

Research Article

In Situ Preparation of Polyether Amine Functionalized MWCNT Nanofiller as Reinforcing Agents

Ayber Yıldırım and Turgay Seçkin

Chemistry Department, Faculty of Arts and Science, İnönü University, Malatya, Turkey

Correspondence should be addressed to Turgay Seçkin; turgayseckin@gmail.com

Received 14 May 2013; Accepted 4 November 2013; Published 20 January 2014

Academic Editor: Jeffrey Glass

Copyright © 2014 A. Yıldırım and T. Seçkin. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In situ preparation of polyether amine functionalized cross-linked multiwalled carbon nanotube (MWCNT) nanofillers may improve the thermal and mechanical properties of the composites in which they are used as reinforcing agents. The reduction and functionalization of MWCNT using ethylenediamine in the presence of polyether amine produced stitched MWCNT's due to the presence of two amine ($-NH_2$) functionalities on both sides of the polymer. Polyether amine was chosen to polymerize the carboxylated MWCNT due to its potential to form bonds with the amino groups and carboxyl groups of MWCNT which produces a resin used as polymeric matrix for nanocomposite materials. The attachment of the polyether amine (Jeffamine) groups was verified by TGA, FT-IR, XRD, SEM, and Raman spectroscopy. The temperature at which the curing enthalpy is maximum, observed by DSC, was shifted to higher values by adding functionalized MWCNT. SEM images show the polymer formation between MWCNT sheets.

1. Introduction

Much attention has been given in recent works on carbon nanotubes (CNTs) either single wall carbon nanotubes (SWCNT) or multiwall carbon nanotubes (MWCNT) because of their small size and unique properties [1–3]. Thus these materials found potential uses mainly in engineering applications and biomedical devices [4–7]. There are two major drawbacks of the MWCNTs: the reactivity of their graphitic structure and the agglomeration affinity due to the large specific surface area. The potential of these new materials in composite materials can be fully explored when these disadvantages are solved, essentially by functionalization. Chemical functionalization of CNTs is very important in different applications. The attachment of functional groups or aliphatic carbon chains to the nanotubes can boost the solubility of nanotubes in organic solvents and compatibilize them with the polymeric matrix [8].

It is well known from many studies that the presence of different purposeful groups is the starting point for binding a mixture of different chemical molecules on the nanotube surfaces [9]. Noncovalent or covalent functionalization are the two ways to modify the surface in which molecules on

the surface are deposited by means of van der Waals forces and latter method is based on direct covalent modification of the MWCNT walls with known synthetic approaches [10, 11]. The advantage of the noncovalent functionalization is that the structure of CNTs walls is not altered and thus their mechanical properties should not change. The disadvantage of the noncovalent functionalization is that the forces between the wrapping molecule and the CNTs are weaker than the covalent bonds. The covalent attachment of amine functional groups [12] to the surface of CNTs can improve the load capacity of the matrix. However, it must be noted that the process for obtaining functional groups may introduce defects on the walls of the nanotubes [13]; another way could be obtaining the functional materials by direct synthesis [14]. Functionalization with amine groups usually leads to an improvement of the mechanical properties. When the content of the MWNTs- NH_2 is 0.6%, the bending strength will increase by 100% and the flexural modulus by 58% [15]. The aim of this study was the improvement of the dispersion state of the MWCNTs reinforcing agent within the epoxy resin matrix and the properties of the nanocomposite materials obtained by diamine attachment on MWCNTs sidewalls.

Chemical functionalization of multiwall carbon nanotube is very important for most of their use in different applications. The attachment of functional groups or aliphatic carbon chains to the MWCNT can increase the solubility of MWCNT in many organic solvents and compatibilize them with polymeric matrices. It is known from many studies that the presence of different functional groups is the starting point for binding a variety of different chemical molecules on MWCNT surfaces.

