pH meter (Schott, Lab860). Then, 0.5 g CNT was added into the solution. The mixture was sonicated for 30 min before its Zeta (ζ) potential was measured using a Zeta meter (Malvern, 300 HS).

2.4. Adsorption isotherm study

The adsorption isotherm of SDS on CNT was obtained by using 1 g CNT in 50 mL SDS solution at pH 4 adjusted by acetate buffer. The initial SDS concentration was varied from 0.2 mM to 10 mM, covering the CMC of SDS at pH 4 (3.2 mM). The mixture was shaken at 75 rpm in a water bath at 30 °C for 24 h. The SDS concentration was measured using a spectrophotometer model CE 2040 at 300 nm fixed wavelength. The amount of adsorbed SDS on 1 g CNT was calculated by the equation

$$[C_{ads}] = \frac{[C_i] - [C_E]}{g_{CNT}} \times \frac{V(\text{ml})}{100}$$

where $[C_{ads}]$ is mole of adsorbed SDS per unit weight of CNT (mol/g_{CNT}), $[C_i]$ and $[C_E]$ are initial and equilibrium concentration of SDS (mol/L), g_{CNT} is weight of CNT powder (g), and V is volume of the solution (mL).

2.5. Admicellar polymerization procedure

Admicellar polymerization of AN on CNT was carried out using 5 mM SDS at pH 4 adjusted by acetate buffer. One g CNT was added into the solution and the mixture was continuously stirred at room temperature for 24 h. AN and PPS were afterward added with the amount of PPS set at 0.3% of AN by mole. The molar ratio of AN to SDS was varied (0.15, 0.30, 0.60, and 0.90) to find the optimum condition. The mixture was then gradually stirred and heated to 90 °C for 3 h for AN polymerization. The CNT samples were subsequently filtered and washed several times with distilled water until the redundant surfactant including surfactant of the upper layers of admicelle were removed. Finally, PAN-coated CNTs were dried in an oven at 70 °C overnight. The schematic of admicellar polymerization steps is illustrated in Fig. 1. For this study, CNT surface was positively charged with surrounding H^+ in the acidic solution to facilitate admicelle formation of the anionic SDS molecules on the CNT surface.

2.6. PAN-coated CNT characterizations

PAN ultrathin film formed on CNT was characterized by ultraviolet spectroscopy (UV), Zeta potential measurement, Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and transmission electron microscopy (TEM). For UV measurement, 0.5 g PAN-coated CNT was extracted by heating in 25 mL DMF at 60 °C for 1 h until the supernatant became yellow and then the solution was filtrated to remove remaining CNT particles. The supernatant was analyzed using spectrophotometer (Unicam, UV500) at 268 nm of PAN absorbance wavelength. The electrostatic surface charge of the as-received CNT, PAN-coated CNT and PAN