



## The Functionalization and Preparation Methods of Carbon Nanotube-Polymer Composites: A Review

Won-Chun Oh<sup>\*,†</sup>, Weon-Bae Ko<sup>\*\*</sup>, and Feng-Jun Zhang<sup>\*\*\*\*</sup>

<sup>\*</sup>Department of Advanced Materials & Science Engineering, Hanseo University, Chungnam, Korea 356-706

<sup>\*\*</sup>Department of Chemistry, Sahmyook University, Seoul, Korea 139-742

<sup>\*\*\*\*</sup>Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture, Anhui Hefei, P. R. China, 230022

(Received May 17, 2010, Revised May 26, 2010, Accepted June 1, 2010)

### 탄소나노튜브-폴리머 복합체의 기능화와 제조방법

오 원 춘<sup>\*,†</sup> · 고 원 배<sup>\*\*</sup> · 장 봉 군<sup>\*\*\*\*</sup>

<sup>\*</sup>한서대학교 신소재공학과,

<sup>\*\*</sup>삼육대학교 화학과,

<sup>\*\*\*\*</sup>안휘건축대학교 화공재료학과

접수일(2010년 5월 17일), 수정일(2010년 5월 26일), 게재확정일(2010년 6월 1일)

**ABSTRACT** : Carbon nanotubes (CNTs) exhibit excellent mechanical, electrical, and magnetic properties as well as nanometer scale diameter and high aspect ratio, which make them an ideal reinforcing agent for high strength polymer composites. The functionalized CNTs are believed to be very promising in the fields such as preparation of functional and composite materials. CNT-Polymer composites are expected to have good processability characteristics of the polymer and excellent functional properties of the CNTs. However, since CNTs usually form stabilized bundles due to Van der Waals interactions, are extremely difficult to disperse and align in a polymer matrix. The biggest issues in the preparation of CNT-reinforced composites reside in efficient dispersion of CNTs into a polymer matrix, and the alignment and control of the CNTs in the matrix. There are several methods for the dispersion of nanotubes in the polymer matrix such as solution mixing, bulk mixing, melt mixing, *in-situ* polymerization and chemical functionalization of the carbon nanotubes, etc. These methods and preparation of high performance CNT-polymer composites are described in this review.

**요약** : 탄소나노튜브는 우수한 기계적 특성, 전기적 및 자기적 성질 뿐만 아니라 나노 크기의 직경 및 높은 종횡비를 나타낸다. 이는 고강도 고분자 복합체의 이상적인 보강제로 사용할 수 있다. 기능성이 부과된 탄소나노튜브는 기능성 재료 및 복합재료의 제조와 같은 분야에서 아주 유력한 재료로 믿어진다. 탄소나노튜브-고분자 복합체는 탄소나노튜브의 우수한 기능성과 고분자의 우수한 가공성을 가질 것으로 기대된다. 그러나, 탄소나노튜브는 보통 반 델 바알스 작용에 의한 안정화된 번들을 형성하기 때문에 고분자 기지에 배열이나 분산이 상당히 어렵다. 탄소나노튜브 강화 복합체의 제조에서 가장 큰 이슈는 고분자내에 탄소나노튜브의 효과적인 분산이며, 기지내에 탄소나노튜브의 배열과 양의 조절이다. 고분자 기지내에 탄소나노튜브의 분산은 용액혼합, 벌크 혼합, 용융혼합, 즉시 고분자화 반응 및 탄소나노튜브의 화학적 기능화 등과 같은 몇 가지 방법이 있다. 본 논평에서는 이들 방법과 고성능 탄소나노튜브-고분자 복합체의 제조에 대하여 서술하고자 한다.

**Keywords** : polymer composites; carbon nanotubes; functionalization; preparation methods

## I. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima,<sup>1</sup> they have received much attention for their many

potential applications, such as nanoelectronics and photovoltaic devices,<sup>2,3</sup> superconductors,<sup>4</sup> and nanocomposite materials.<sup>5,6</sup> There are two types of CNTs: multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). The former consists of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core with interlayer separations as in graphite. In con-

<sup>†</sup>Corresponding Author. E-mail: wc\_oh@hanseo.ac.kr

trast, SWCNT comprises a single graphene cylinder. Both SWCNTs and MWCNTs have physical characteristics of solids and are micro-crystals with high aspect ratios of 1000 or more, although their diameter is close to molecular dimensions. CNTs have unique mechanical, electrical, magnetic, optical and thermal properties.

