

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

M. Seneewong-Na-Ayuttaya and T. Pongprayoon

Abstract—The nanofiber sheet of Multiwall Carbon Nanotube (MWCNTs)/Polyacrylonitrile (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 in 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 large variety of products such as ultrafiltration membrane, textile and carbon paper in fuel cell. In this work, to improve the dispersion of MWCNTs and to prevent the aggregation of MWCNTs in PAN matrix, MWCNTs were chemically modified by two different surface treatment techniques, admicellar polymerization and functionalization [2], [3].

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 adsorption, 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 10 μ m, and 5-8 $\times 10^{-1}$ Ω .cm, respectively. Polyacrylonitrile (PAN) with the average molecular weight of 150,000g/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). 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 5,000 μ M SDS in acetic acid/sodium acetate buffer (pH 3.8) then it was continuously rotated for 24 hrs at room temperature afterward 0.28% K₂S₂O₈ (based on mole of AN) and AN were added into the mixture solution of 1:30 SDS:AN. The vial was sealed by parafilm 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-cm³ duran bottle. Then the duran bottle was continuously

Montira Seneewong-Na-Ayuttaya is with the Department of Chemical Engineering, Center of Eco-Materials and Cleaner Technology, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand.

Thirawudh Pongprayoon is with the Department of Chemical Engineering, Center of Eco-Materials and Cleaner Technology, King Mongkut's University of Technology North Bangkok, Bangkok, Thailand. (e-mail: tpongprayoon@yahoo.com, thp@kmutnb.ac.th http://www.kmutnb.ac.th).

stirred and heated up to 60°C in a hot plate for 15min. 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 150°C during 4 hours.

D. MWCNTs/PAN Nanofiber Sheet Fabrication

The mixture solution containing of 16%(w/v) PAN, 10cm³ 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 0.5cm³/hour, 10cm, and 10kV, respectively. After spinning, the nanofiber composites sheet was fabricated with 5cm × 10cm dimension.

E. Modified MWCNTs Characterization

Colloidal stability was studied by investing the dispersion of modified MWCNTs in DMF organic solvent. Laser particle size (Malvern Mastersizer X ver. 2.15) was used to measure the modified MWCNTs. Fourier-transformed Raman spectroscopy (FT-Raman) (Perkin Elmer, Spectrum GX) was used to characterize an effective conductivity of the MWCNTs.

F. MWCNTs/PAN Nanofiber Sheet Measurement

Differential scanning calorimeter (DSC) (Netzsch, 204 F1 Pheoenix, Germany) was used to measure the dispersion of MWCNTs in PAN nanofiber. Scanning electron microscopy (SEM) (JEOL, JSM-5410L, Japan) was used to obtain the surface and structure of MWCNTs/PAN nanofiber composites. Universal Testing Machine (Shimadzu, DSS-10T) was used to examine the mechanical properties of MWCNTs/PAN nanofiber sheet.

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

CLaser 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.

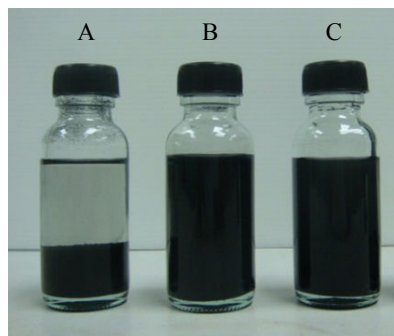


Fig. 1 Colloidal dispersion of (A) un-modified (B) admicellar polymerization and (C) functionalization treated MWCNTs in DMF after 24 hours

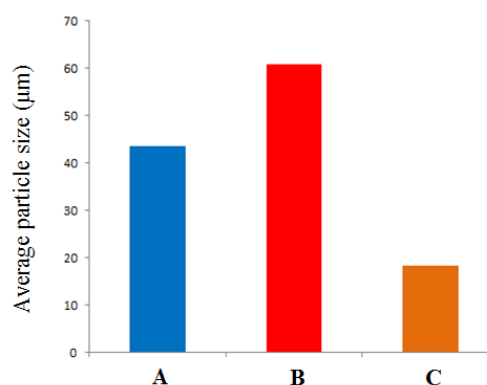


Fig. 2 Laser particle size of treated MWCNTs with (A) un-modified, (B) admicellar polymerization and (C) functionalization

3. Fourier-Transformed Raman Spectroscopy

Raman spectroscopy was used to characterize the destruction and electrical conductivity of modified MWCNTs. Raman spectra show G-band (double bound) and D-band (single bound). Normally the intensity ratio of I_G/I_D (Table I) is used to imply the electrical conductivity and surface destroyed. From the result, it shows that modified MWCNTs by functionalization had the least of the I_G/I_D ratios, which supports the destruction structure and surface of the MWCNTs. Therefore, the electrical conductivity of this MWCNTs had decreased.

B. Testing of MWCNTs/PAN Nanofiber Sheet

1. Differential Scanning Calorimeter

In Fig. 3, all DSC curves displayed an exothermic peak, which indicated thermal stabilizaing and cyclization of nitrile

group of PAN. The exothermic peak of pure PAN displayed at 289.6°C, 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 13°C, 2.6°C, and 0.3°C 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.

