The Effect of Mixing Process on Linear Viscoelastic and Electrical Properties of ABS/MWNT Nanocomposites

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ABSTRACT: The aim of this article was to study the microstructure development and the linear melt viscoelastic properties of ABS/MWNT nanocomposites. The nanocomposite samples varying in nanotube concentration (1, 2, 4, and 8 wt %) were prepared using two different methods; solution method and direct melt compounding. Results of the melt linear viscoelastic measurements performed on the nanocomposite samples prepared by both methods showed a pronounced low frequency nonterminal behavior in storage modulus along with the viscosity upturn with greater extent for the samples prepared by the solution method. The values of low frequency storage modulus for the solution processed samples were found to be increased with increasing the nanotube content up to 3 wt % above which it is increased more significantly. These results could be related to a 3D microstructure development, the extent of which was found to be enhanced in the samples prepared by the solution method due to the improving interfacial interaction and promoting the nanotube dispersion in ABS matrix. This was supported by the SEM results of the samples. Dynamic mechanical thermal analysis results of the melt-mixed and solution-processed samples showed that Tg of the SAN is increased about 20°C at the presence of nanotube. The results are related to the chain mobility restrictions caused by physical interaction between carbon nanotubes (CNT) and polymer chains. The electrical conductivity versus CNT content for the nanocomposite samples prepared by solution method showed a percolation behavior with CNT concentration above 4 wt % which attributed to the 3D network between nanotubes. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: E260–E267, 2012

Key words: ABS; carbon nanotube; microstructure; rheological properties; electrical properties; solution method

INTRODUCTION

In recent years, carbon nanotube (CNT) reinforced polymer composites have been widely studied due to their superior mechanical and electrical properties. CNT with high aspect ratio up to 100–1000 enables the electrical percolation at very low content of CNT. CNT has also shown unique mechanical properties, e.g., tensile strength as high as 20 GPa and Young's modulus about 1 TPa.[1–4] The extent of improvements in mechanical and electrical properties of the CNT reinforced composites depends on the CNT loading and the state of CNT dispersion in polymer matrices. However, homogeneous dispersion of nanotubes is difficult to achieve due to the high van der Waals interactions between the nanotubes and the tendency to the formation of aggregates. Several kinds of preparation methods have been developed for dispersion of CNT into polymer matrices. The melt compounding, in situ polymerization of monomer in the presence of CNTs, and solution processing are among the most important methods used for preparation of CNT composites.[5–11]

Several studies have been carried out on CNT reinforced polymer composites, focusing on fundamental understanding of the tube–matrix interactions. Barrera compared the mechanical properties of single-walled CNT containing ABS composites with those of ABS/carbon fiber composites and showed greater mechanical enhancement in SWNT composites. The results of the thermal analyses of ABS/SWNT composites showed that the addition of SWNTs destabilized ABS and the composite began to degrade at lower temperatures.[12–14]

Pötschke et al. studied the melt rheological and electrical properties of polycarbonate/CNT composites to determine the state of nanotube dispersion. They observed a nonterminal behavior of storage modulus (G′) at low oscillation frequency range. It can be related to the formation of percolated structure and liquid–solid transition with increasing CNT content in polymer matrix.[15–19] The results of electrical conductivity of nanocomposite sample were also correlated with the interconnected network and percolation threshold of CNTs.[20–22]

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The relation between molecular structure of polymer and nanotube dispersion was investigated by Fangming using dynamic rheological measurements and electrical conductivity measurements. They showed that increasing the degree of nanotube dispersion leads to more individual CNT, which allows the formation of 3D network structure at lower nanotube concentration.[23]

The aim of this article was to study the relationship between the CNT content and its interaction with the "physical network" formed by entangled polymer chains. In addition, the effect of resulted network structure on the dynamic-mechanical and electrical properties of the samples was investigated.