Herein, we report the simultaneous reduction and polymerization of MWCNT using ethylenediamine ($\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$) and polyether amine (Jeffamine). Moreover, the reduction and functionalization of MWCNT using ethylenediamine in the presence of polyether amine produce sutured MWCNT due to the presence of two amine ($-\text{NH}_2$) functionalities on both sides of the polymer and the carboxyl groups of MWCNT sheets. The as-prepared functionalized MWCNT sheets were characterized by a variety of conventional methods to corroborate the structure and properties of the as-prepared nanocomposites. It was found that the mechanical properties of MWCNT-based composites were strongly influenced by the processing method and the interactions between multiwall carbon nanotube and polymers. Therefore, it is expected that the stitched, layered structures produced with polyether amine will be an effective reinforcing material for polymer composite applications. The cross-linking between the multiwall carbon nanotube sheets should eliminate the problems associated with multiwall carbon nanotube sliding that leads to poor mechanical properties with conventional functionalized multiwall carbon nanotube filled polymer composites.

2. Materials and Methods

2.1. Materials. MWCNT was supplied by Grafen Company; N,N-dicyclohexylcarbodiimide (DCC) Fluka Analytical; potassium permanganate (KMnO_4) (Merck); sodium nitrate (NaNO_3) Merck. Polyether amine (Jeffamine D230) and other chemical reagents nitric acid (68%), concentrated HCl (37%), concentrated sulfuric acid (98%), and tetrahydrofuran (THF, 95%) were analytically pure and purchased from Sigma-Aldrich Co.

2.2. Characterization. The thermogravimetric and DTA analyses were performed on a Shimadzu Instruments system with a heating rate of $10^\circ\text{C}/\text{min}$. The Raman spectra were collected using a Raman spectrometer (Thermo Scientific NXR) with a 1064 nm laser with 1303 W power and 128 scan rate. Scanning electron microscopic (SEM) images were taken on a Nova NanoSEM 600, while X-ray diffraction (XRD) was measured on a Miniflex II X-ray diffraction (XRD) for the crystal structure, average particle size, and the concentration of impurity compounds present. A Rigaku Rad B-Dmax II powder X-ray diffractometer was used for X-ray diffraction patterns of these samples. The 2θ values were taken from 20°C to 110°C with a step size of 0.04° using $\text{Cu K}\alpha$ (λ value of 2.2897 Å). The dried samples were dusted onto plates with low background. A small quantity of 30 mg (± 2 mg) spread over

5 cm^2 is used to minimize error in peak location and also the broadening of peaks due to reduction in sample thickness. These data illustrate the crystal structure of particles and also provide the interplanar space, d . The broadening of the peak was related to the average diameter (L) of the particle according to Scherrer's formula, that is, $L = 0.9\lambda/\Delta \cos \theta$, where λ is the X-ray wavelength, Δ is the line broadening measured at half-height, and θ is the Bragg angle of the particles.

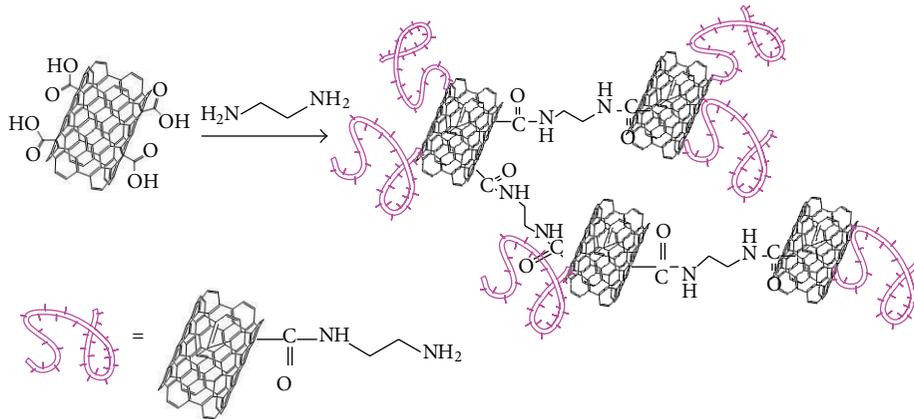
TEM analysis was made on JEOL JEM 2100F HRTEM 80–200 kV with ultrahigh vacuum.