In some special applications, such as space explorations, high-performance lightweight structural materials are required, and they can be developed by adding CNTs to polymers or other matrix materials. The superior properties of CNTs offer exciting opportunities for new composites. The NASA has invested large sums of money to develop carbon nanotube-based composites for applications such as the Mars mission.<sup>7</sup> In particular, this combination of properties makes them ideal candidates as advanced filler materials in composites. Researchers have envisaged taking advantage of their conductivity and high aspect ratio to produce conductive plastics with exceedingly low percolation thresholds.<sup>8</sup> In another area, it is thought that their massive thermal conductivity can be exploited to make thermally conductive composites.<sup>9</sup>

Recently, polymer/CNT composites have attracted considerable attention owing to their unique mechanical and conductivity, surface and multi-functional properties, and strong interactions with the matrix resulting from the nano-scale microstructure and extremely large interfacial area. Our review given below is complementary to theirs and we focus on recent progress made towards the functionalization of CNT and preparation methods of CNT polymer composites.

## II. Functionalization of CNT

Since CNTs usually agglomerate due to Van der Waals force, they are extremely difficult to disperse and align in a polymer matrix. Thus, a significant challenge in developing high performance CNT polymer composites is to introduce the individual CNTs in a matrix in order to achieve better dispersion and alignment and strong interfacial interactions, and to improve the load transfer across the CNT-polymer matrix interface. The functionalization of CNT is an effective way to prevent nanotube aggregation, which helps to better disperse and stabilize the CNTs within a matrix. These functionalization procedures will be summarized here.

### 2.1 Chemical functionalization

In addition, the surfaces of CNTs have to be chemically functionalized (including grafting copolymerization) to achieve good dispersion in CNT composites and strong interface adhesion between surrounding polymer chains, even though the interface area is very large. CNTs are assembled as ropes or bundles, and there are some catalyst residuals, bucky onions,

spheroidal fullerenes, amorphous carbon, polyhedron graphite nano-particles, and other forms of impurities in as grown CNTs. Thus, purification, cutting or disentangling, and activation treatments are needed before chemical functionalization.

#### 2.1.1 Purification

The first method to purify MWCNTs is based on oxidation,<sup>10</sup> which is observed to occur preferentially at the nanotube ends and on nano-particles that have a high concentration of topological defects. Hiura et al.<sup>11</sup> purified CNTs by a mixture of concentrated sulfuric acid and potassium permanganate, but this is still not proven to be a good method for large-scale separation. Tohji et al.<sup>12</sup> suggested a purification method that included hydrothermal treatment along with extraction of fullerenes, thermal oxidation and dissolution in 6 M hydrochloric acid. Liu et al.<sup>13</sup> developed a purification method that consisted of refluxing in 2.6 M nitric acids and re-suspending CNTs in pH 10 water with surfactant followed by filtration with a cross-flow filtration system. This may be an efficient method to purify CNTs owing to the combined advantages of the chemical and physical methods.

#### 2.1.2 Cutting or disentangling

CNTs are long and entangled as ropes or in bundles. The cutting process is necessary for CNTs to disentangle, open up the tubes and provide active sites for chemical functionalization. Liu et al.<sup>13</sup> chose a 3:1 mixture of concentrated sulfuric acid and nitric acid to cut CNTs into ~150 nm in length. The short and open-ended CNTs are then treated by a 4:1 mixture of concentrated sulfuric acid and 30% aqueous hydrogen peroxide. Thus, more functional groups such as carboxylic acid and hydroxyl groups are formed on the CNT surface. Later, Shaffer et al.<sup>14,15</sup> used a 3:1 mixture of concentrated sulfuric acid and nitric acid to cut CNTs and produce an electrostatic stabilized dispersion of CNTs in water with an average length of 1.1  $\mu\text{m}$ . Chen et al.<sup>16</sup> also obtained disentangled SWCNTs with an average length >1  $\mu\text{m}$ . Obviously, it is necessary to control and adjust the processing conditions to obtain short CNTs with different length.

#### 2.1.3 Activation treatments

In general, carboxylic acid and hydroxyl groups could be formed on the surface or open ends of CNTs during the oxidation process by oxygen, air, concentrated sulfuric acid, nitric acid and 30% aqueous hydrogen peroxide, and concentrated sulfuric acid and its mixture. To further activate the carboxylic acid groups on the surface of CNTs, they are converted into acyl chloride groups by reaction with thionyl chloride at room temperature. Ramanathan et al.<sup>17</sup> functionalized SWCNT with amino groups via chemical modification of carboxyl groups introduced on the carbon nanotube surface. The amino termi-

nation further allows the functionalized SWCNTs possible for covalent bonding to polymers and biological systems such as DNA and carbohydrates. By using a redox initiating system, which consists of cerium ions and hydroxymethyl groups ( $-\text{CH}_2\text{OH}$ ) on the surface of CNTs, free radical graft polymerization of vinyl monomers could occur. Besides the above activation methods, Chen et al.<sup>18</sup> activated CNTs surface by plasma modification. Acetaldehyde and ethylenediamine vapors were plasma polymerized on the surface of CNTs, thereby introducing active aldehyde ( $-\text{CHO}$ ) and amino ( $-\text{NH}_2$ ) groups.