MATERIALS AND METHODS

Materials

A commercial grade of ABS, SD (MFI = 1.7 g/10 min, $\rho = 1.04$ g/cm^3) supplied by Tabriz Petrochemical Company in Iran was used as the polymeric matrix. Multiwalled CNT with purity of 90%, diameter changing from 40 to 100 nm, and length around 15 microns purchased from Iranian Institute of Petroleum Industry was used.

Methods

Two sets of samples prepared by two different methods were considered:

1. Direct melt compounding: The first set of nanocomposite samples with MWNT concentrations at 0, 1, 2, 4, and 8 wt % was prepared by melt mixing in an internal mixer equipped with a Banbury type rotor. All the melt compoundings were carried out at rotor speed of 60 rpm and 190°C for 15 min.
2. Masterbatch dilution (Solution method): solution method was used to obtain samples with better dispersion of nanotube. The nanocomposite samples were prepared in two steps. First, ABS/MWNT masterbatch containing 16 wt % MWNT was produced using solution method: multiwalled CNTs were dispersed in toluene by sonicating for 5 min followed with 18-h stirring and the resulting solution was sonicated for 10 min. The solution was then mixed with ABS which was dissolved in toluene. The resulting solution mixture was dried through thermal drying at 110°C in an oven and freeze drying at −40°C. Second, the nanocomposite samples containing 2, 4, and 8 wt % MWNT were prepared by melt mixing of masterbatch with the appropriate amount of ABS matrix in a Banbury type internal mixer at 60 rpm and 190°C for 15 min.

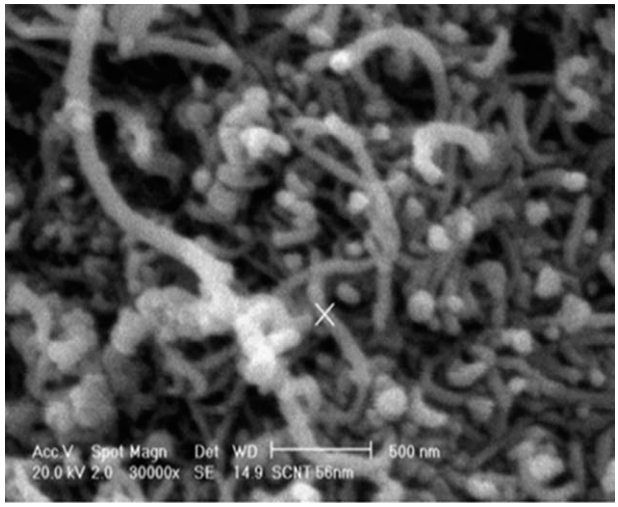

Figure 1 SEM micrograph of neat MWNTs.

Characterization

The melt linear viscoelastic behavior of the samples was studied using a rheometric mechanical spectrometer (Paar Physica MCR300). All the measurements were conducted at 200°C utilizing a parallel-plate fixture with a diameter of 25 mm. Frequency sweep tests were taken in the angular frequency range between 600 and 0.01 rad/s at 1% amplitude strain to be within the linear viscoelastic range. Specimens were allowed to equilibrate for approximately 10 min prior to each frequency sweep run.

A Vega©Tescan microscope was used to study the microstructure of the samples. SEM images were made in the cryofractured surface.

For the electrical conductivity measurements, the samples containing 2, 4, 8 wt % MWNT were cut in dimension 10 mm × 10 mm × 2mm from compression moulded sheets and their surfaces were covered by silver paste. To find out the concentration of CNT above which the conductivity become independent of CNT content, the conductivity measurement was also performed on the ABS/MWNT masterbatch containing 16 wt % CNT. The electrical conductivity was measured in thickness direction using a four-probe electrometer at different voltages.

The dynamic mechanical properties of the samples (dimension 30 mm × 10 mm × 2 mm) were investigated using a DMA-Triton model: Tritec 2000 DMA under nitrogen, at 1% strain, and a frequency of 1 Hz. The temperature was scanned between −100 and 150°C at a rate of 5°C/min.

