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Carbon Nanotubes-Polymer Nanocomposites

¹M. Rabiatul Manisah and ²Y. Kamal

¹Faculty of Chemical Engineering Technology, TATI University College, 24000 Terengganu, MALAYSIA.

²Faculty of Chemical & Natural Resources Engineering, University of Malaysia Pahang, 26300 Kuantan, MALAYSIA.

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ABSTRACT

Carbon nanotubes (CNTs) has attracted both academic and industrial interest because it can produce a dramatic improvement in properties at very low filler content. This paper reviews the current understanding of CNTs and CNTs polymer nanocomposites. The modification of CNTs and the utilization of these materials in the fabrication of nanocomposites have been explored. The mechanical properties of CNT/polymer nanocomposites are also highlighted.

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INTRODUCTION

The field of nanoscience has blossomed over the last twenty years and the emergence of polymer nanocomposites has become more important in enormous area and applications. In particular, the use of nanomaterials as fillers in the preparation of polymer nanocomposites has attracted increasing interest owing to their unique properties and numerous potential applications in the automotive, aerospace, construction and electronic industries (Marvin L. Cohen, 2001). Polymer nanocomposites are two phase systems consisting of polymer matrix loaded with high surface area reinforcing fillers. The systems have attracted many interest because they theoretically promise substantial improvement of material's properties at very low filler loadings (D. A. Schaefer, R. S. Justice, 2001). There are many types of fillers incorporated in polymer matrix such as nanoclays, nano-oxides, CNTs as well as metallic oxides.

CNTs are one dimensional carbon materials which can have an aspect ratio greater than 1000 (J. N. Coleman, U. Khan, W. J. Blau, Y. K. Gun'ko, 2006). Due to their special electrical, mechanical, thermal and optical properties, CNTs have been shown to have various potential applications. Many research dedicated on utilizing CNTs have proven that CNTs to be very effective fillers in polymer nanocomposites (E. T. Thostenson, Z. F. Ren, T. W. Chou, 2001, J. N. Coleman, U. Khan, Y. K. Gunko, 2006). However, the full potential of employing CNTs as reinforcements has been limited because of the difficulties associated with dispersion of entangled CNTs during processing and poor interfacial interaction between CNTs and polymer matrix.

Carbon Nanotubes:

Carbon nanotubes (CNTs), one of the carbon allotropes, has been investigated for more than two decades since it was first discovered. Due to their special electrical, mechanical, thermal and optical properties, CNTs have been shown to have various potential applications. CNTs are one dimensional carbon materials which can have an aspect ratio greater than 1000. They can be envisioned as cylinders composed of rolled-up graphite planes with diameters in nanometer scale. The cylindrical nanotube usually has at least one end capped with a hemisphere of fullerene structure. Depending on the process for CNT fabrication, there are two types of CNTs; single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). SWCNTs consist of a single graphene layer rolled up into a seamless cylinder whereas MWCNTs consist of two or more concentric cylindrical shells of graphene sheets coaxially arranged around a central hollow core with van der Waals forces between adjacent layers (P.-C. Ma, N. a. Siddiqui, G. Marom, and J.-K. Kim, 2010). According to the rolling angle of the graphene sheet, CNTs have three chiralities: armchair, zigzag and chiral one. The chirality of nanotubes has significant impact on their transport properties, particularly the electronic properties, metallic or semiconductors.

Corresponding Author: M. Rabiatul Manisah, Faculty of Chemical Engineering Technology, TATI University College, 24000 Terengganu, MALAYSIA.

2. Properties of CNTs:

The chemical bonding of CNTs is composed entirely of sp^2 carbon-carbon bonds. This bonding structure - stronger than the sp^3 bonds found in diamond - provides CNTs with extremely high mechanical properties. Although there is no consensus on the exact mechanical properties of CNTs, theoretical and experimental results have shown unusual mechanical properties of CNTs with Young's modulus as high as 1.2 TPa and tensile strength of 50–200 GPa (J. N. Coleman, U. Khan, W. J. Blau, and Y. K. Gun'ko, 2006).

In addition to the exceptional mechanical properties associated with CNTs, they also possess other useful physical properties. CNTs have many advantages over other carbon materials in terms of electrical and thermal properties. These properties offer CNTs great potential for wide applications in field emission, conducting plastics, thermal conductors, energy storage, conductive adhesives, thermal interface materials, structural materials, fibers, catalyst supports, biological applications, air and water filtration, ceramics and so on.

