A Novel Manufacturing Method for Carbon Nanotube/Aramid Fiber Filled Hybrid Multi-component Composites

Young Seok Song [a], **Hwajin Oh** [b], **Taikyeong T. Jeong** [c] **and Jae Ryoun Youn** [b,*]

[a] Department of Mechanical Engineering, MIT, Cambridge, MA 02139, USA

[b] School of Materials Science and Engineering, Seoul National University, 56-1, Shinlim-Dong, Gwanak-Gu, Seoul, Korea

[c] Department of Communications Eng., Myongji University, San 38-2, Nam-Dong, Cheoin-Gu, Yongin, Korea

Abstract
A novel manufacturing method for hybrid composites filled with carbon nanotubes (CNTs) and aramid fibers is proposed. To disperse the CNTs in the epoxy matrix with the presence of aramid fibers, CNT/polyethyleneoxide (PEO) composites are prepared and utilized because PEO is miscible in the epoxy resin. After thin films are made of the CNT/PEO composite and placed together with the aramid fibers, the epoxy resin is infused to them. The PEO is dissolved in the epoxy and then the CNTs are dispersed in the PEO/epoxy matrix between aramid fibers before the pre-heated matrix is cured. It is found that the PEO is completely miscible with the epoxy resin and CNTs are dispersed well in the space between the aramid fibers.
© Koninklijke Brill NV, Leiden, 2008

Keywords
Composite material, carbon nanotube, nanocomposite

1. Introduction

Fiber-reinforced composites have been widely used in aerospace, automotive and marine industries because they have attractive advantages such as outstanding mechanical properties, light weight, low fabrication cost and easy handling. Many fiber composites are manufactured by the liquid composite molding (LCM), which encompasses resin transfer molding (RTM) [1–9], vacuum assisted resin transfer molding (VARTM), resin film infusion (RFI), and structural reaction injection

---

molding (SRIM) [10]. To sustain the fiber preform, pure polymer resins have been commonly employed as matrices but the polymer resins have some limitations in physical and thermal properties. Hence, polymers with high cross-linking density are proposed or elasticizers such as powder, viscous liquid, and monomer mixture are introduced into the resin to get over the shortcomings [11]. Moreover, some studies on application of polymer nanoclay composites have been reported [12, 13]. However, there still exist several problems to be resolved, namely, viscosity increase of the matrix resin, difficulty in particle dispersion and onset of the matrix monolithization. Since carbon nanotubes (CNTs) possess fascinating mechanical, thermal and electrical properties, composites with high stiffness and toughness could be achieved at even low loading of the CNTs [14–16]. However, few studies on the fiber-reinforced composites with the CNT-filled matrix have been reported [17, 18].

Thermosetting polymer matrices have been used in fiber-reinforced composites. Among the thermosets, epoxy resin is one of the most important resins and thermoplastic resins are blended with the epoxy resin to improve the toughness [19, 20]. In general, it is difficult to obtain homogeneous blends because intermolecular interactions are more complicated in thermosetting blends than those in linear polymer blends. Recently, several miscible epoxy blends have been reported and one of them is the epoxy/PEO blend. The epoxy/PEO blend is found to be miscible when cured with 4,4′-diaminodiphenylmethane (DDM) and phthalic anhydride (PA). In aromatic amine curing systems, the miscibility is attributed to formation of intermolecular hydrogen-bonding interactions [21, 22].

Figure 1 depicts the main idea of the current study schematically. Hybrid composites reinforced by aramid fibers and CNTs are manufactured by using a thermoplastic/epoxy blend. First of all, thermoplastic nanocomposites are filled with CNTs and nanocomposite films are prepared with good CNT dispersion. Then, the
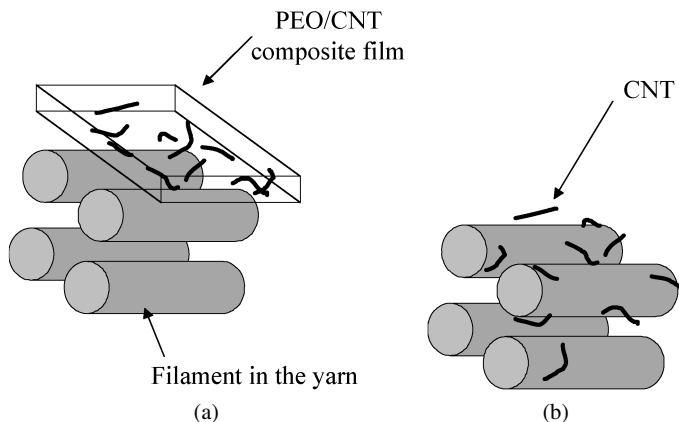
Figure 1. Schematic description of the manufacturing process for CNT/fiber hybrid composites: (a) before infusion and (b) after infusion of epoxy resin. The CNT particles are dispersed into the epoxy resin as the PEO is blended with the epoxy resin.