RESULTS AND DISCUSSION

Morphology

Figure 1 shows a typical SEM micrograph of neat MWNT used. As it can be noticed, the MWNTs are

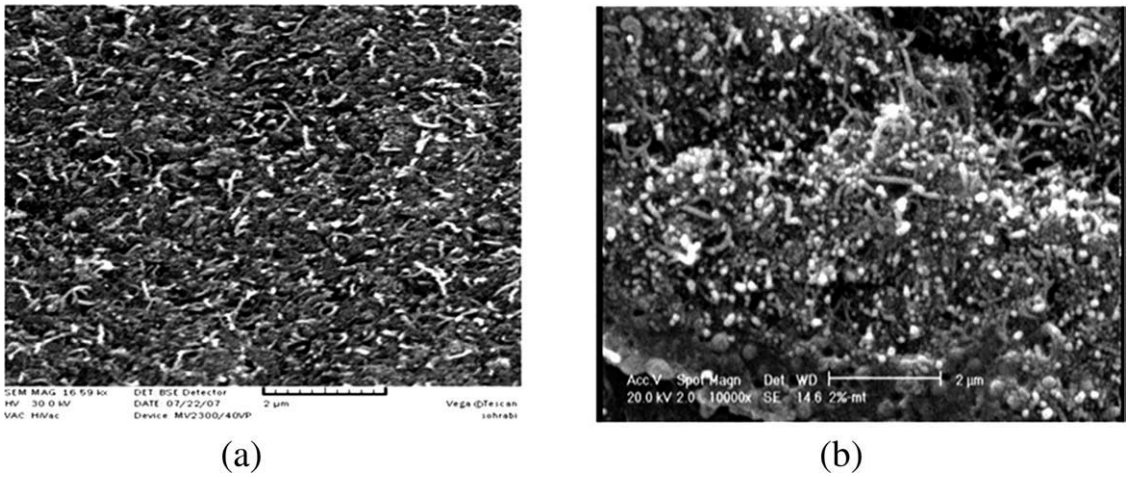

Figure 2 The fracture surface of the composites containing (a) 2 wt % and (b) 4 wt % MWNT prepared by melt-mixing method.

aggregated and curved as a result of van der Waals interactions. Few bright species can also be observed in this micrograph that could be related to impurities such as amorphous carbon.

Figure 2 shows the SEM micrographs of nanocomposite samples containing 2 and 4 wt % MWNT both prepared by melt-mixing method.

Figure 3 shows SEM micrographs of the nanocomposite samples containing 4 wt % MWNT prepared by the solution methods. By comparing these micrographs with that shown in Figure 2, one may notice a great improvement in dispersion of nanotube for the samples prepared by solution method.

Rheology

Figure 4 indicates the results of complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') as a function of frequency obtained for the ABS/MWNT composite samples with different CNT concentrations prepared by melt-mixing method. As it can be seen, the nanocomposite samples exhibit a pronounced low frequency nonterminal storage modulus and viscosity upturn, whose values were increased by increasing the nanotube concentration. This behavior can be related to a network-type microstructure resulted from CNT/CNT interconnectivity and/or CNT/matrix interaction. Slightly lower viscosity and dynamic moduli of 1 and 2% of CNT containing nanocomposites can be attributed to the flow-induced alignment of CNTs. The results obtained from similar experiments performed on the samples prepared by solution method are shown in Figure 5. By comparing these results with those obtained for the samples prepared by the melt-mixing method as shown in Figure 4, one can clearly notice that at the same nanotube concentration, the low-frequency solid body response of the samples prepared by solution process is