Dispersion of CNTs:

In order to obtain the best performance from carbon nanotube-polymer nanocomposites, several challenges should be overcome. For example, purification of nanotubes is a necessary step to remove metallic and amorphous carbon impurities, while avoiding serious damage to the nanotubes. Furthermore, carbon nanotube content and alignment as well as the void content in the nanocomposite should be controlled. The dispersion of carbon nanotubes in the polymer matrix plays an important role in the nanocomposite's performance. Obtaining the optimum dispersion is a challenge which requires detailed studies at different scales, particularly for nanocomposites with relatively high nanotube content (M. Rahmat and P. Hubert, 2011, L. Vaisman, H. D. Wagner, and G. Marom, 2006).

The nature of dispersion problem for CNTs is rather different from other conventional fillers, such as spherical particles and carbon fibers, because CNTs are characteristic of small diameter in nanometer scale with high aspect ratio (>1000) and thus extremely large surface area. In addition, the commercialized CNTs are supplied in the form of heavily entangled bundles, resulting in inherent difficulties in dispersion. The large quantity of particles and their size effect will lead to an exceptionally large surface area of nano-scale fillers in the composite. A large surface area of fillers means a large interface area present between the filler and matrix.

The performance of a CNT/polymer nanocomposite depends on the dispersion of CNTs in the matrix and interfacial interactions between the CNT and the polymer. However, the carbon atoms on CNT walls are chemically stable because of the aromatic nature of the bond. As a result, the reinforcing CNTs are inert and can interact with the surrounding matrix mainly through van der Waals interactions, unable to provide an efficient load transfer across the CNT/matrix interface. The chemistry of functionalized CNTs and the reaction mechanisms between the CNTs and functional groups can be divided into chemical functionalization and physical methods based on the interactions between the active molecules and carbon atoms on the CNTs.

2. Chemical Functionalization:

Chemical functionalization is based on the covalent linkage of functional entities onto carbon scaffold of CNTs. It can be performed at the termini of the tubes or at their sidewalls. Direct covalent sidewall functionalization is associated with a change of hybridization from sp^2 to sp^3 and a simultaneous loss of π -conjugation system on graphene layer. This process can be made by reaction with some molecules of a high chemical reactivity, such as fluorine (Z. Spitalsky, D. Tasis, K. Papagelis, and C. Galiotis, 2010). It was shown that the fluorination of purified SWCNTs occurred at temperatures up to 325 °C and the process was reversible using anhydrous hydrazine that could remove the fluorine. The fluorinated CNTs have C-F bonds that are weaker than those in alkyl fluorides and thus providing substitution sites for additional functionalization. Successful replacements of the fluorine atoms by amino, alkyl and hydroxyl groups have been achieved.

Defect functionalization is another method for covalent functionalization of CNTs. This process takes advantage of chemical transformation of defect sites on CNTs. Defect sites can be the open ends and/or holes in the sidewalls, pentagon or heptagon irregularities in the hexagon graphene framework. Oxygenated sites can also be considered as defects. Defects can be created on the sidewalls as well as at the open ends of CNTs by an oxidative process with strong acids such as HNO_3 , H_2SO_4 or a mixture of them, or with strong oxidants such as $KMnO_4$, ozone, reactive plasma. The defects on CNTs created by oxidants are stabilized by bonding with carboxylic acid ($-COOH$) or hydroxyl ($-OH$) groups. These functional groups have rich chemistry and the CNTs can be used as precursors for further chemical reactions, such as silanation, polymer grafting, esterification, thiolation, alkylation and arylation and even some biomolecules. The CNTs functionalized in this way are soluble in many organic solvents because the hydrophobic nature of CNTs is changed to hydrophilic one due to the attachment of polar groups. The chemically functionalized CNTs can produce strong interfacial bonds with many polymers, allowing CNT-based nanocomposites to possess high mechanical and functional properties.