#### 2.1.4 Chemical functionalization

Lin et al.<sup>19</sup> synthesized polymer grafted CNTs based on acylated CNTs with poly(propionylethylenimine-co-ethylenimine) (PPEI-EI), poly(vinyl acetate-co-vinyl alcohol) (PVA-VA) and poly(vinyl alcohol) (PVA), respectively. They found that PVA grafted CNTs were soluble in PVA solution, PVA-CNT nanocomposite films so-formed are of high optical quality without any observable phase separation. The result indicates that chemical graft functionalization of CNTs by matrix polymer was an effective way to achieve homogeneous dispersion for high-performance polymer/CNT nanocomposites. Meanwhile, Mitchell et al.<sup>20</sup> synthesized 4-(10-hydroxydecyl) benzoate-SWCNTs by in situ reaction of organic diazonium compounds, and prepared the composites based on the functionalized SWCNTs and PS. These nanocomposites show a percolated SWCNT network structure at 1 vol. % nanotubes, whilst for the unfunctionalized SWCNT/PS nanocomposites this occurs at twice SWCNTs loading. The reason is because the chemical functionalization of CNTs enhances their interaction with the polymer matrix and improves their dispersion in the composites. Recently, Viswanathan et al.<sup>21</sup> reported that introduction of carbanions on the SWCNTs surface by treatment with an anionic initiator served to exfoliate bundles of SWCNTs, and provided initiating sites for polymerization of styrene. Qin et al.<sup>22</sup> grafted poly (n-butyl methacrylate) (PBMA) brushes on the ends and sidewalls of SWCNTs by using atom transfer radical polymerization (ATRP).

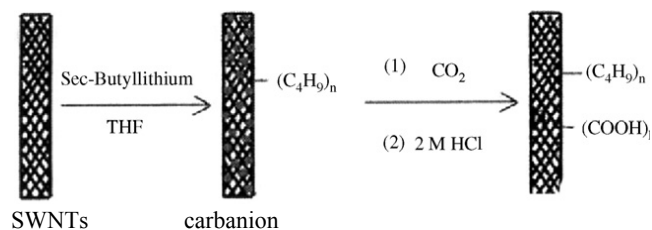
In summary, chemical functionalization can promote good dispersion in the polymer/CNT composites and will play a dominant role in future development and applications of these nanocomposites. Also nanotubes have distinct inner and outer surfaces, which can be functionalized either chemically or biochemically. Thus, the development of simple and cost effective chemical methods for covalent functionalization of carbon nanotube materials is becoming an area of growing fundamental and industrial importance.

#### 2.2 Samples of functionalization of CNTs

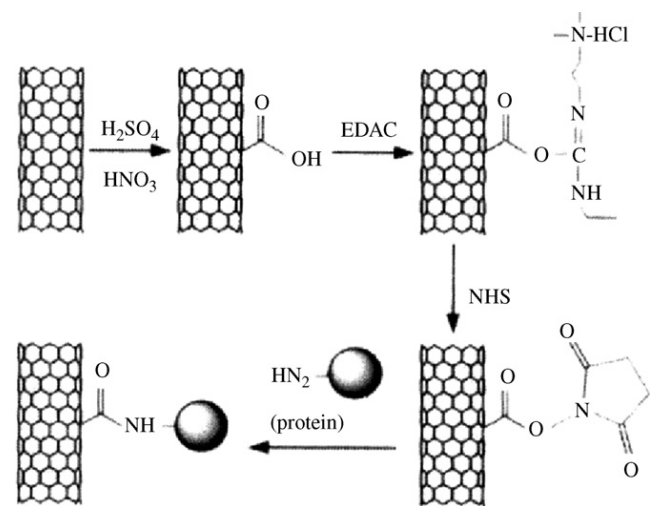
Hu et al.<sup>23</sup> functionalized CNT with the molecules contain-

ing thiol group and halogen. The chemical methods for the covalent functionalization of CNTs involve direct fluorination, organic free radical addition, fluorine displacement in fluoro nanotubes producing amino, hydroxyl and carboxy group terminated derivatives. The carboxylation is conducted via oxidation of defect sites in CNTs by strong oxidants. The alkylation and acylation of CNTs can be realized by making use of fluorine displacement reactions of fluoronanotubes with alkyl lithium reagents or by employing diazonium chemistry for attaching acyl groups to the sidewalls.<sup>24</sup> By treating the CNT with secondary butyl lithium firstly and reacting the generated carbanions with carbon dioxide secondly, it can be alkylated and carboxylated and its schematic representation is given in Figure 1.