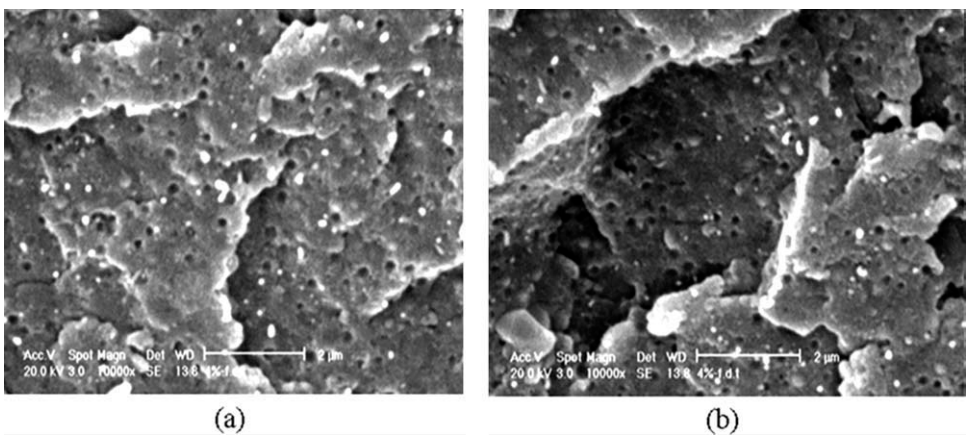

Figure 3 SEM micrograph of the samples with 4 wt % MWNT prepared by solution methods: (a) freeze-drying method and (b) thermal-drying method.

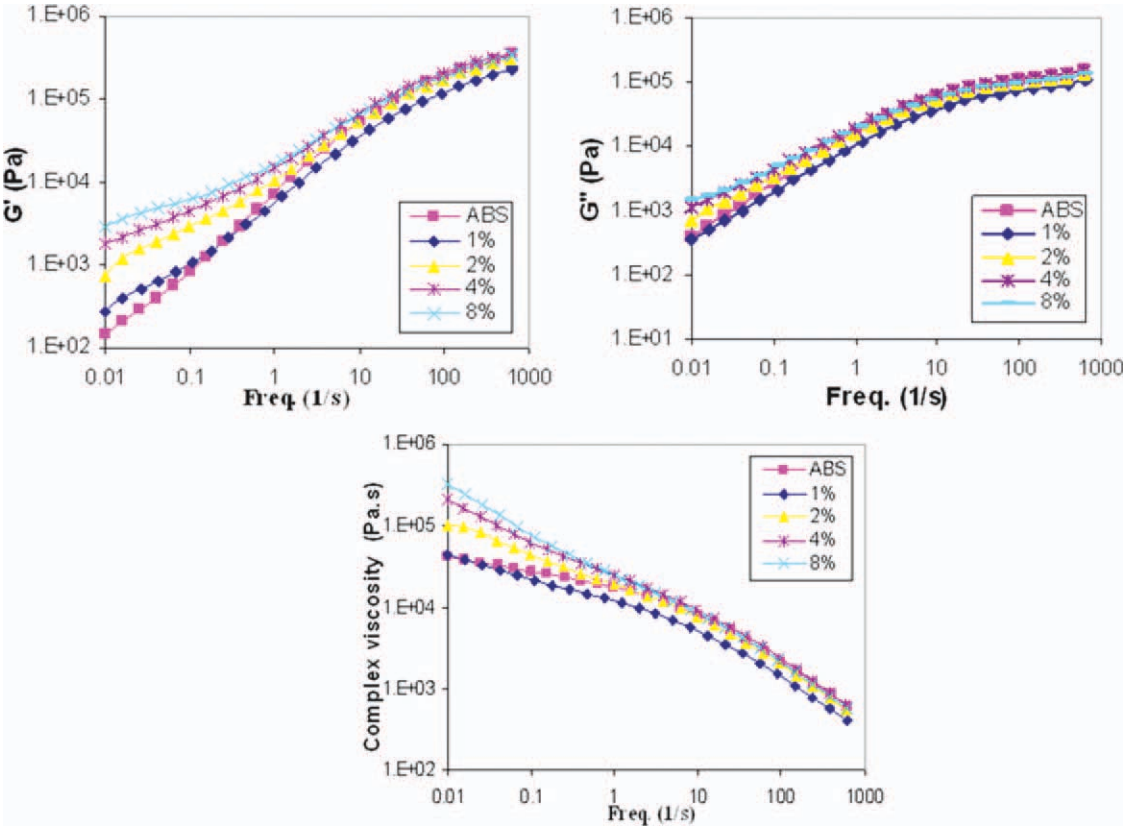

Figure 4 Storage modulus, loss modulus, and complex viscosity versus frequency for the nanocomposites prepared by direct melt-mixing method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