nanocomposite film is placed selectively in the region where additional reinforce-
ment is required. The epoxy resin that has been heated up to melting point of the
thermoplastic resin is infused into the fiber preform and the nanocomposite film is
dissolved by the epoxy resin. The CNT particles embedded in the nanocomposite
are dispersed in the region between aramid fibers. It is expected that the shear stress
generated by the resin flow in LCM is large enough to drive CNT particles into
the matrix [18]. Finally, the epoxy resin is cured, and the CNT/aramid fiber hybrid
composite is prepared.

In this study, PEO is adopted as the thermoplastic polymer for the nanocom-
posite because CNTs are dispersed well in PEO that is miscible with the epoxy.
Furthermore, the PEO can lower processing temperature and time, which has re-
cently become one of the vital issues in the aerospace industry [23]. Thermal and
morphological characterization of the CNT/PEO composites are made to verify dis-
persion state of the CNTs by using differential scanning calorimetry (DSC) and
field emission scanning electron microscopy (FESEM). The CNT/aramid fiber hy-
brid composites consist of four components, i.e. carbon nanotubes, aramid fibers,
PEO and epoxy resin.

2. Experimental

Muti-walled carbon nanotubes [24–29] with the average diameter of 13 nm and the
length of 10 µm and aramid fibers with the diameter of 12 µm were utilized. PEO
resin with molecular weight of 100 000 g/mol was purchased from Aldrich and its
melting temperature is 65°C. Epoxy resin selected in this study was diglycidyl ether
of bisphenol A (DGEBA, YD-128) with the epoxide equivalent weight of 185–190
and 4,4′-diaminodiphenylmethane (DDM) was used as the curing agent.

Because the pristine CNTs included many impurities, such as amorphous car-
bon, metal catalysts, and graphite particle, the CNTs were purified in a 3:1 mixture
of 65% H_2SO_4/HNO_3 at 100°C for 30 min. The purified CNTs were dispersed in
ethanol under sonication for 2 h and then distilled water and PEO were added to the
solution. The mixture was sonicated for 1 h at 100°C again and kept in a vacuum
oven for 2 days to remove the water and the ethanol. The CNT/PEO mixture was
processed into 20 µm thickness film containing CNTs of 2.0 wt% by using com-
pression molding. To prepare CNT/aramid fiber hybrid composites, aramid fibers
were placed in a Petri dish and the film and strings made of the CNT/PEO compos-
ites were placed together with aramid fibers as shown in Fig. 2. To verify blending
of the epoxy and the PEO, PEO film without the CNTs was prepared and employed.
Then, the mixture of the epoxy resin and the curing agent that had been heated up to
100°C was cast in the Petri dish, which was smoothly shaken to dissolve the PEO
in the epoxy. Finally, the Petri dish was kept in a vacuum oven to cure the epoxy
resin.

Differential scanning calorimetric (DSC) measurements were performed using
a TA instruments DSC 2010 to characterize the CNT/PEO composites. Field emis-

sion scanning electron microscope (FESEM) images were obtained with JEOL JSM-6700F to verify hybridization of CNTs and aramid fibers morphologically as well as to observe the dispersion state of the CNTs. Cross-sectional areas of the specimens fractured under liquid nitrogen were examined by the FESEM.

3. Results and Discussion

Figure 3 shows the PEO/epoxy composite specimen filled with aramid fibers and the PEO/epoxy hybrid composite specimen filled with CNTs and aramid fibers after the epoxy resin is cured. Figure 3(a) illustrates that the PEO is miscible with the epoxy