One of the universal methods for connecting biomolecules to CNTs is diimide activated amidation by direct coupling of carboxylic acid to proteins using *N*-ethyl-*N*-(3-dimethylamino-propyl) carbodiimide hydrochloride (EDAC) or *N,N*-dicyclohexyl carbodiimide (DCC) as a coupling agent.<sup>25</sup> The schematic view of the attachment of proteins to CNTs via diimide activated amidation is given in Figure 2.



**Figure 1.** Schematic representation of the carboxylation of CNTs.<sup>24</sup>



**Figure 2.** Schematic view of the attachment of proteins to CNTs via diimide activated amidation.<sup>25</sup>

### III. Preparation methods of CNT-polymer composites

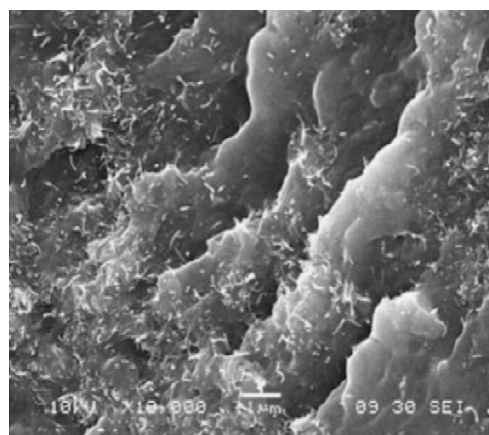
The dispersion of CNTs in polymer matrices is a critical issue in the preparation of CNT/polymer composites. Better reinforcing effects of CNTs in polymer composites will be achieved if they do not form aggregates and as such, they must be well dispersed in polymer matrices. Several processing methods available for fabricating CNT/polymer composites based on either thermoplastic or thermosetting matrices have been described in past review articles.<sup>26,27</sup> They mainly include solution mixing, bulk mixing, melt mixing, and in situ polymerization. Although inherently different processing routes have been attempted, they all address important issues that affect composite properties, such as exfoliation of CNT bundles and ropes, homogeneous dispersion of the individual tubes into the matrix, alignment and interfacial bonding.

The effective utilization of CNT material in composite applications depends strongly on their ability to be dispersed individually and homogeneously within a matrix. An optimized interfacial interaction between the CNT sidewalls and the matrix should result in an efficient load transfer to the “hard” component of the composite. All processing methods known thus far for CNT-based composites are described below. Due to the huge volume of related literature, only the seminal works will be discussed for each processing method.

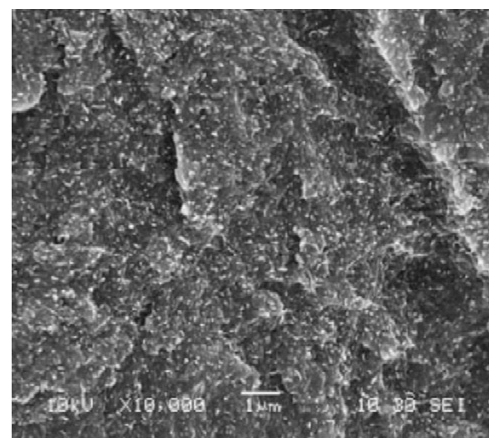
#### 3.1 Solution mixing

In this approach, a dispersion of CNTs in a suitable solvent and polymers are mixed in solution. The CNT/polymer composite is formed by precipitation or by evaporation of the solvent. It is well known that it is very difficult to properly disperse pristine CNTs in a solvent by simple stirring. A high power ultrasonication process is more effective in forming a dispersion of CNTs. Ultrasonic irradiation has been extensively used in dispersion, emulsifying, crushing, and activating the particles. By taking advantage of the multi-effects of ultrasound, the aggregates and entanglements of CNTs can be effectively broken down.