3. Physical Functionalization:

Functionalization of CNTs using covalent method can provide useful functional groups onto the CNT surface. However, these methods have two major drawbacks: firstly, during the functionalization reaction, especially along with damaging ultrasonication process, a large number of defects are inevitably created on the CNT sidewalls, and in some extreme cases, CNTs are fragmented into smaller pieces. These damaging effects result in severe degradation in mechanical properties of CNTs as well as disruption of π electron system in nanotubes. The disruption of π electrons is detrimental to transport properties of CNTs because defect sites scatter electrons and phonons that are responsible for the electrical and thermal conduction of CNTs, respectively. Secondly, concentrated acids or strong oxidants are often used for CNT functionalization, which are environmentally unfriendly. Therefore, many efforts have been put forward to developing methods that are convenient to use, of low cost and less damage to CNT structure.

Non-covalent functionalization is an alternative method for tuning the interfacial properties of nanotubes. The suspension of CNTs in the presence of polymers, such as poly(phenylene vinylene) or polystyrene, lead to the wrapping of polymer around the CNTs to form supermolecular complexes of CNTs. This is a typical example of non-covalent functionalization of CNTs. The polymer wrapping process is achieved through the van der Waals interactions and π - π stacking between CNTs and polymer chains containing aromatic rings. Besides polymers, surfactants have also been employed to functionalize CNTs. Several studies have contributed to studying the effects of surfactant on dispersibility and other property of CNTs. The surfactants studied previously include:

- (i) **non-ionic surfactants**, such as polyoxyethylene 8 lauryl ($\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{-CH}_2)_7\text{OCH}_2\text{CH}_3$), nonylphenol ethoxylate (Tergitol NP-7), polyoxyethylene octylphenylether (Triton X-100);
- (ii) **anionic surfactants**, such as sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), poly(styrenesulfate) (PSS);
- (iii) **cationic surfactants**, such as dodecyltri-methyl ammoniumbromide (DTAB), cetyltrimethylammonium 4-vinylbenzoate (CTVB).

In particular, a recent study shows that the physical adsorption of surfactant on the CNT surface lowered the surface tension of CNT, effectively preventing the formation of aggregates. Furthermore, the surfactant-treated CNTs overcome the van der Waals attraction by electrostatic/steric repulsive forces. The efficiency of this method depended strongly on the properties of surfactants, medium chemistry and polymer matrix. It was concluded that in water-soluble polymers such as polyethylene glycol, cationic surfactants had some advantages, whereas in water-insoluble polymers like polypropylene, CNT dispersion was promoted by a non-ionic surfactant. The treatment of non-ionic surfactants is based on a strong hydrophobic attraction between the solid surface and the tail group of surfactant.

Another non-covalent method for CNT functionalization is the so-called endohedral method. In this method, guest atoms or molecules are stored in the inner cavity of CNTs through the capillary effect. The insertion often takes place at defect sites localized at the ends or on the sidewalls. The insertion of inorganic nanoparticles into the tubes, such as C_{60} , Ag, Au and Pt, is a typical example of endohedral functionalization. Small biomolecules, such as proteins, DNA, can also be entrapped in the inner hollow channel of nanotubes by simple adsorption, forming natural nano-test tubes. The combination of these two materials (i.e. CNTs and guest molecules) is particularly useful to integrate the properties of the two components in hybrid materials for use in catalysis, energy storage, nanotechnology and molecular scale devices.

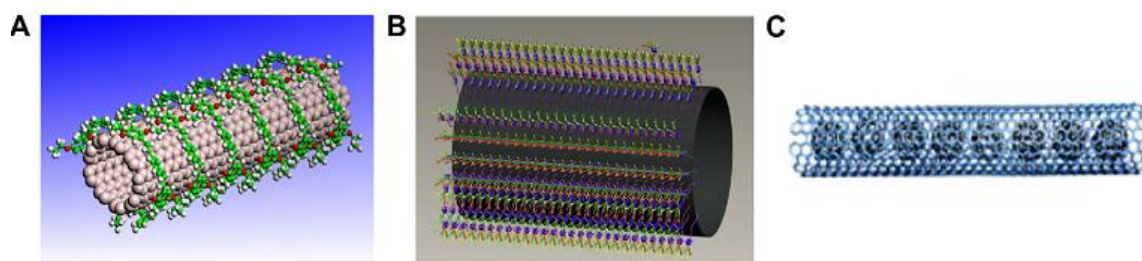


Fig. 1: Schematics of CNT functionalization using non-covalent methods (A: polymer wrapping; B: surfactant adsorption; C: endohedral method). Reproduced from (P.-C. Ma, N. a. Siddiqui, G. Marom, and J.-K. Kim, 2010).