2.3. MWCNT Functionalization. The reason for functionalization was the debundling and dispersion improvement of the MWCNT during composite processing. Thus, the functionalization process consisted of two steps. Firstly, the oxidation of MWCNT accomplished by using a 3:1 (vol.) mixture of H_2SO_4 : HNO_3 in order to purify the raw material from catalyst traces to adsorb carboxylic groups on their surface, as well as at the end by capping the hemispherical ends. Thus 100 mg of MWCNT was added to 12 mL H_2SO_4 : HNO_3 mixture, heated at 70°C in silicon oil bath, and kept under stirring for 12 h and then the product was filtered on $0.22\ \mu\text{m}$ pore Teflon membrane and washed until the pH reached neutral value. Carboxylated carbon multiwalled carbon nanotubes (MWCNT-COOH) were dried under vacuum for 48 h at room temperature (RT). The second step consisted of amine attachment at these MWCNT surfaces by acylation with thionyl chloride (SOCl_2) at 65°C for 24 h, followed by amidation of the resulted MWCNT-COCl with an excess of polyether amine at room temperature for 48 h to complete the functionalization process.

2.4. Composite Precursor Preparation. Composite precursor materials were obtained by mixing polyether amine resin with the reinforcing agents (MWCNT, MWCNT-COOH, and MWCNT-EA) using ultrasonication for 2 h at room temperature. Postcuring steps were necessary to obtain final products, so the curing process was done for 3 h at 60°C and the second one for 1.5 h at 100°C to complete the reaction. The method used to obtain the nanocomposites samples is illustrated in Scheme 1.

3. Results and Discussion

The mechanism for the reduction of MWCNT using ethylamine and polyether amine has been proposed and is shown in Scheme 1. The surface of the MWCNT contains several oxygen containing functionalities, such as epoxide, hydroxyl, and carboxyl groups. It is expected that the $-\text{NH}_2$ functionalities of the ethylamine molecules might attack the epoxide carbon to convert it to a hydroxyl group accompanying a proton transfer on the multiwall carbon nanotube sheet, as evidenced by the Raman, FT-IR data. In the case of ethylenediamine, the two $-\text{NH}_2$ functional groups attack the epoxide carbon of two different MWCNT sheets and help form a stitched structure.



SCHEME 1: Composite synthesis.

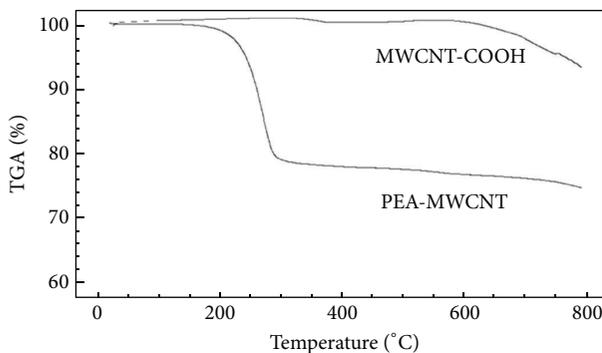


FIGURE 1: TGA thermograms of MWCNT-COOH, PEA-MWCNT.

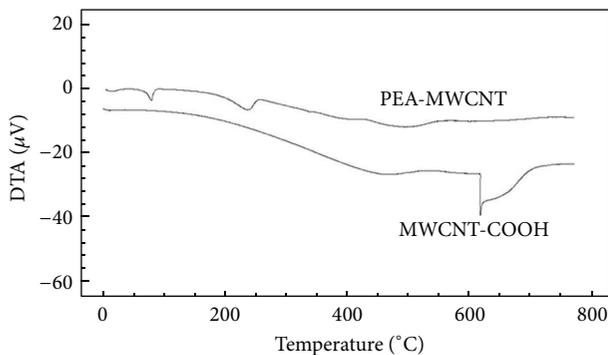


FIGURE 2: DTA of MWCNT-COOH, PEA-MWCNT.

