Properties of MWCNTs/PAN Nanofiber Sheet Prepared from Chemically Modified MWCNTs

M. Seneewong-Na-Ayuttaya and T. Pongprayoon

Abstract—The nanofiber sheet of Multiwall Cabon Nanotube (MWCNTs)/Polyacrylonitile (PAN) composites was fabricated from electrospun nanofiber. Firstly the surface of MWCNTs was chemically modified, comparing two different techniques consisting of admicellar polymerization and functionalization to improve the dispersion and prevent the aggregation of the PAN matrix. The modified MWCNTs were characterized by the dispersion in dimethylformamide (DMF) solvent, Laser particle size, and FT-Raman. Lastly, DSC, SEM and mechanical properties of the nanofiber sheet were examined. The results show that the mechanical properties of the nanofiber sheet prepared from admicellar polymerization-modified MWCNTs were higher than those of the others.

Keywords— Multiwall carbon nanotube, admicellar polymerization, functionalization, nanofiber sheet.

I. INTRODUCTION

MULTIWALLED carbon nanotubes (MWCNTs) are interested in the community of scientists, technologists and engineers due to their excellence in mechanical strength and electrical conductivity. Therefore many researches have improved the MWCNTs properties of MWCNTs/polymer compound. However, MWCNTs always aggregate due to effect of Van Der Waal force that are difficult to fabricate homogeneous MWCNTs/polymer compound [1]. Polyacrylonitrile (PAN) is a versatile polymer used to produce ultrafine fiber with fibrous structure and easily fabricated [6].

Admicellar polymerization is one of in-situ polymerization techniques to modify material surface by coating with polymeric nanofilm on the material surface. The benefit of this technique is a non-destroy material technique that also does not destroy its structure. This technique normally consists of four steps: admicell formation, monomer adsolubilization, polymer formation and removing the upper layer of surfactant [4]. The other one technique used in this work was functionalization technique that was used to add the functional group onto materials surface with the oxidation reaction of the high concentration acid. Oxygenated functional group (OH, C=O, and COOH) may render the ability of dispersion of MWCNTs in organic solvent. Functionalization is recognized as an efficient method for purification, dispersion and surface activation of MWCNTs to fabric compound [5]. The disadvantage of this technique is that the surface and structure of materials are possibly destroyed. Electrospinning was used to fabricate nanofiber of MWCNTs/PAN composites before making the nanofiber sheet due to the ultrafine fiber with fibrous structure and easily fabricated [6].

II. EXPERIMENTAL

A. Chemical and Materials

Multiwalled carbon nanotubes (MWCNTs) were prepared from department of physic and material science, Chiang Mai University (Thailand). The average diameter, average length and electrical resistivity of the MWCNTs were approximately 27nm, greater than 10µm, and 5-8×10⁷Ωcm, respectively. Polyacrylonitrile (PAN) with the average molecular weight of 150,000g/mol and Acrylonitrile (AN) were purchased from Sidma 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). Nitric acid (HNO₃) and Sulfuric acid (H₂SO₄) were purchased from J.T. Baker analyzed (Thailand).

B. Admicellar Polymerization Modification

One gram of purified MWCNTs was added into a vial containing 50ml of 5,000µM SDS in acetic acid/sodium acetate buffer (pH 3.8) then it was continuously rotated for 24 hrs at room temperature afterward 0.28% K₂S₂O₇ (based on mole of AN) and AN were added into the mixture solution of 1:30 SDS:AN. The vial was sealed by paraffin and wrapped with aluminum foil, respectively, to prevent AN vaporization. The vial was rotated for 24 hrs at room temperature. After that, the mixture was continuously stirred and heated up to 90 °C for 2hrs for polymerization then the vial was cooled down and the MWCNT was kept and washed with distilled water several times to remove the excess SDS. Lastly, the MWCNTs were dried in the oven at 70°C for a day.

C. Functionalization Modification

70ml of acid solution was prepared from the mixture acid solution of H₂SO₄ and HNO₃ 8.0 M in ratio 1:1. Then, 3.0g purified MWCNTs was add in to the mixture acid solution in a 100-cml’duran bottle. Then the duran bottle was continuously...
stirred and heated up to 60ºC in a hot plate for 15 min. After that, the mixture was sonicated in an ultrasonic bath (35 kHz) for 2 hours. Then, the MWCNTs was taken out from the duran bottle with filtered and thoroughly washed with distilled water. Finally, the MWCNTs was dried in a convection oven at 150ºC during 4 hours.

D. MWCNTs/PAN Nanoifiber Sheet Fabrication

The mixture solution containing of 16%(w/v) PAN, 10 cm³ DMF and 0.5% (w/v) modified MWCNTs was spun to obtain nanofiber mat by electrospinning process. The parameters; flow rate, distance between injector and target, and applied voltage were set at 0.5 cm³/hour, 10 cm, and 10 kV, respectively. After spinning, the nanofiber composites sheet was fabricated with 5 cm × 10 cm dimension.