(a)   (b)
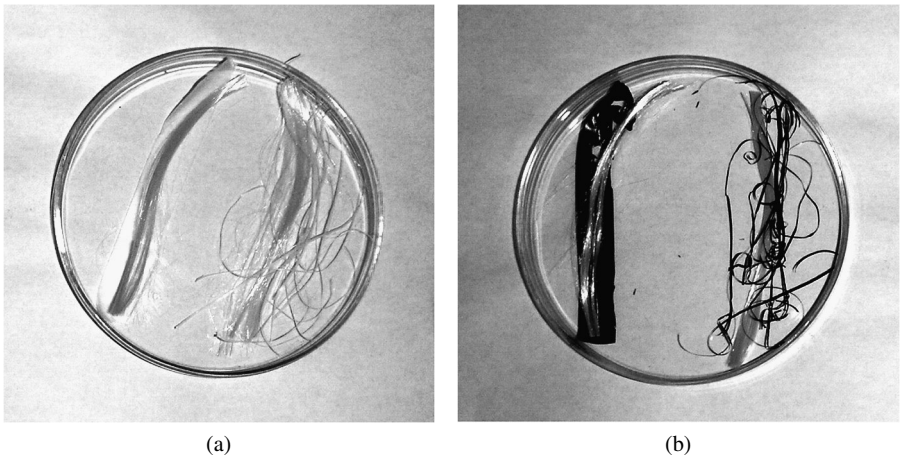
Figure 2. (a) A film and strings of PEO resin together with aramid fibers and (b) a film and strings of the CNT/PEO composite with aramid fibers before the epoxy resin is cast in the Petri dish.



(a)   (b)
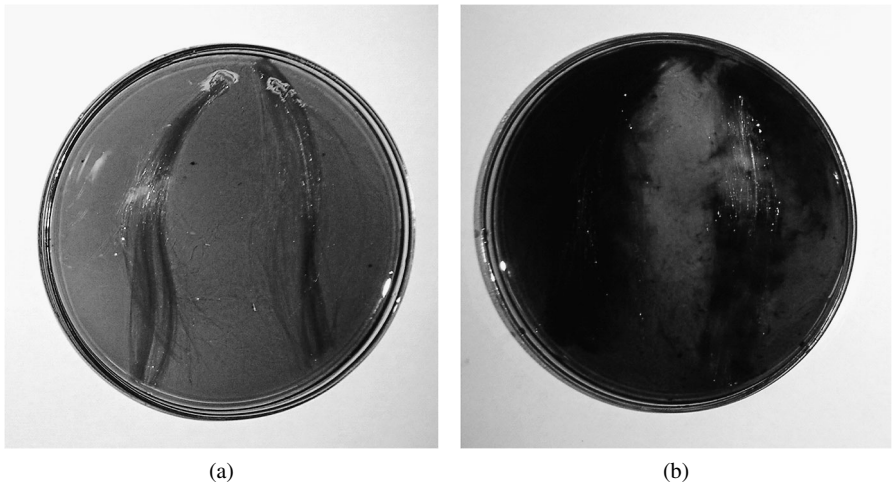
Figure 3. Photographs of (a) PEO/epoxy composite filled with aramid fibers and (b) PEO/epoxy hybrid composite filled with CNTs and aramid fibers after the epoxy resin is cured.

resin and that both thin PEO films and strings are appropriate for dissolving the PEO resin in the epoxy. In contrast to Fig. 3(a), the matrix for the hybrid composite looks darker as shown in Fig. 3(b) because the CNTs are dispersed in the epoxy resin, which is blended with the PEO. In addition, the fractured surface of the PEO/epoxy blend is examined by using FESEM to provide further validation of miscibility between PEO and epoxy resin. As shown in Fig. 4(a), the PEO/epoxy blend has no phase boundaries or phase separation, which is apparently similar to neat cured epoxy resin [30]. This result is also in good agreement with the previous studies [31, 32]. Figure 4(b) shows that the acid-treated CNTs are dispersed well in the PEO resin, which proves that the method used in this study is effective for preparing CNT/PEO nanocomposites. As a result, CNTs dispersed in the thin film can provide selective reinforcements to local weak areas in the composite in that the PEO films which contain dispersed CNTs are miscible with the epoxy resin.
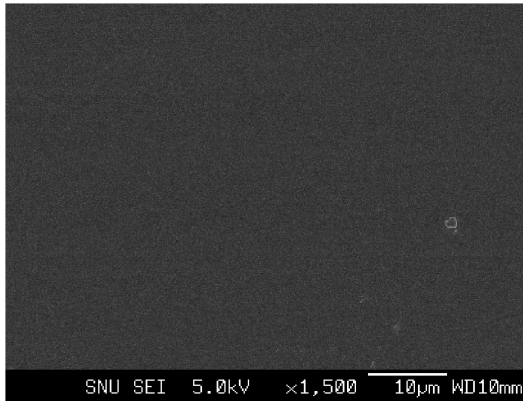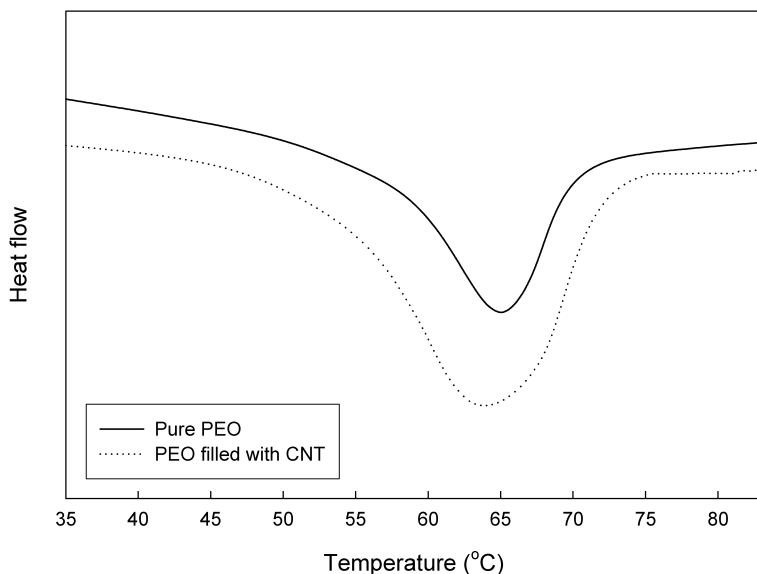