For example, Li et al.<sup>28</sup> used a simple solution-precipitation technique to improve the dispersion of CNTs in a polycarbonate solution by sonication at a frequency of 20 kHz for 10 min. They showed that the CNTs were uniformly dispersed in polycarbonate matrix on its consolidation. In this case, ultrasonic wave as well as mechanically stirring played important roles in the formation of the composites with a uniform particle size. The chemical effects of ultrasound are associated with the rapid (microsecond time scale), violent collapse of cavitation bubbles created as the ultrasonic waves pass through a liquid medium. Safadi et al.<sup>29</sup> dispersed MWNTs in PS using



(a)



(b)

**Figure 3.** SEM micrographs of PU/CNT composites: (a) 10 wt% pristine MWNT and (b) 20 wt% MWNT-COOH.<sup>30</sup>

ultrasonication and dismembrator at 300W for 30 min. Uniform dispersions of CNTs in PS were achieved by using sonication.

Recently Cho and co-workers successfully prepared PU/MWNTs composites with better dispersion of CNTs up to 20 wt% in PU.<sup>30</sup> In the research, the necessary weight fractions of carboxylate MWNTs were first dispersed in DMF solution under sonication at room temperature for 1 h using a high power ultrasonic processor. Thereafter, PU was added into this solution and stirred for 1 h. The mixtures were then sonicated again for 1 h. The SEM photographs of the cross-sectional fracture of composites of the achieved dispersion for the investigated MWNTs are shown in Figure 3.

#### 3.2 Bulk mixing

Milling is a mechanical process that leads to local generation of high pressure as a result of collisions throughout the grinding media. Concerning applications in CNT nanotechnology,

this method has been used to shorten the lengths of carbon nanostructures.<sup>31</sup> A solid state mechanochemical pulverization process, namely pan milling, was used to prepare a CNT/polypropylene composite powder.<sup>32</sup> This powder was subsequently melt-mixed with a twin-roll masticator to obtain a homogeneous composite. The length of the CNTs was reduced from a few micrometers to  $\sim 500$  nm. Similarly, high energy ball milling was utilized to incorporate CNTs into polymer matrices.<sup>33</sup> In this way, a satisfactory level of dispersion of CNTs into the polymer matrix was obtained, resulting in an improvement of the physical properties of the samples. In addition, a mechanical-chemical high-speed vibration milling technique was applied for solubilizing CNTs in various media due to the formation of non-covalent-type complexes with species, such as cyclodextrins.<sup>34</sup>

### 3.3 Melt mixing

While solution processing is a valuable technique for both nanotube dispersion and composite formation, it is completely unsuitable for many polymer types that are insoluble. Melt processing is a common alternative, which is particularly useful for dealing with thermoplastic polymers. This range of techniques makes use of the fact that thermoplastic polymers soften when heated. Amorphous polymers can be processed above their glass transition temperature while semi-crystalline polymers need to be heated above their melt temperature to induce sufficient softening. Due to the fact that thermoplastic semicrystalline polymers soften when heated above their melting point, melt processing has been a very valuable technique for the fabrication of CNT-based composites. In addition, the method is suitable for polymers that cannot be processed with solution techniques due to their insolubility in common solvents.

In general, melt mixing involves the blending of polymer melt with CNT material by application of intense shear forces. Depending on the final morphology/shape of the composites, the bulk samples can then be processed by several techniques, such as extrusion.<sup>35</sup> An early study on the melt mixing of SWCNTs and PMMA matrix was carried out by Winey and co-workers.<sup>36</sup> CNTs and PMMA were first blended in dimethylformamide (DMF) and the resulting suspension was casted onto Teflon dishes and dried. The resultant films were broken up in small pieces and hot pressed to form a new film. This was then broken up and hot pressed, a process that was repeated as many as 25 times. The authors observed that the CNT dispersion improved with each melting step. The final composite film was then extruded through a melt spinning apparatus to form a fiber. In the final step, the composite fibers were melt spun to achieve draw ratios between 20 and 3600. Due to the alignment of tubes along the fiber axis, the elastic

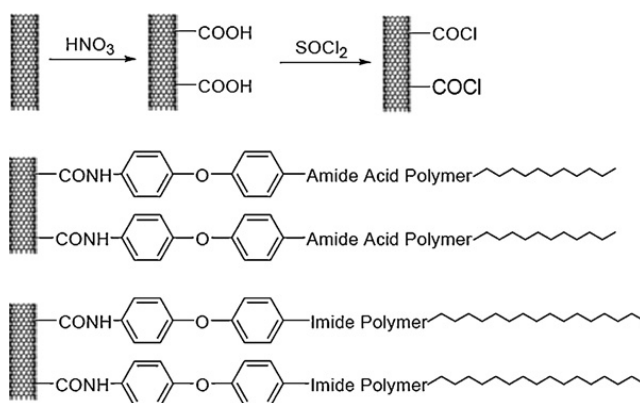
modulus and yield strength of the composite fibers increased with nanotube loading and draw ratio.