3.1. Thermal Analysis (TGA and DSC). The enhancement of thermal stability for PEA-MWCNT nanofiller is desired for future applications. In Figure 1, the thermal degradation of MWCNT and the PEA-MWCNT were given. It is well known that the graphitic structure of carbon nanotubes is stable up to 500–600°C, when thermal oxidative processes occur [3–5]. The oxidation of MWNTs with strong acids introduces carboxylic groups at the nanotube surface by creating defects in the hexagonal or pentagonal structures from the graphene sheet or by etching the hemispherical ends of the CNTs. The degradation process of MWCNT occur in two steps,

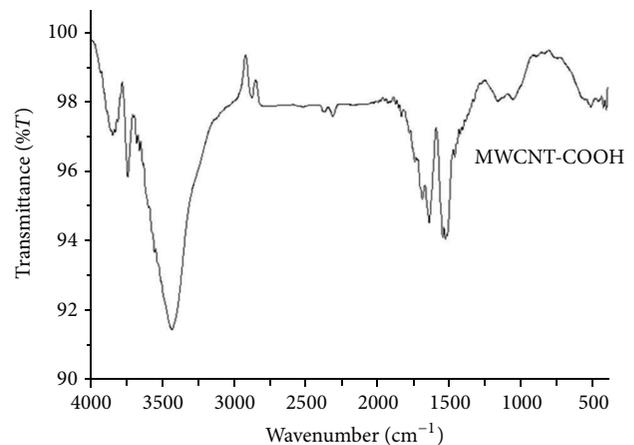


FIGURE 3: Fourier transform infrared (FTIR) spectra of MWCNT-COOH.

one at $\sim 173^\circ\text{C}$ assigned to the broken amidic groups and another at $\sim 538^\circ\text{C}$ normally attributed to graphite structure degradation. Nanocomposite PEA-MWCNT samples reinforced with polyether amine show a higher stability than the corresponding analogs. This evidence is supported by DSC analysis (Figure 2). Differential scanning calorimetry curves show an exothermic peak representing the cure process of the PEA, meaning that the presence of MWNT-PEA enhances the thermal stability.

3.2. FT-IR Measurements. FT-IR spectra of pure MWCNT and PEA-MWCNT are shown in Figures 3 and 4. After the reduction of MWCNT with ethylamine in the presence of polyether amine, there is a dramatic decrease in the intensities of the peaks corresponding to the oxygen functionalities, such as the $-\text{COOH}$ stretching vibration peak at 1727 cm^{-1} and the $-\text{OH}$ deformation vibration peaks (3425 cm^{-1} and 1399 cm^{-1}). The intensity of the epoxy and alkoxy peaks at 1224 and 1060 cm^{-1} also decreases in MWCNT and PEA-MWCNT. The appearance of new peaks in the region of 1564 cm^{-1} and 1260 cm^{-1} is attributed to the presence of

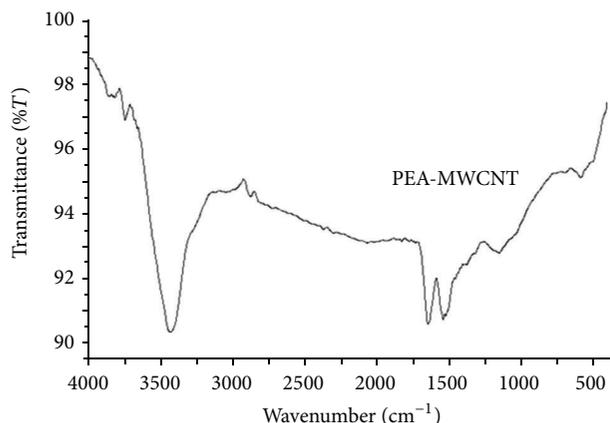


FIGURE 4: Fourier transform infrared (FTIR) spectra of PEA-MWCNT.

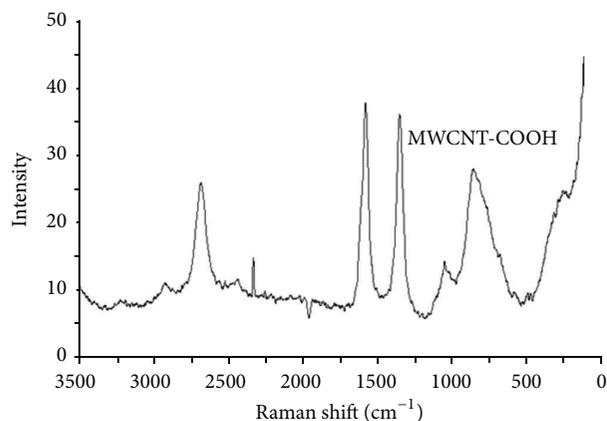


FIGURE 5: Raman spectra of MWCNT-COOH.

strong in-plane C–N scissoring absorptions and C–O stretching vibrations. These findings confirm not only the removal of oxygen functionalities from the surface of MWCNT but also the information of nanocomposites.