Mechanical Properties of CNTs Filled Polymer Nanaocomposites:

Polymer composites based on CNTs as nanofillers, have been widely reported. This section discusses the effectiveness of functionalized CNTs in polymer nanocomposites, on the mechanical properties. Composites

based on functionalized nanotubes are expected to have large interfacial shear strengths. Covalently grafted long-chain molecules entangle with the polymer matrix creating a very strong bond. In addition the functional groups act to make the nanotubes more compatible both with polymer hosts and solvents. This tends to dramatically improve the nanotube dispersion and hence further improve composite properties.

Yang *et al.* (Yang J, Hu J, Wang C, Qin Y, Guo Z, 2004) fabricated composites from CVD-MWNT in p(MMA-co-EMA). The stiffness increased from 1.64 to 2.62 GPa on introduction of 10 wt.% nanotubes. While the strength also increased from 55 to 73 MPa, the material became very brittle at higher nanotube contents. Furthermore there was no significant difference between functionalised and pristine nanotubes. Blake *et al.* (Fig. 2) covalently attached chlorinated PP to CVD-MWNT and blended with chlorinated PP (Blake R, Gun'ko YK, Coleman J, Cadek M, Fonseca A, Nagy JB, *et al.*, 2004). Stiffness increased from 0.22 to 0.68 GPa, corresponding to a reinforcement of 72 GPa. Moreover both strength and toughness increased from 12.5 to 49 MPa and from 24 to 108 J/g, respectively.

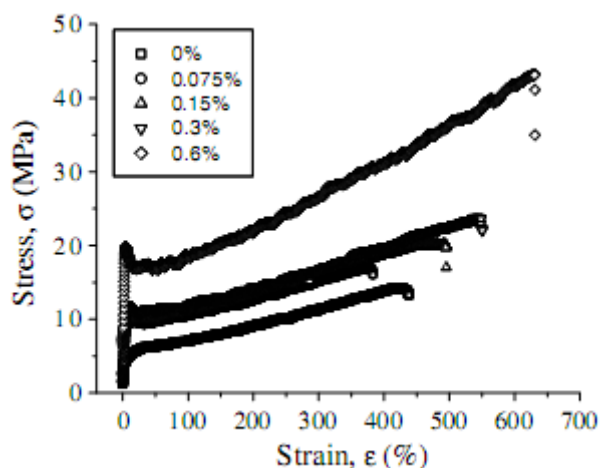


Fig. 2: Stress–strain curves for a range of composites fabricated from functionalised MWNT and CL-polypropylene. Reproduced from (Blake R, Gun'ko YK, Coleman J, Cadek M, Fonseca A, Nagy JB, *et al.*, 2004)

In two papers Zhu *et al.* demonstrated covalent grafting of large organic molecules to SWNT (Zhu J, Kim J, Peng H, Margrave JL, Khabashesku VN, Barrera EV, 2001, Zhu J, Peng H, Rodriguez-Macias F, Margrave JL, Khabashesku VN, Imam AM, *et al.*, 2004). These were then dispersed in epoxy resin and treated to covalently attach the functionalities to the resin. The modulus increased from 2.02 to 3.4 GPa on addition of 4 wt.% SWNT. In addition the strength improved from 83 to 102 MPa. The high level of stress transfer was suggested by the fact that many tubes fractured on composite failure. Melt-spun fibres from PA6 grafted SWNT in a PA6 matrix were produced by Gao *et al.* (Gao J, Itkis ME, Yu A, Bekyarova E, Zhao B, Haddon RC, 2005). The fibres were stiffened from 440 MPa to 1200 MPa on addition of 1.5 wt.% tubes. The strength was doubled from 41 to 86 MPa.

Conclusions:

Polymer nanocomposites are one of the most important applications of carbon nanofillers including CNTs. Nanocomposites are suitable for applications as high performance composites, where good dispersion of the filler can be achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix. The most important basis in polymer nanocomposites is the interaction between the polymer matrix and the nanostructures that contribute directly to the mechanical and functional properties of the nanocomposites. The interface adhesion between the two materials may affect the effectiveness of load transfer from the polymer matrix to nanostructures. Thus, good surface interactions of nanostructures is needed to promote better dispersion of fillers and to enhance the interfacial adhesion between the two phases. For the study of CNTs as nanofillers, the direction of the research is to look into the methods of polymer nanocomposites preparation. Further testing to gain understanding of the behavior of the material must be conducted.

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