(a)
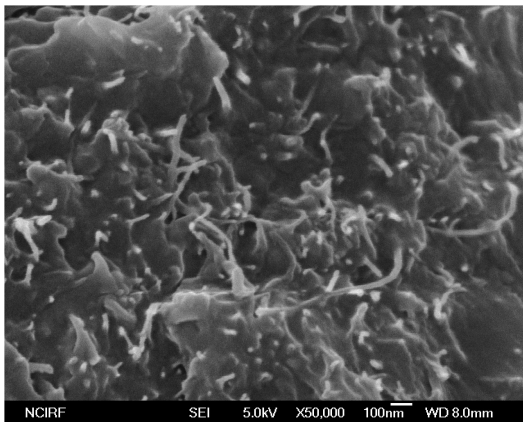
(b)

Figure 4. FESEM images of (a) PEO/epoxy blends and (b) CNT/PEO nanocomposites.

Figure 5. DSC curves at a heating rate of 10°C/min.

To investigate effects of the filled CNT on the thermal properties of the PEO, thermal analysis is performed with DSC. Figure 5 shows that endothermic peak for pure PEO is located at 65°C but the presence of the CNT affects crystallization and particle–particle interactions between the CNTs serve as a chain confinement. Therefore, the melting temperature is decreased by around 2°C. It is well known that DSC results can be utilized to understand the dispersion state of CNTs [33]. It can be confirmed from Fig. 6 that the CNTs have good dispersion in the PEO matrix.
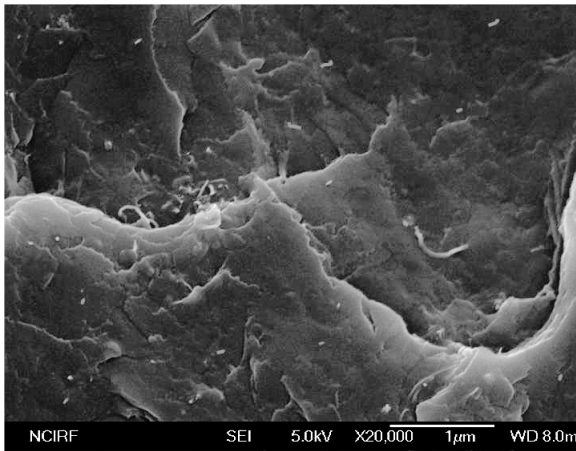
The fractured surface of the composite specimen is shown in Fig. 6. Aramid fibers are broken and pulled out from the matrix. The weight fraction of the aramid fiber is 0.15. Since only a small amount of the PEO is mixed with the epoxy resin and a homogeneous mixture is obtained, it is impossible to detect the PEO phase in the epoxy. To observe the existence of the CNTs, the small highlighted region indicated in Fig. 6(a) is magnified as shown in Fig. 6(b). Even though the CNT loading is very low, CNTs are dispersed in the matrix relatively well. Figure 6 indicates that CNTs are dispersed between aramid fibers which are impregnated by the PEO/epoxy mixture.