3.3. Raman Spectroscopy. The disorder (*D*) band in MWCNTs is observed when the symmetry of hexagonal lattice is disrupted due to, for example, covalent side-wall functionalization. The *G* mode at $\sim 1588\text{ cm}^{-1}$ represents the tangential vibration mode of the graphitic structure of the nanotubes [16]. As shown in the spectra from Figures 5 and 6, the form of these bands is not modified during functionalization, which means that the global structure of the graphene sheet does not suffer major damages during functionalization treatments. The ratio between the intensities of these two characteristic bands is a quantification of the introduction of functional groups via measurement of *sp*³ carbon. The Raman data show an increase of the *ID/IG* ratio value as the functionalization by oxidation and then amidation occurs. This tendency is maintained also for the shifting of the *D* and *G* bands positions.

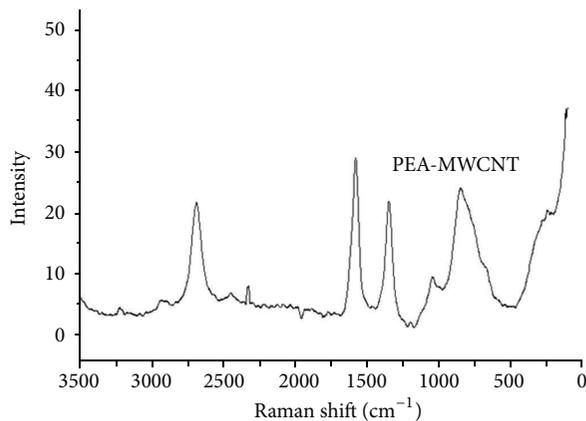


FIGURE 6: Raman spectra of MWCNT-PEA.

3.4. SEM-TEM Analysis. The surface morphology of MWCNT and PEA-MWCNT was studied by SEM (Figure 7) and graphene morphology was studied with TEM (Figure 8) and SEM analysis. It is clearly observed that PEA-MWCNT are quite uniformly dispersed in the polymer matrix due to the MWCNT compatibility between the two components. The few bright areas observed in the figure are considered to be the broken ends of MWCNT pulled out from the matrix during fracture process, suggesting that not all the multiwall carbon nanotubes are functionalized.

3.5. XRD Analysis. Figure 9 shows XRD spectra for MWCNT-PEA and MWCNT-COOH. The sharp diffraction peaks seen for PEA indicate a well-defined crystal structure. The structures of MWCNT-COOH showed diffraction peak at 26.7° , implying the grapheme oxide sheets. Diffraction peaks of PEA-MWCNT are found at 19.9° (amin), 23.1° , and 33.2° (minor). The result indicated that MWCNT-COOH has been extensively reacted efficiently with Jeffamine by forming mildly cross-linked matrix. In addition the crystalline structure of the matrix was slightly affected due to the incorporation of the grapheme platelets.

Covalently bonded PEA moieties increased the interlayer space of MWCNT as evidenced by XRD profile

4. Conclusions

In summary, polyether amine in the presence of ethylene diamine as reducing agent gave us a simple, cost-effective, and efficient reduction of MWCNT and PEA-MWCNT nanocomposites in which MWCNT sheets were cross-linked with polyether amine. Raman FT-IR analysis showed that most of the oxygen functionalities were removed from the surface of MWCNT. The covalent bonds between the MWCNT and amine compounds are also clearly visible from the FTIR analysis. XRD analysis confirms the stitching of multiwall carbon nanotube layers using polyether amine as evidenced by SEM analysis. In contrast, almost single layer multiwall carbon nanotube is formed with ethylamine functionalization. Both ethylamine and ethylenediamine attach to the surface of MWCNT through covalent bonding and