Using a different protocol for bulk composites, Goh and co-workers<sup>37</sup> have melt-blended MWCNTs and PMMA in a laboratory mixing molder at a speed of 120 rpm (blending temperature  $\sim 200$  °C). The mixed samples were then compressed under pressure at 210 °C using a hydraulic press to yield composite films. Electron microscopy images showed that the nanotubes are well dispersed in the polymer matrix. Concerning the upscaled fabrication of composites, Potschke et al.<sup>38</sup> have fabricated 1 kg batches of MWCNTs/polycarbonate composites by melt extrusion and compression molding. Rheology measurements of the composites at 260 °C showed that viscosity increases significantly with increasing CNT concentration, especially for CNT weight fractions above 2%.

### 3.4 *In-situ* polymerization

Since 1999, *in-situ* polymerisation in the presence of carbon nanotubes has been intensively explored for the preparation of polymer grafted nanotubes and processing of corresponding polymer composite materials. The main advantage of this method is that it enables grafting of polymer macromolecules onto the walls of carbon nanotubes. In addition, it is a very convenient processing technique, which allows the preparation of composites with high nanotube loading and very good miscibility with almost any polymer type. This technique is particularly important for the preparation of insoluble and thermally unstable polymers, which cannot be processed by solution or melt processing. Depending on required molecular weight and molecular weight distribution of polymers, chain transfer, radical, anionic, and ring-opening metathesis polymerizations can be used for *in situ* polymerization processing. Here we consider only recent advances in *in situ* polymerization processing, which resulted in new polymer-carbon nanotube composites.

In this polymerization method, the CNTs are dispersed in monomer followed by polymerization. A higher percentage of CNTs may be easily dispersed in this method, and form a strong interaction with the polymer matrixes. This method is useful for the preparation of composites with polymers that can not be processed by solution or melt mixing, e.g., insoluble and thermally unstable polymers. Hu et al.<sup>39</sup> synthesized MWNT-reinforced polyimide nanocomposites by *in-situ* polymerization of monomers in the presence of acylated MWNTs, as shown in Scheme 1. In this work, MWNTs were functionalized with acyl groups, and then reacted with biphenyltetracarboxylic dianhydride to form MWNT-poly(amic acid). The final MWNT-polyimide nanocomposite films were obtained by imidization of MWNT-poly(amic acid) at 350 °C for 1 h under vacuum. In this method, the CNTs were uniformly dispersed in polymer matrix.



**Scheme 1.** Outline of the preparation of MWNT-polyimide nanocomposite films.<sup>39</sup>

Concerning the fabrication of CNT-based silicone elastomer composites, Liu et al.<sup>40</sup> dispersed the graphitic nanostructures into a viscous mixture of monomers by mechanical grinding of the components. Most probably, the thermal energy given by the grinding process caused the efficient condensation of the precursor substances. The thermal conductivities were found to increase with the CNT amount. There was a 65% enhancement with 3.8 wt% CNT loading.

Similarly, Gojny et al.<sup>41</sup> studied the dispersion of CNTs into viscous epoxy monomers via a common shear mixing technique that is, calendaring. In a first step, the nanoparticles were manually mixed into the resin while in the following step they were homogeneously dispersed using of a three-roll calender. A first primary dispersion of the agglomerates could be achieved by the knead-vortex between the rolls, while the final exfoliation and dispersion of the CNTs occurs in the area between the rolls. The suspension was collected and then mixed with the curing agent to obtain a homogeneous composite.

#### IV. Conclusion

In conclusion, much progress has been made over the last few years in polymer composite using carbon nanotubes. In addition, many researchers are branching out with the fabrication of novel structures by innovative processing techniques. Enhanced dispersion and alignment of CNTs in polymer matrices greatly improve mechanical, electric, thermal, electrochemical, optical and super-hydrophobic properties of polymer/CNT composites. Thus, the critical challenge is the development of means and ways to promote and increase the dispersion and alignment of CNTs in the matrix. Chemical functionalization could improve the dispersion of CNTs. If this progress continues apace, we can expect a continuing bright future in this fascinating and potentially very useful area.

