Effect of Plasma Polymerization Coating of CNTs on the Tensile Strength of PEI/CNT Composites

K. C. Song and T. H. Yoon[†]

Department of Materials Science and Engineering, Gwangju Institute of Science & Technology, Gwangju 500-712, Korea

Abstract: Multi-walled carbon nanotubes (CNTs), which were purified by etching in 25% H_2SO_4/HNO_3 solution at 60°C for 2 h, were modified via plasma polymerization coating of acrylic acid, allylamine or acetylene, and then utilized to prepare PEI/CNT composites. First, plasma polymerization conditions were optimized by measuring the solvent resistance of coatings in THF, chloroform and NMP, and the tensile strength of PEI/CNT (0.5%) composites as a function of plasma power (20~50 W) and monomer pressure (20~50 mTorr). The tensile strength of PEI/CNT composites was further evaluated as a function of CNT loading (0.2, 0.5 and 1%). Finally, FT-IR was utilized to provide a better understanding of the improved tensile properties of PEI/CNT composites via plasma polymerization coating of CNTs. Plasma polymerization of acrylic acid greatly enhanced the tensile strength of PEI/CNT composites, as did allylamine but to a lesser degree, while acetylene plasma polymerization coating decreased tensile strength.

Keywords: *CNT, plasma polymerization, composites*

1. Introduction

Since their discovery by Iijima, carbon nanotubes (CNT) have received great attention due to their unique mechanical, electrical and thermal properties[1], making them very attractive materials for high performance composites, electronics and biological applications[2,3]. In particular, the most challenging area of their application is that of high performance composites material due to their high aspect ratio and high Young's modulus[4]. Consequently, there has been considerable volume of research conducted on CNT reinforced polymer composites[5,6]. As expected, however, it proved to be quite difficult to achieve good dispersion and alignment of CNTs in the composite, owing to their chemically inert and highly hydrophobic nature[3], which also resulted in poor adhesion between the CNT and polymer.

To date, a number of attempts to modify CNTs have been made to afford good dispersion and adhesion, including acid etching, covalent/noncovalent bonding, *in situ* polymerization, high power sonication and physical blending [7,8]. In acid etching, CNTs are etched by a strong acid to generate various functional groups[9,10]. But this process, in general, degrades CNTs, resulting in decreased

Young's modulus and thus, lowers composite properties. In comparison, covalent/noncovalent bonding does not affect the physical property of CNTs. Instead, the CNT surface is covered by polymer wrapping, polymer absorption (noncovalent bonding), or polymer grafting (covalent bonding). Recently, micelle encapsulation of CNTs was also introduced to modify CNTs[11]. However, problem with noncovalent bonding is unstable polymer coating due to weak van der Waals or π-π stacking, while that of covalent bonding is limited availability of such molecules for covalent bonding.

Recently, there has been an increasing demand for a new process that can afford excellent dispersion and adhesion of CNTs without detracting from CNT properties. A possible method may be plasma polymerization since the process is known to provide pinhole free thin films with functional groups[12,13], in addition to being environmentally friendly. In fact, it has been widely utilized in the modification of carbon fibers[14] and silica[15]. Unfortunately, there have been only few studies on the modification of CNTs via plasma polymerization[16,17], and thus further research is needed to gain a better understanding.

In this study, therefore, plasma polymerization was utilized in modifying multi-walled carbon nanotubes (CNTs) in order to provide functional groups, and thus resulting in

[†] Corresponding author: e-mail: thyoon@gist.ac.kr

excellent dispersion and adhesion, which in turn, lead to good composite properties. First, CNTs purified by acid etching were modified via plasma polymerization coating of acrylic acid, allylamine or acetylene. Plasma polymerization conditions were optimized by measuring the solvent resistance and tensile strength of PEI/CNT (0.5%) composites as a function of plasma power (20~50 W) and monomer pressure (20~50 mTorr). Next, the tensile strength of PEI/CNT composite was further evaluated as a function of CNT loading (0.2, 0.5 and 1%). Finally, FT-IR was utilized to gain an understanding of the improved tensile properties of PEI/CNT composites.