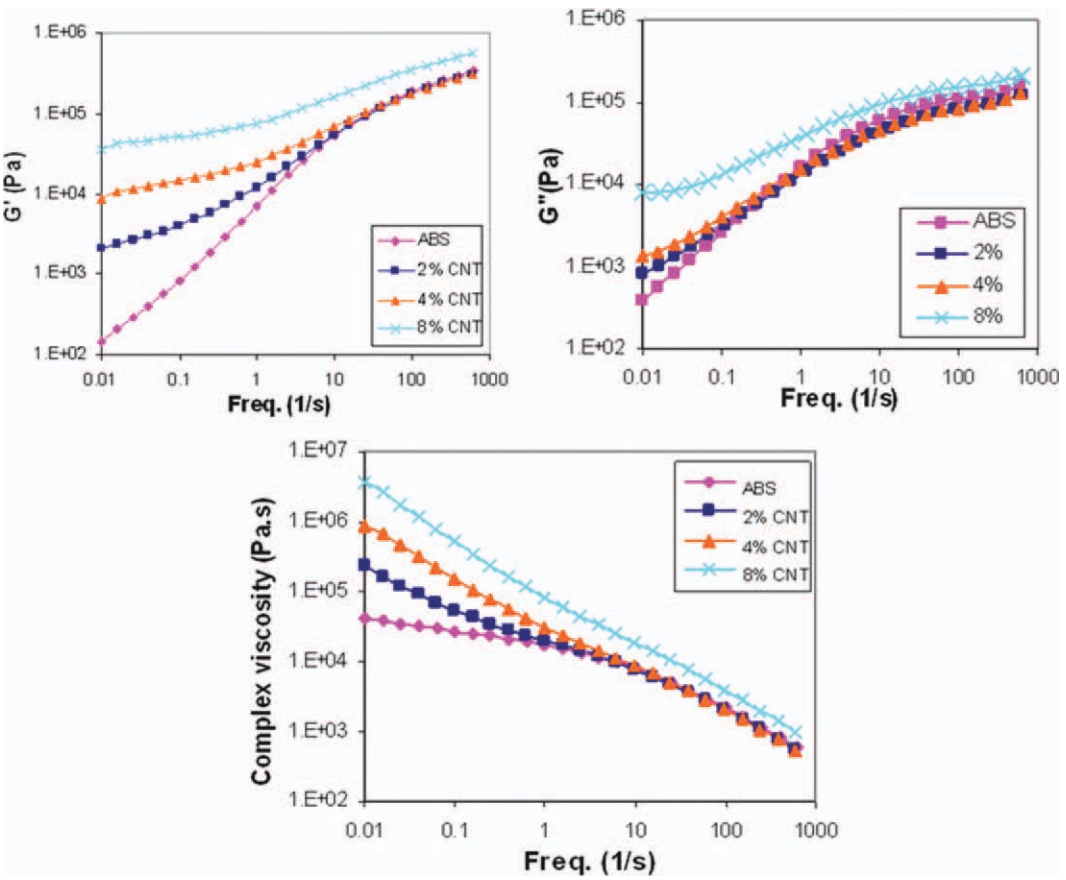

Figure 5 Storage modulus, loss modulus, and complex viscosity versus frequency for the nanocomposites prepared by solution method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