4. Conclusion

The objective of the present study is to introduce a novel manufacturing method for CNT/aramid fiber hybrid composites, which may make it possible to tailor mechanical properties by means of selective reinforcements. Because it is not easy to infuse the epoxy resin embedded with CNTs into the fiber preform directly, a CNT/PEO
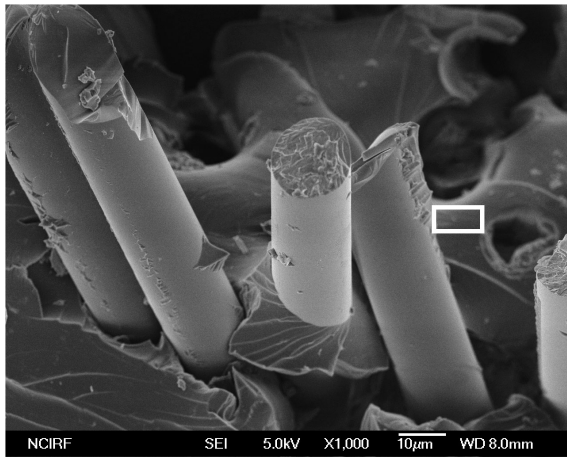
(a)

(b)

Figure 6. FESEM images of the fractured surface for CNT/aramid hybrid composites: (a) Kevlar fibers and (b) carbon nanotubes.

composite film is employed in order to distribute the CNTs in the desired region between fibers. Since the PEO has a melting temperature lower than other thermoplastic polymers, the PEO is blended with epoxy effectively before postcuring is completed. It is shown that the CNTs are well dispersed in the matrix between aramid fibers and that the PEO/epoxy blends are thoroughly miscible. FESEM observation also indicates that the CNT/PEO composite has good CNT dispersion.

Acknowledgement

References

1. D. G. Seong, K. Chung, T. J. Kang and J. R. Youn, A study on resin flow through a multi-layered preform in resin transfer molding, *Polym. Polym. Compos.* **10**, 493–509 (2002).

2. W. Lee, J. H. Kim, H. Shin, K. Chung, T. J. Kang and J. R. Youn, Constitutive equations based on cell modelling method for 3D circular braided fiber-reinforced composites, *Fiber Polym.* **4**, 77–83 (2003).

3. Y. S. Song, K. Chung, T. J. Kang and J. R. Youn, Prediction of permeability tensor for plain woven fabric by using control volume finite element method, *Polym. Polym. Compos.* **11**, 465–476 (2003).

4. Y. J. Cho, Y. S. Song, T. J. Kang, K. Chung and J. R. Youn, Permeability measurement of a circular braided preform for resin transfer molding, *Fiber Polym.* **4**, 135–144 (2003).

5. Y. S. Song, K. Chung, T. J. Kang and J. R. Youn, Numerical prediction of permeability tensor for three-dimensional circular braided preform by considering intra-tow flows, *Polym. Polym. Compos.* **13**, 323–334 (2005).

6. Y. S. Song and J. R. Youn, Asymptotic expansion homogenization of permeability tensor for plain woven fabrics, *Composites, Part A* **37**, 2080–2087 (2006).

7. K. S. Shin, Y. S. Song and J. R. Youn, Radial flow advancement in multi-layered preform for resin transfer molding, *Korea–Australia Rheol. J.* **18**, 217–224 (2006).

8. H. S. Chae, Y. S. Song and J. R. Youn, Transverse permeability measurement of a circular braided preform in liquid composite molding, *Korea–Australia Rheol. J.* **19**, 17–25 (2007).

9. Y. S. Song and J. R. Youn, Flow advancement through multi-layered preform with sandwich structure, *Composites, Part A* **38**, 1082–1088 (2007).

10. Y. S. Song, K. Chung, T. J. Kang and J. R. Youn, Prediction of permeability tensor for three dimensional circular braided preform by applying a finite volume method to a unit cell, *Compos. Sci. Technol.* **64**, 1629–1636 (2004).

11. R. E. Shalin, *Polymer Matrix Composites*. Chapman and Hall, London, UK (1995).

12. A. Haque, M. Shamsuzzoha, F. Hussain and D. Dean, S2-glass/epoxy polymer nanocomposites: manufacturing, structures, thermal and mechanical properties, *J. Compos. Mater.* **37**, 1821–1837 (2003).