#### Reference

1. S.Iijima, "Helical microtubules of graphitic carbon", *Nature*, **354**, 56 (1991).
2. A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, "Logic circuits with carbon nanotube transistors", *Science*, **294**, 1317 (2000).
3. H. Ago, K. Petritsch, M.S.P. Shaffer, A.H. Windle, and R.H. Friend, "Composites of carbon nanotubes and conjugated polymers for photovoltaic devices", *Adv. Mater.*, **11**, 1281 (1999).
4. A.Y. Kasumov, R. Deblock, M. Kociak, B. Reulet, H. Bouchiat, and I. Khodos, "Supercurrents through single-walled carbon nanotubes", *Science*, **284**, 1508 (1999).
5. X.L. Xie, Y.W. Mai, and X. Ping, "Dispersion and alignment of carbon nanotubes in polymer matrix: a review", *Mater. Sci. Eng. Rep.*, **49**, 89 (2005).
6. R. Andrews, and M.C. Weisenberger, "Carbon nanotube polymer composites", *Curr. Opin. Solid. State. Mater. Sci.*, **8**, 31 (2004).
7. M.S. Dresselhaus, G. Dresselhaus, and P. Avouris, "Carbon Nanotubes: Synthesis, Structure, Properties and Application", Springer, Berlin, Germany, 2001, pp.11-28.
8. B.E. Kilbride, J.N. Coleman, J. Fraysse, P. Fournet, M. Cadek, and A. Drury, "Experimental observation of scaling laws for alternating current and direct current conductivity in polymer-carbon nanotube composite thin films", *J. Appl. Phys.*, **92**, 4024 (2002).
9. M.J. Biercuk, M.C. Llaguno, M. Radosavljevic, J.K. Hyun, and A.T. Johnson, "Carbon nanotube composites for thermal management", *Appl. Phys. Lett.*, **80**, 2767 (2002).
10. T.W. Ebbesen, P.M. Ajayan, H. Hiura, and K. Tanigaki, "Purification of nanotubes", *Nature*, **367**, 519 (1994).
11. H. Hiura, T.W. Ebbesen, and K. Tanigaki, "Opening and purification of carbon nanotubes in high yields", *Adv. Mater.*, **7**, 275 (1995).
12. K. Tohji, H. Takahashi, Y. Shinoda, N. Shimizu, B. Jeyadevan, I. Matsuoda, Y. Saito, A. Kasuya, S. Ito, and Y. Nishina, "Purification Procedure for Single-Walled Nanotubes", *J. Phys. Chem. B*, **101**, 1974 (1997).
13. J. Liu, A.G. Rinzier, H.J. Dai, J.H. Hafner, R.K. Bradley, P.J. Boul, 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, "Fullerene pipes", *Science*, **280**, 1253 (1998).
14. M.S.P. Shaffer, X. Fan, and A.H. Windle, "Dispersion and packing of carbon nanotubes", *Carbon*, **36**, 1603 (1998).
15. M.S.P. Shaffer, and A.H. Windle, "Fabrication and Characterization of Carbon Nanotube/Poly(vinyl alcohol) Composites", *Adv. Mater.*, **11**, 937 (1999).
16. J. Chen, A.M. Rao, S. Lyuksyutov, M.I. Itkis, M.A. Hamon, H. Hu, R.W. Cohn, P.C. Eklund, D.T. Colbert, R.E. Smalley, and R.C. Haddon, "Dissolution of full-length single-walled carbon nanotubes", *J. Phys. Chem. B*, **105**, 2525 (2001).