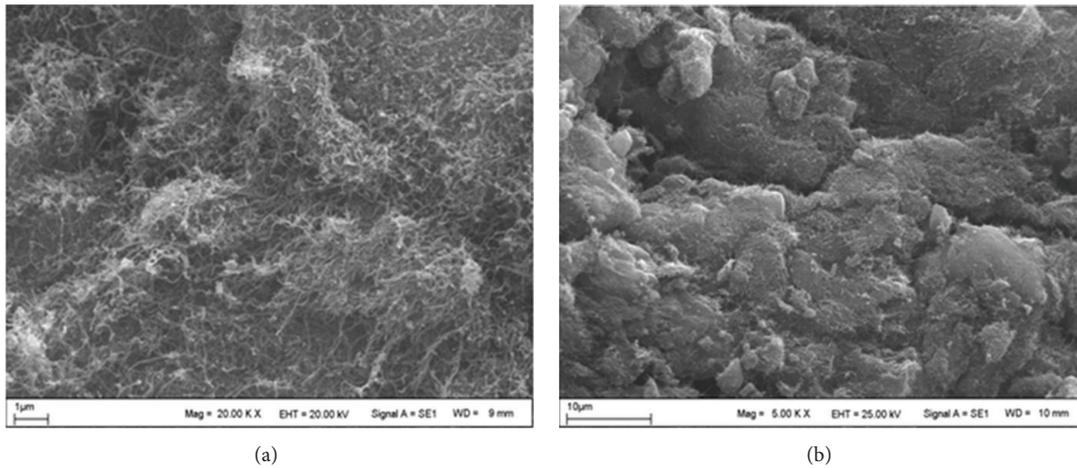


FIGURE 7: SEM images of MWCNT-COOH (a), PEA-MWCNT (b).

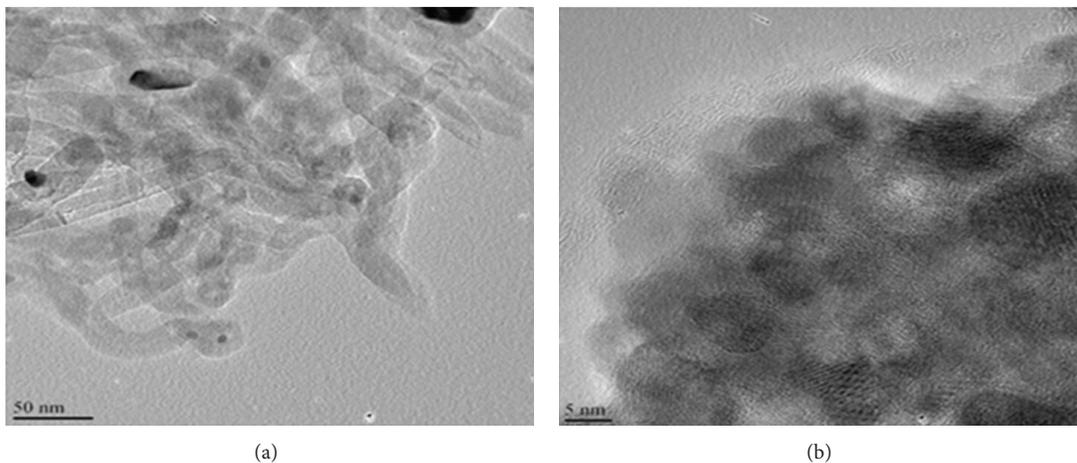


FIGURE 8: TEM images of MWCNT-COOH.

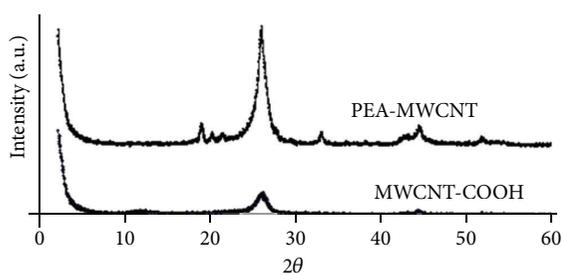


FIGURE 9: XRD diffractions of MWCNT-COOH, PEA-MWCNT.

prevent the agglomeration of MWCNT layers. The morphological structures of composites have been confirmed by SEM analysis.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of the paper.

Acknowledgment

This study was fully supported by the TÜBİTAK Turkish Research Council, Chemistry and Biology Division KBAG, 110T153.