13. D. P. N. Vlasveld, P. P. Parlevliet, H. E. N. Bersee and S. J. Picken, Fiber–matrix adhesion in glass-fibre reinforced polyamide-6 silicate nanocomposites, *Composites, Part A* **36**, 1–11 (2005).

14. J. K. W. Sandler, J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer and A. H. Windle, Ultra-low electrical percolation threshold in carbon-nanotube–epoxy composites, *Polymer* **44**, 5893–5899 (2003).

15. Y. S. Song and J. R. Youn, Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites, *Carbon* **43**, 1378–1385 (2005).

16. A. Allaoui, S. Bai, H. M. Cheng and J. B. Bai, Mechanical and electrical properties of a MWNT/epoxy composites, *Compos. Sci. Tech.* **62**, 1993–1998 (2002).

17. E. T. Thostenson, W. Z. Li, D. Z. Wang, Z. F. Ren and T. W. Chou, Carbon nanotube/carbon fiber hybrid multiscale composites, *J. Appl. Phys.* **91**, 6034–6037 (2002).

18. Z. Fan, K. T. Hsiao and S. G. Advani, Experimental investigation of dispersion during flow of multi-walled carbon nanotube/polymer suspension in fibrous porous media, *Carbon* **42**, 871–876 (2004).

19. L. Meynie, F. Fenouillot and J. P. Pascault, Influence of the gel on the morphology of a thermoset polymerized into a thermoplastic matrix, under shear, *Polymer* **45**, 5101–5109 (2004).

20. B. Kulshreshtha, A. K. Ghosh and A. Misra, Crystallization kinetics and morphological behavior of reactively processed PBT/epoxy blends, *Polymer* **44**, 4723–4734 (2003).

21. Q. Guo, C. Harrats, G. Groeninckx and M. H. J. Koch, Miscibility, crystallization kinetics and real-time small-angle X-ray scattering investigation of the semicrystalline morphology in thermosetting polymer blends of epoxy resin and poly(ethylene oxide), *Polymer* **42**, 4127–4140 (2001).

22. Z. Sixun, Z. Naibin, L. Xiaolie and M. Dezhu, Epoxy resin/poly(ethylene oxide) blends cured with aromatic amine, *Polymer* **36**, 3609–3613 (1995).

23. J. T. Carter, G. T. Emmerson, C. L. Faro, P. T. McGrail and D. R. Moore, The development of a low temperature cure modified epoxy resin system for aerospace composites, *Composites, Part A* **80**, 83–91 (2003).

24. Y. S. Song and J. R. Youn, Properties of epoxy nanocomposites filled with carbon nanomaterials, *e-Polymers* **080**, 1–11 (2004).

25. Y. S. Song and J. R. Youn, Modeling of rheological behavior of nanocomposites by Brownian dynamics simulation, *Korea–Australia Rheol. J.* **16**, 201–212 (2004).

26. Y. S. Song and J. R. Youn, Modeling of effective elastic properties for polymer based carbon nanotube composites, *Polymer* **47**, 1741–1748 (2006).

27. Y. S. Song and J. R. Youn, Evaluation of effective thermal conductivity for carbon nanotube/polymer composites using control volume finite element method, *Carbon* **44**, 710–717 (2006).

28. J. A. Kim, D. G. Seong, T. J. Kang and J. R. Youn, Effects of surface modification on rheological and mechanical properties of CNT/epoxy composites, *Carbon* **44**, 1898–1905 (2006).

29. S. H. Lee, E. Cho, S. H. Jeon and J. R. Youn, Rheological and electrical properties of polypropylene composites containing functionalized multi-walled nanotubes and compatibilizers, *Carbon* **45**, 2810–2822 (2007).

30. T. J. Horng and E. M. Woo, Effect of network segment structure on the phase homogeneity of crosslinked poly(ethylene oxide)/epoxy networks, *Polymer* **39**, 4115–4122 (1998).

31. E. Schauer, L. Berglund, G. Peña, C. Marieta and I. Mondragon, Morphological variations in PMMA-modified epoxy mixtures by PEO addition, *Polymer* **43**, 1241–1248 (2002).

32. L. Hu, H. Lü and S. Zheng, Effect of crosslinking on intermolecular interactions in thermosetting blends of epoxy resin with poly(ethylene oxide), *J. Polym. Sci., Part B: Polym. Phys*. **42**, 2567–2575 (2004).

33. Y. H. Hyun, S. T. Lim, H. J. Choi and M. S. Jhon, Rheology of poly(ethylene oxide)/organoclay nanocomposites, *Macromolecules* **34**, 8084–8093 (2001).