TABLE I
IG/ID INTENSITY RATIOS FOR THE TREATED MWCNTs

MWCNTs	G-Band (cm ⁻¹)	D-band (cm ⁻¹)	I _G	I _D	I _G /I _D
Un-treated	1594	1290	1.485	3.210	0.462
Admicellar	1594	1290	0.718	1.770	0.404
Functional	1590	1290	1.105	3.300	0.334

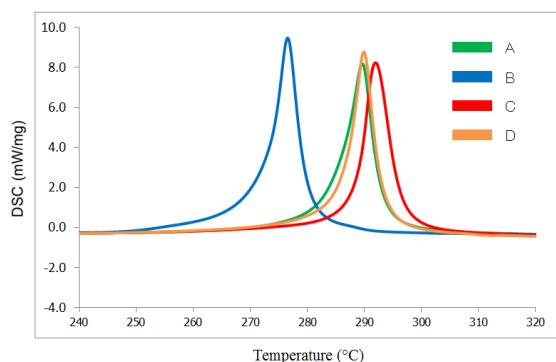


Fig. 3 DSC curves (A) pure PAN nanofiber, (B) un-modified (C) admicellar polymerization and (D) functionalization MWCNTs/PAN nanofiber

2. Scanning Electron Microscopy CNTs/PAN

SEM images of nanofiber 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.

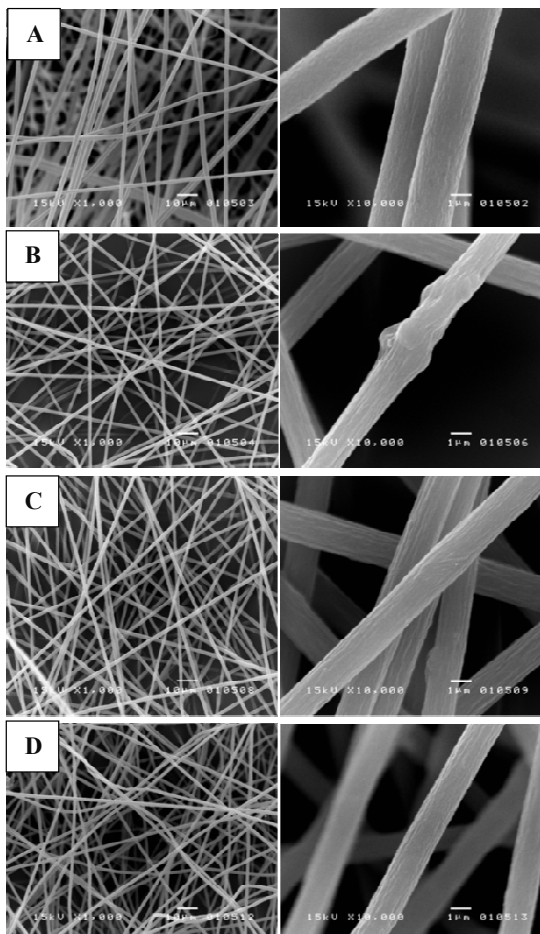


Fig. 4 SEM images of (A) pure PAN nanofiber, (B) unmodified MWCNTs/PAN nanofiber (C) admicellar MWCNTs/PAN nanofiber and (D) functionalization MWCNTs/PAN nanofiber

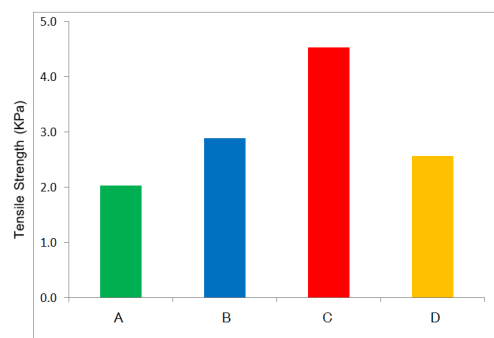


Fig. 5 Tensile strength of (A) pure PAN, (B) unmodified MWCNTs/PAN, (C) admicellar MWCNTs/PAN and (D) functionalization MWCNTs/PAN nanofiber sheet

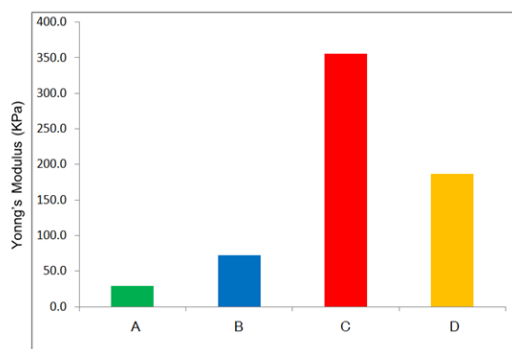


Fig. 6 Young Modulus of (A) pure PAN, (B) unmodified MWCNTs/PAN, (C) admicellar MWCNTs/PAN and (D) functionalization MWCNTs/PAN nanofiber sheet

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

- [1] P.J.F. Harris, *Carbon Nanotube and Related Structure: New Materials for the 21 st Century*, Cambridge University, 1999.
- [2] H.G. Chae, Y. H. Choi, M.L. Minus and S. Kumar, "Carbon nanotube reinforced small diameter polyacrylonitrile based carbon fiber," *IEEE J. composites Science and Technology*, vol. 69, pp. 406–413, 2009.
- [3] R.B. Mathur, P.H. Maheshwari, T.L. Dhami, R.K. Sharma and C.P. Sharma, "Processing of carbon composite paper as electrode for fuel cell," *IEEE J. Power Sources*, vol. 161, pp. 790–798, 2006.
- [4] T. Pongprayoon, N. Yanumet and E.A. O'Rear, "Admicellar polymerization of Styrene on Cotton," *IEEE J. Colloid and Interface Science A*, vol. 329, pp. 227–234, 2009.
- [5] F. Aviles, J.V. Cauich-Rodriguez, L. Mii-Tah, A. May-Pat and R. Vargas-Coronado, "Evaluation of mild acid oxidation treatments for MWCNTs functionalization," *IEEE J. Carbon*, vol. 47, pp. 2970–2975, 2009.
- [6] Z.M. Huang, Z.Y.Z., M. Kotaki and S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites," *IEEE J. composites Science and Technology*, vol. 63, pp. 2223–2253, 2003.