2. Experimentral

2.1. Materials

Multi-walled carbon nanotubes (CNTs) with a diameter of 15 nm, prepared by CVD method, were provided by ILJIN Nanotech (Korea). Prior to plasma polymerization coating, CNTs were purified by sonicating in 25% H_2SO_4/HNO_3 solution at $60^{o}C$ for 2 hrs (Figure 1), as previously reported[9]. They were then filtered and washed with deionized water until the filtrate became neutral and dried under vacuum. Monomers such as acrylic acid, allylamine and acetylene were utilized for plasma polymerization coating of CNTs. Ultem® 1000 poly(ether imide), provided by GE plastics (USA), was used as the polymer matrix for composite preparation.

2.2. Optimization of Plasma Polymerization Coating

For the plasma polymerization coating of CNTs, a radio frequency (13.56 MHz) electroless plasma reactor (Hanatek, HPPS-300) consisting of a tubular type reactor, manual impedance matching and mass flow controller was used[15]. The reactor, which was made of quartz, had a length of 430 mm and a diameter of 100 mm. To supply the monomer, a gas inlet pipe was inserted into the quartz tube, which was designed to rotate in order to provide good mixing, and thus uniform coating of the CNTs. Plasma polymerization coating was carried out by charging CNTs (0.2 g) into the reactor, followed by evacuating to 1 mTorr, and introducing the monomer for plasma polymerization.

The conditions for plasma polymerization coating were optimized by first measuring the solvent resistance, followed by tensile strength as a function of plasma power (20~50 W) and monomer pressure (20~50 mTorr) for each monomer. For the solvent resistance test, a plasma polymer coated slide glass was immersed into solvents such as THF, CHCl₃ and NMP for 2 hrs. After

drying, the slide was scratched with a razor blade, while the solutions were inspected by naked eye to evaluate the solubility of coatings.

2.3. Tensile Property Measurement of CNT/PEI Composites

The PEI/CNT composite was prepared by solution casting of PEI/CNT mixture. First, a PEI solution (10 wt% in NMP) was prepared, and then a calculated amount of CNTs (0.2, 0.5, 1.0 wt%) were added, followed by sonication for 3 hrs in $40^{o}C$ water bath. Second, the mixture was cast onto a glass plate; dried at $60^{o}C$ for 12 hrs; and slowly heated to $240^{o}C$. Further drying at $240^{o}C$ *in vacuo* for 2 hrs resulted in 40~50 μm thick composite films. The samples for tensile test were prepared from composite films according to ASTM D-638 (#5), while tensile properties were measured with Instron 5567 at a crosshead speed of 5 mm/min at RT. Five or more specimens were tested and the results were averaged.

2.4. Characterization of Plasma Polymerization Coating

FT-IR (SHIMADZU, FTIR-8400S) was utilized to provide a better insight into the functional groups on the CNT surface. However, due to the difficulty of FT-IR analysis of CNTs, KBr powder was used instead of CNTs for plasma polymerization coating, despite some anticipated discrepancies. Prior to the plasma polymerization coating, KBr powder was dried in vacuum at $100^{o}C$ for 24 hrs. For all samples, 12 scans were recorded at a resolution of 4 cm⁻¹.

3. Results and Discussion

3.1. Optimization of Plasma Polymerization Conditions
3.1.1. Optimization via Solvent Resistance Test

Plasma polymerization conditions were first optimized by measuring the solubility of plasma polymer coatings (Table 1), since coatings should have good solvent resistance, and therefore be stable during preparation of PEI/CNT composites. The solubility of coatings was evaluated by scraping the surface of the slide glass, which was plasma polymer coated and immersed in a solvent. In addition, the solvent was inspected by naked eye after the immersion of plasma polymer coated slide glass.