17. T. Ramanathan, F.T. Fischer, and R.S. Ruoff, "Amino functionalized carbon nanotubes for binding to polymers and biological systems", *Chem. Mater.*, **17**, 1290 (2005).
18. Q.D. Chen, L.M. Dai, M. Gao, S.M. Huang, and A. Mau, "Plasma activation of carbon nanotubes for chemical modification", *J. Phys. Chem. B*, **105**, 618 (2001).
19. Y. Lin, B. Zhou, K.A.S. Fernando, P. Liu, and Y.P. Sun, "Polymeric carbon nanocomposites from carbon nanotubes functionalized with matrix polymer", *Macromolecules*, **36**, 7199 (2003).
20. C. Mitchell, J.L. Bahr, S. Arepalli, J.M. Tour, and R. Krishnamoorti, "Dispersion of functionalized carbon nanotubes in polystyrene", *Macromolecules*, **35**, 8825 (2002).
21. G. Viswanathan, N. Chakrapani, H. Yang, B. Wei, H. Chung, K. Cho, C.Y. Ryu, and P.M. Ajayan, "Single-Step in Situ Synthesis of Polymer-Grafted Single-Wall Nanotube Composites", *J. Am. Chem. Soc.*, **125**, 9258 (2003).
22. S. Qin, D. Qin, W.T. Ford, D. Resasco, and J.E. Herrera, "Polymer Brushes on Single-walled Carbon Nanotubes by Atom Transfer Radical Polymerization of n-Butyl Methacrylate", *J. Am. Chem. Soc.*, **126**, 170 (2004).
23. J. Hu, J. Shi, S. Li, Y. Quin, Z. Guo, Y. Song, and D. Zhu, "Efficient method to functionalize carbon nanotubes with thiol groups and fabricate gold nanocomposites", *Chem. Phys. Lett.*, **401**, 352 (2005).
24. S. Chen, W. Shen, G. Wu, D. Chen, and M. Jiang, "A new approach to the functionalization of single-walled carbon nanotubes with both alkyl and carboxyl groups", *Chem. Phys. Lett.*, **402**, 312 (2005).
25. K. Jiang, L.S. Schadler, R.W. Siegel, X. Zhang, H. Zhang, and M. Terrones, "Protein immobilization on carbon nanotubes via a two-step process of diimide-activated amidation", *J. Mater. Chem.*, **14**, 37 (2004).
26. O. Breuer and U. Sundararaj, "Big returns from small fibers: a review of polymer/carbon nanotube composites", *Polym. Compos.*, **25**, 630 (2004).
27. M. Moniruzzaman and K.I. Winey, "Polymer nanocomposites containing carbon nanotubes", *Macromolecules*, **39**, 5194 (2006).
28. C. Li, X.J. Pang, M.Z. Qu, Q.T. Zhang, B. Wang, and B.L. Zhang, "Fabrication and characterization of polycarbonate/carbon nanotubes composites", *Compos. Part A*, **37**, 1485 (2005).
29. B. Safadi, R. Andrews, and E.A. Grulke, "Multiwalled carbon nanotubes polymer composites: synthesis and characterization of thin films", *J. Appl. Polym. Sci.*, **84**, 2660 (2002).
30. N.G. Sahoo, Y.C. Jung, H.J. Yoo, and J.W. Cho, "Effect of functionalized carbon nanotubes on molecular interaction and properties of polyurethane composites", *Macromol. Chem. Phys.*, **207**, 1773 (2006).
31. N. Pierard, A. Fonseca, Z. Konya, I. Willems, G. Van Tendeloo, and J.B. Nagy, "Production of short carbon nanotubes with open tips by ball milling", *Chem. Phys. Lett.*, **335**, 1 (2001).
32. H. Xia, Q. Wang, K. Li, and G.H. Hu, "Preparation of CNT/polypropylene composite powder with a solid state mechanochemical pulverization process", *J. Appl. Polym. Sci.*, **93**, 378 (2004).
33. S. Ghose, K.A. Watson, K.J. Sun, J.M. Criss, E.J. Siochi, and J.W. Connell, "High temperature resin carbon nanotube composite fabrication", *Compos. Sci. Technol.*, **66**, 1995 (2006).
34. A. Ikeda, K. Hayashi, T. Konishi, and J.I. Kikuchi, "Solubilization and debundling of purified single-walled carbon nanotubes using solubilizing agents in an aqueous solution by high-speed vibration milling technique", *Chem. Commun.*, **11**, 1334 (2004).
35. C.A. Cooper, D. Ravich, D. Lips, J. Mayer, and H.D. Wagner, "Distribution and alignment of carbon nanotubes and nanofibrils in a polymer matrix", *Compos. Sci. Technol.*, **62**, 1105 (2002).
36. R. Hagenmueller, H.H. Gommans, A.G. Rinzler, J.E. Fischer, and I. Winey, "Aligned single-wall carbon nanotubes in composites by melt processing methods", *Chem. Phys. Lett.*, **330**, 219 (2000).
37. Z. Jin, K.P. Pramoda, G. Xu, and S.H. Goh, "Dynamic mechanical behavior of melt-processed multiwalled carbon nanotube/poly(methyl methacrylate) composites", *Chem. Phys. Lett.*, **337**, 43 (2001).
38. P. Potschke, T.D. Fomes, and D.R. Paul, "Rheological behaviour of multiwalled carbon nanotubes/polycarbonate composites", *Polymer*, **43**, 3247 (2002).
39. N. Hu, H. Zhou, G. Dang, X. Rao, C. Chen, and W. Zhang, "Efficient dispersion of multi-walled carbon nanotubes by in situ polymerization", *Polym. Int.*, **56**, 655 (2007).
40. C.H. Liu, H. Huang, Y. Wu, and S.S. Fan, "Thermal conductivity improvement of silicone elastomer with CNT loading", *Appl. Phys. Lett.*, **84**, 4248 (2004).
41. F.H. Gojny, M. Wichmann, U. Kopke, B. Fiedler, and K. Schulte, "CNT-reinforced epoxy composites: enhanced stiffness and fracture toughness at low nanotube content", *Compos. Sci. Technol.*, **64**, 2363 (2004).