References

- [1] D. Y. Kim, C.-M. Yang, H. Noguchi et al., "Enhancement of H₂ and CH₄ adsorptivities of single wall carbon nanotubes produced by mixed acid treatment," *Carbon*, vol. 46, no. 4, pp. 611–617, 2008.
- [2] G. Kalita, S. Adhikari, H. R. Aryal et al., "Functionalization of multi-walled carbon nanotubes (MWCNTs) with nitrogen plasma for photovoltaic device application," *Current Applied Physics*, vol. 9, no. 2, pp. 346–351, 2009.
- [3] D. Wang, J. Lu, J. Zhou et al., "Selective adsorption of cations on single-walled carbon nanotubes: a density functional theory study," *Computational Materials Science*, vol. 43, no. 4, pp. 886–891, 2008.
- [4] C. Peng, S. Zhang, D. Jewell, and G. Z. Chen, "Carbon nanotube and conducting polymer composites for supercapacitors," *Progress in Natural Science*, vol. 18, no. 7, pp. 777–788, 2008.

- [5] S. Kawasaki, T. Hara, Y. Iwai, and Y. Suzuki, "Metallic and semiconducting single-walled carbon nanotubes as the anode material of Li ion secondary battery," *Materials Letters*, vol. 62, no. 17-18, pp. 2917–2920, 2008.
- [6] A. Bianco, K. Kostarelos, and M. Prato, "Applications of carbon nanotubes in drug delivery," *Current Opinion in Chemical Biology*, vol. 9, no. 6, pp. 674–679, 2005.
- [7] G. A. Rivas, M. D. Rubianes, M. C. Rodríguez et al., "Carbon nanotubes for electrochemical biosensing," *Talanta*, vol. 74, no. 3, pp. 291–307, 2007.
- [8] U. Dettlaff-Weglikowska, J.-M. Benoit, P.-W. Chiu, R. Graupner, S. Lebedkin, and S. Roth, "Chemical functionalization of single walled carbon nanotubes," *Current Applied Physics*, vol. 2, no. 6, pp. 497–501, 2002.
- [9] C.-E. Hong, J.-H. Lee, P. Kalappa, and S. G. Advani, "Effects of oxidative conditions on properties of multi-walled carbon nanotubes in polymer nanocomposites," *Composites Science and Technology*, vol. 67, no. 6, pp. 1027–1034, 2007.
- [10] E. Lee, D. W. Park, J. O. Lee, D. S. Kima, B. H. Lee, and B. S. Kima, "Molecularly imprinted polymers immobilized on carbon nanotube," *Colloids and Surfaces A*, vol. 313-314, pp. 202–206, 2008.
- [11] G.-W. Lee, J. Kim, J. Yoon et al., "Structural characterization of carboxylated multi-walled carbon nanotubes," *Thin Solid Films*, vol. 516, no. 17, pp. 5781–5784, 2008.
- [12] J. Shen, W. Huang, L. Wu, Y. Hu, and M. Ye, "Thermo-physical properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes," *Composites A*, vol. 38, no. 5, pp. 1331–1336, 2007.
- [13] S. Goyanes, G. R. Rubiolo, A. Salazar, A. Jimeno, M. A. Corcuera, and I. Mondragon, "Carboxylation treatment of multi-walled carbon nanotubes monitored by infrared and ultraviolet spectroscopies and scanning probe microscopy," *Diamond and Related Materials*, vol. 16, no. 2, pp. 412–417, 2007.
- [14] F. D. Balacianu, R. Bartoş, and A. C. Nechifor, "Organic-inorganic membrane materials," *Science Bulletin*, vol. 71, pp. 37–54, 2009.
- [15] Z. Yaping, Z. Aibo, C. Qinghua, Z. Jiaoxia, and N. Rongchang, "Functionalized effect on carbon nanotube/epoxy nanocomposites," *Materials Science and Engineering A*, vol. 435-436, pp. 145–149, 2006.
- [16] M. S. Dresselhaus, G. Dresselhaus, and A. Jorio, "Raman spectroscopy of carbon nanotubes in 1997 and 2007," *Journal of Physical Chemistry C*, vol. 111, no. 48, pp. 17887–17893, 2007.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