The acrylic acid plasma polymerization coatings prepared at 20 W exhibited two different behaviors depending on the solvent used. In the first group, the samples provided no scrapings of coating, and no changes were observed in the solvent after immersion in CHCl₃, demonstrating the insolubility of the coating. In the second group, coatings were partially scraped off, with some portions floating in the solvent after immersion in NMP and THF, indicating
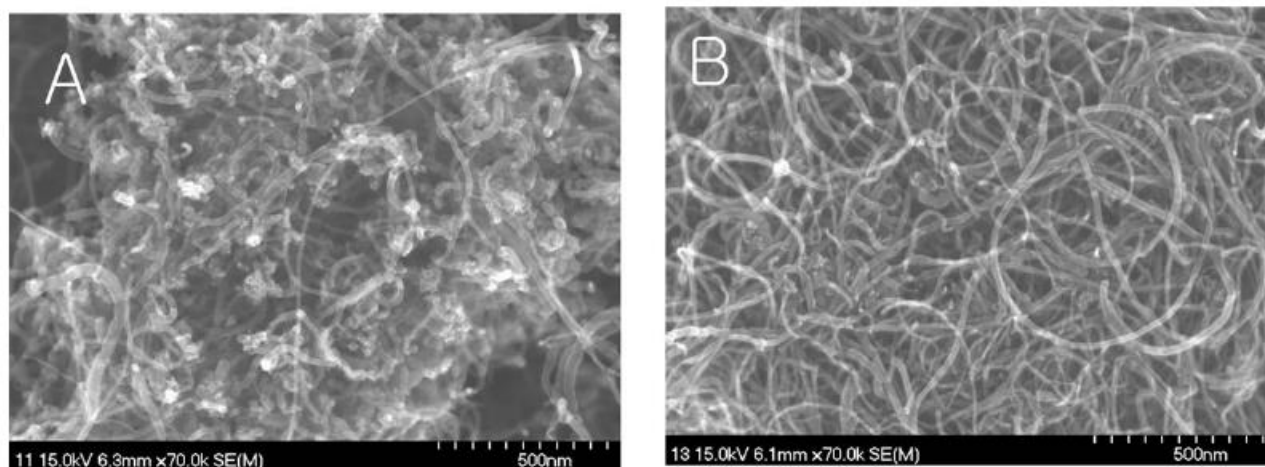
Figure 1. SEM micrographs of as-received (A) and purified (B) CNTs.

Table 1. Solubility of acrylic acid, allyl amine and acetylene plasma polymer films as a function of plasma power in CHCl₃, NMP and THF

Monomer	Acrylic Acid				Allylamine				Acetylene			
Solvent Power (W)	20	30	40	50	20	30	40	50	20	30	40	50
Chloroform	I	I	I	I	I	I	I	I	I	I	I	I
NMP	P	I	I	I	P	I	I	I	I	I	I	I
THF	P	I	I	I	P	I	I	I	P	I	I	I

I: insoluble, P: partially soluble (Plasma polymerization at 40 mTorr for 1 min)

partial solubility. The plasma polymer coatings of acrylicacid at 30, 40 and 50 W were insoluble in CHCl₃, NMP and THF, irrespective of plasma power used, suggesting highly cross-linked thin films.

The plasma polymer coatings from allyamine exhibited the same trend as that of acrylic acid, resulting in partially soluble films in NMP and THF if prepared at 20 W, with all other films being insoluble. In comparison, acetylene plasma polymer coatings prepared at 20 W were insoluble in CHCl₃ and NMP, but partially soluble in THF, while those prepared at 30, 40 and 50 W were all insoluble in CHCl₃, NMP and THF. Based on the results from the solvent resistance test, the films prepared at 30 W or higher power were insoluble in CHCl₃, NMP and THF, demonstrating highly cross-linked plasma polymer films[12]. Therefore, the films prepared at 20 W were excluded from tensile strength measurements for further optimization of conditions.