E. Modified MWCNTs Characterization

Colloidal stability was studied by investing the dispersion of modified MWCNTs in DMF organic solvent. Laser particle size analyzer was used to determine the dispersion and degradation of modified MWCNTs, by determine average particle size of before and after MWCNTs treatment process. From Fig. 2, admicellar polymerization (B) had a larger average particle size than the unmodified MWCNTs (A) had, because there was PAN nanofilm coated on the surface of MWCNTs. The laser particle size of modified MWCNTs by functionalization (C) had the smallest size due to the damage of structure and surface of MWCNTs from this treatment. From these results, it was found that admicellar polymerization less destroyed structure and surface of the MWCNTs than functionalization did.

III. RESULTS AND DISCUSSION

A. Characterization of Modified MWCNTs Particle

1. Colloidal Stability of MWCNTs Suspensions

Dispersion of MWCNTs in the DMF solution was showed in Fig. 1. The MWCNTs without treatment (A) sedimented completely in approximately 10 minutes after sonication. The modified MWCNTs with admicellar polymerization (B) and with functionalization (C) remained as a colloidal solution (well dispersion more than 24 hours). From this result, it is clear that the presence existence of functional groups in PAN nanofilm coated on MWCNTs surface (B) and the oxidized MWCNTs (C), which both led to a reduction of van der Waals interactions in MWCNTs surface. Therefore, the MWCNTs modified with two methods were very well dispersion in the DMF. This also implied that MWCNTs were coated with PAN by admicellar polymerization and completed with oxidation reaction by functionalization differential.

2. Laser Particle Size Analysis

A laser particle size analyzer was used to determine the dispersion and degradation of modified MWCNTs, by determine average particle size of before and after MWCNTs treatment process. Form Fig. 2, admicellar polymerization (B) had a larger average particle size than the unmodified MWCNTs (A) had, because there was PAN nanofilm coated on the surface of MWCNTs. The laser particle size of modified MWCNTs by functionalization (C) had the smallest size due to the damage of structure and surface of MWCNTs from this treatment. From these results, it was found that admicellar polymerization less destroyed structure and surface of the MWCNTs than functionalization did.
group of PAN. The exothermic peak of pure PAN displayed at 289.6ºC, while the exothermic peaks of unmodified MWCNTs/PAN (A), PAN-coated MWCNTs/PAN (B) and functional MWCNTs/PAN (C) composites were shifted to lower the initiation temperature about 13ºC, 2.6ºC, and 0.3ºC respectively. These results described that the incorporated MWCNTs, making the dense crystalline structure of PAN fiber, had been deteriorated. The exothermic peaks of pristine MWCNTs/PAN nanofiber was more negatively shifted than of PAN-coated MWCNTs/PAN and of pure PAN due to higher agglomeration of the unmodified MWCNT, inside the matrix of PAN nanofiber than that of the PAN-coated and functional MWCNTs.

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<th>TABLE I: IG/ID INTENSITY RATIOS FOR THE TREATED MWCNTS</th>
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<td>MWCNTs</td>
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Fig. 3 DSC curves (A) pure PAN nanofiber, (B) unmodified PAN-coated MWCNTs/PAN and (D) functionalization MWCNTs/PAN nanofiber

2. Scanning Electron Microscopy CNTs/PAN
SEM images of nonfiber morphology are displayed in Fig. 4. The images show that the surface of modified MWCNTs/PAN nanofibers of both admicellar polymerization treatment (C) and functionalization treatment (D), respectively, was smoother and smaller roughness than that of unmodified MWCNTs/PAN nanofiber (B) due to the aggregation of unmodified MWCNTs in PAN matrix of its composites nanofiber.

3. Mechanical Properties of Nanofiber Sheet
The mechanical properties of MWCNTs/PAN nanofiber sheet are shown in Fig. 5 (tensile strength) and Fig. 6 (Young modulus). The admicellar modified MWCNTs/PAN nanofiber sheet had higher tensile strength and young's modulus than those of functionalization MWCNTs/PAN nanofiber sheet also due to the destroyed structure and surface of MWCNTs treated by functionalization. However both modifications gave the better mechanical properties of nanofiber sheet, comparing with unmodified MWCNTs due to good dispersion in PAN matrix. All nanofiber sheets using MWCNTs gave higher mechanical properties than those of pure PAN nanofiber sheet from reinforcement action of MWCNTs in the PAN composite.

Fig. 4 SEM images of (A) pure PAN nanofiber, (B) unmodified MWCNTs/PAN nanofiber (C) admicellar MWCNTs/PAN nanofiber and (D) functionalization MWCNTs/PAN nanofiber

Fig. 5 Tensile strength of (A) pure PAN, (B) unmodified MWCNTs/PAN, (C) admicellar MWCNTs/PAN and (D) functionalization MWCNTs/PAN nanofiber sheet
IV. CONCLUSION

The studied properties of modified MWCNTs/PAN nanofiber sheet prepared from admicellar polymerization were higher than those of the composites nanofiber sheet prepared from functionalization because admicellar polymerization did not destroy the structure and surface of MWCNTs, whereas functionalization did.

REFERENCES