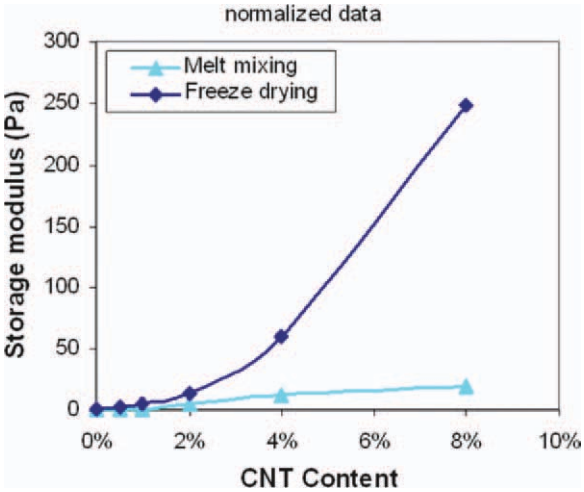

Figure 6 The storage modulus versus nanotube content at Freq = 0.01 s^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stronger than that observed for melt-mixed samples. This can be attributed to the better dispersion–distribution of CNT in the samples prepared by solution method as a result of mutual specific interactions of both CNT and matrix with the solvent.

Figure 6 illustrates the results of storage modulus as a function of nanotube concentration for the solution processed and melt-mixed samples. It is obvious that the samples prepared by solution method exhibit a pronounced percolation as the CNT content exceeds 3 wt %. While in samples prepared by melt-mixing method, the G′ slightly increases with increasing nanotube concentration. These results suggest that while better dispersion–distribution of CNT is in the favor of both CNT/CNT and CNT/matrix interconnectivities, the contribution of the network structure due to the CNT/CNT interconnectivity becomes greater at higher CNT concentration.

The freeze-dried samples indicate complex viscosity (η*) and storage modulus (G′) higher than those of the thermal-dried samples at lower CNT concentrations (Fig. 7). A possible reason behind this is that in contrary to forced-thermal drying, the freeze drying is a thermodynamic process that proceeds in equilibrium manner and consequently it does not perturb the formed dispersion–distribution state upon the slow removal of the solvent.

Electrical measurements

The results of electrical conductivity versus CNT content for the nanocomposite samples prepared by solution method are presented in Figure 8(a,b). As it can be observed in this figure, there is a critical nanotube concentration (i.e., 4 wt %) above which the conductivity of the samples increases remarkably up to some extent where it remains unchanged. A similar percolation threshold at different nanotube concentrations has been reported for other polymer-based CNT containing nanocomposite. These results are in agreement with those shown in Figure 6.

Pötschke et al. have reported the same rheological and electrical percolation at lower CNT concentrations (i.e., 1–2 wt %) for polycarbonate/MWNT nanocomposites prepared by melt-mixing and master-batch-dilution methods in the extruder. It was due to good dispersion of CNTs resulted from using master-batch feeding and thin nanotubes.[18,24] On the other hand, Chen et al. observed a greater percolation threshold (i.e., 5 wt %) for polycarbonate/MWNT nanocomposites and considered it as the reduction of nanotubes' length during melt mixing in extruder.[25]

The relatively higher percolation threshold obtained for ABS/MWNT nanocomposites compared with those reported for other CNT containing samples