3.1.2. Optimization via Tensile Strength Measurements

Plasma polymerization conditions were further optimized by measuring the tensile strength of PEI/CNT composites with 0.5 wt% CNT as a function of plasma power (30~50 W) and monomer pressure (20~50 mTorr). As shown in Figure 2-A, PEI/CNT composites with acrylic acid coating provided tensile strength of 116 MPa at 30 W, which increased to 129 MPa at 40 W and then decreased to 105 MPa at 50 W. As the plasma power increased, the degree of cross-linking increased, while the number of functional groups decreased. The former has a negative effect on tensile strength, while the latter has a positive effect. Consequently, the maximum tensile strength was obtained at 40 W, demonstrating optimum power of 40 W at 40 mTorr and 1 min.

Upon varying the monomer pressure, the tensile strength of 108, 138, 129 and 123 MPa were obtained at 20, 30, 40 and 50 mTorr, respectively, providing maximum tensile strength of 138 MPa at 30 mTorr (Figure 2-B). At 20 mTorr, the monomers receive more than enough energy, leading to highly dissociated monomers, which in turn results in highly cross-linked films with few functional groups left, providing poor tensile strength of composites. On the other hand, at 50 mTorr, there is less than sufficient plasma power for each monomer, and monomer dissociation is small. However, poor tensile strength of composites is again obtained despite the large number of functional groups due to the poor mechanical property of films[12].

At 30 mTorr, however, each monomer receives plasma energy that is high enough to form a lightly cross-linked polymer film with good mechanical property, but not too high to affect most functional groups, leading to maximum tensile strength. Based on the tensile strength of PEI/CNT composites, 40 W and 30 mTorr were chosen to be the optimum conditions for acrylic acid polymer coating. Similarly, condition optimization was also carried out forallylamine and acetylene, resulting in 40 W and 40
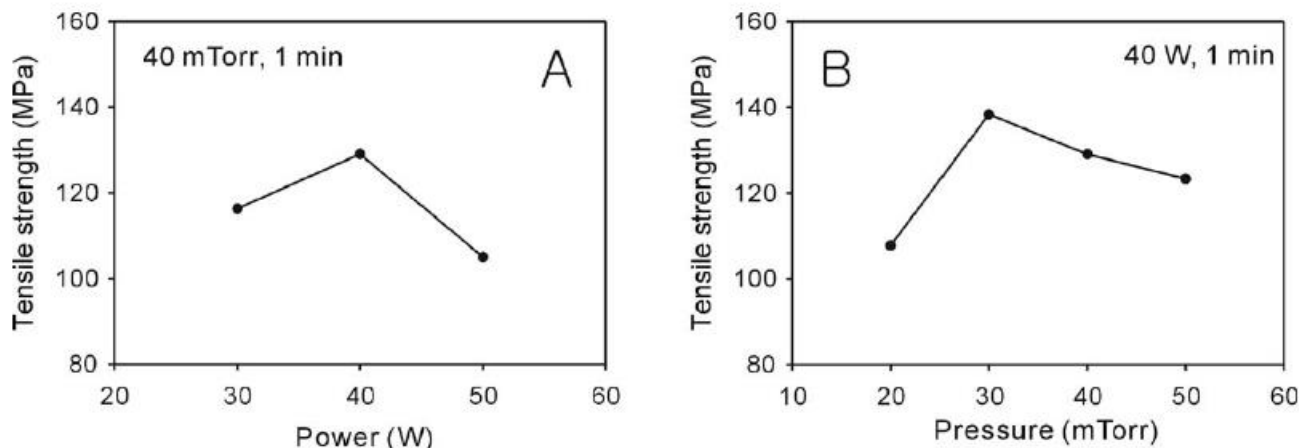
Figure 2. Condition optimization for acrylic acid plasma polymerization by measuring tensile strength as a function of (A) plasma power at 40 mTorr and 1 min (B) monomer pressure at 40 W and 1 min.
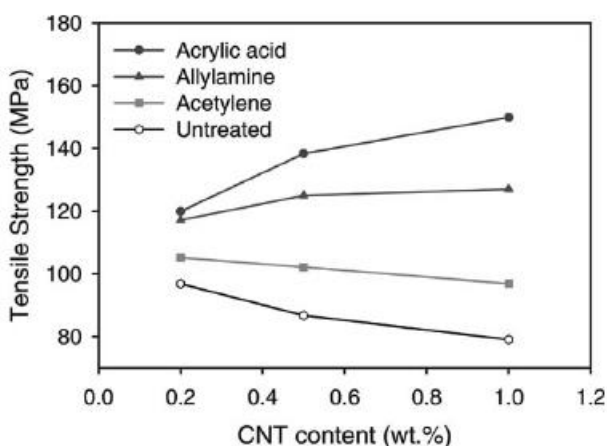

Figure 3. Tensile properties of PEI/CNTs composites as a function of CNT loading.

mTorr, and 40 W and 30 mTorr, respectively.

3.2. Tensile Strength of the PEI/CNT Composites

Under optimized conditions, CNTs were modified via plasma polymerization and subjected to composite preparation with PEI by varying the CNT loading ($0.2 \sim 1$ wt%). As shown in Figure 3, PEI/CNT composites with acrylic acid plasma polymer coated CNTs provided the highest tensile strength (120 MPa), followed by allylamine coated CNTs (118 MPa), acetylene coated CNTs (105 MPa) and the control CNTs (97 MPa). As the loading increased, there were two different behaviors; increased tensile strength with acrylic acid and allylamine coating, but decreased tensile strength with acetylene coating and control CNTs.

The increased tensile strength with acrylic acid and allylamine coatings can be attributed to the enhanced adhesion between the CNT and the PEI, which in turn,

can be attributed to functional groups introduced onto the CNT surface by plasma polymerization coating. In particular, acrylic acid plasma polymer coating was much better than allylamine coating in enhancing the tensile strength of PEI/CNT composites, possibly due to the strong polarity of acrylic acid monomer.

On the other hand, the PEI/CNT composites with acetylene plasma polymer coated CNTs exhibited decreased tensile strength as the CNT loading increased from 0.2 to 1.0%. A similar behavior was also observed from the PEI/CNT composites with control CNTs, demonstrating poor adhesion of CNTs with PEI polymer. The acetylene plasma polymer coatings do not have polar moiety and thus, cannot induce interaction, resulting in poor interfacial adhesion and decreased tensile strength. The same is true for PEI/CNT composites with control CNTs, which have an inert CNT surface.

3.3. FT-IR Analysis of Plasma Polymer Coatings

Since each plasma polymer coating provided a characteristic tensile strength when applied to CNTs, the plasma polymer coatings were analyzed by FT-IR with KBr powder (Figure 4). The plasma polymer coatings of acrylic acid and allylamine provided very similar bands at around 1450 and 2930 cm^{-1}, which can be assigned to CH_2 bending and CH_2 stretching, demonstrating hydrocarbon backbone chains[15]. However, there were also differences; C=O (1700 cm^{-1}) and -OH (3410 cm^{-1}) from acrylic acid; C=N (1660 cm^{-1}) and primary/secondary amine (3340 cm^{-1}) from allylamine.

On the other hand, the acetylene plasma polymer coatings provided all hydrocarbon type bands at around 1380, 1450, 2870, 2930 and 2960 cm^{-1}, which are assigned to CH_3 bending, CH_2 bending, CH_3 symmetric stretching,
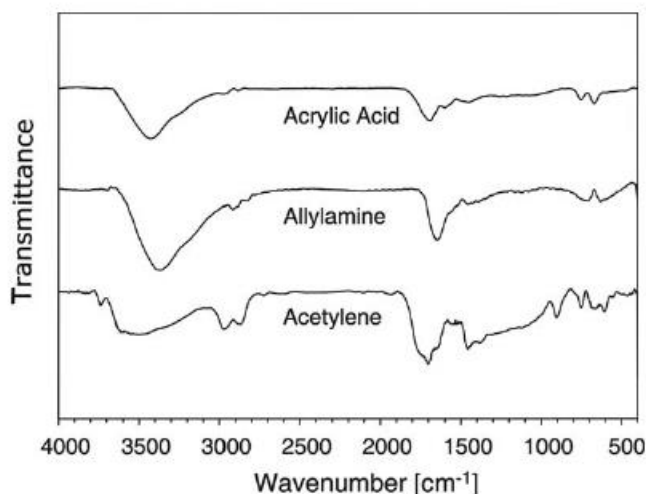
Figure 4. FT-IR of plasma polymer films of acrylic acid, allyl amine and acetylene under optimized conditions.

CH$_2$ stretching and CH$_3$ asymmetric stretching, respectively. In addition, the bands are broader than usual, which is a typical phenomenon found in plasma polymerization coatings. As expected, the acrylic acid and allylamine plasma polymerization coatings provided polar groups such as acid and amine, respectively, which may be responsible for the enhanced tensile strength, owing to the increased adhesion and dispersion of CNTs. However, acetylene plasma polymer coatings only provided hydrocarbon type coatings, given the nature of acetylene monomer.

4. Conclusions

CNTs were successfully modified by plasma polymerization coatings of acrylic acid, allylamine and acetylene, and utilized to prepare PEI/CNT composites. The major findings are summarized as follows:

1) The optimum conditions for the plasma polymerization coating of CNT with acrylic acid and acetylene were 40 W and 30 mTorr, while those for allylamine were 40 W and 40 mTorr, which resulted in tensile strength values of 138 (acrylic acid), 125 (allylamine) and 102 MPa (acetylene) at 0.5% CNT loading.

2) As the loading of CNT increased, the tensile strength of PEI/CNT composites increased with acrylic acid and allylamine plasma polymerization coating, but decreased with acetylene coating and control CNTs.

3) Enhanced tensile strength with the plasma polymerization coating of acrylic acid and allylamine can be attributed to the functional groups provided by the monomers, as evidenced by FT-IR, wh1ich induced interaction with the PEI matrix and thus, enhanced interfacial adhesion.

References

1. S. Iijima, *Nature*, **354**, 56 (1991).
2. R. H. Baughman, A. A. Zakihidof, and W. A. De Heer, *Science*, **297**, 787 (2002).
3. M. Dresselhaus, G. Dresselhaus, and Ph. Avouris, Carbon Nanotubes; synthesis, properties and applications, Springer, Berlin (2001).
4. M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, *Nature*, **381**, 678 (1996).
5. E. T. Thostenson, Z. Ren, and T. W. Chou, *Compo Sci. Techn.*, **61**, 1899 (2001).
6. C. Park, Z. Ounaies, K. A. Watson, K. Pawlowski, S. E. Lowther, J. W. Cobbell, E. J. Soichi, J. S. Harrison, and T. L. St. Clair, *Mat. Res. Soc. Sympo. Proc.*, **706**, 91 (2002).
7. X. L. Xie, Y. W. Mai, and X. P. Zhou, *Mater. Sci. Eng.*, R**49**, 89 (2005).
8. P. Liu, *European Polym J*, **41**, 2693 (2005).
9. T. W. Ebbeson, P. M. Ajayan, H. Hiura, and K. Tanigaki, *Nature*, **367**, 679 (1996).
10. J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boil, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y. S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley, *Science*, **280**, 1253 (1998).
11. Y. Kang and T. A. Taton, *J. Am. Chem. Soc.*, **125**, 5650 (2003).
12. H. Yasuda, Plasma Polymerization, Academic Press, Orlando (1985).
13. R. d'Agostino, P. Favia, and F. Fracassi, Plasma Processing of Polymers, Academic Press, Boston (1990).
14. H. M. Kang, N. I. Kim, and T. H. Yoon, *J. Adhes. Sci. Technol.*, **16**, 1809 (2002).
15. J. H. Roh, J. H. Lee, and T. H. Yoon, *J. Adhes. Sci. Technol.*, **16**, 1529 (2002).
16. Q. Chen, L. Dai. M. Gao, S. Huang, and A. Mau, *J. Phys. Chem.*, **105**, 618 (2001).
17. D. Shi, J. Lian, P. He, L. M. Wang, W. J. van Ooij, M. Schulz, Y. Liu, and D. B. Mast, *Appl. Phys. Lett.*, **81**, 5216 (2002).