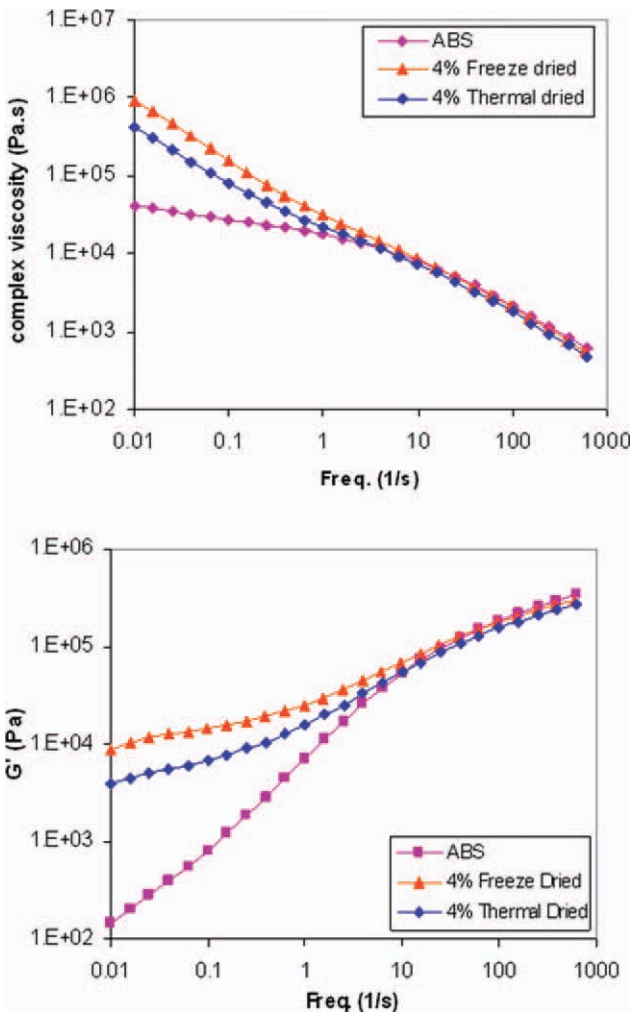

Figure 7 Effect of drying method on the storage modulus for the samples prepared by solution method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

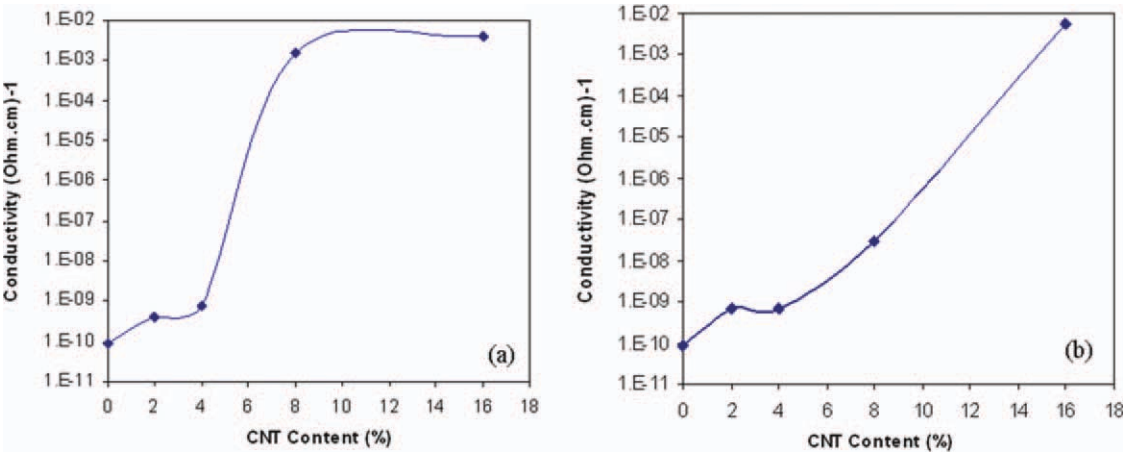

Figure 8 The effect of CNT content on the electrical properties: (a) thermal dried and (b) freeze-dried nanocomposite samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

using different matrices can be attributed to partitioning a fraction of nanotubes within the SAN–rubber interface, which do not contribute to the nanotube-network formation (Fig. 9).

Figure 8(b) shows the results of conductivity for the nanocomposite samples as a function of CNT content prepared by freeze-drying method. Comparing these results with those shown in Figure 8(a), one may notice that the rate of increasing conductivity obtained for the freeze-dried samples is less sensitive to CNT concentration. These results also show that for the thermal-dried sample, there is a CNT concentration (8%) above which, the conductivity remains unchanged while for the freeze-dried samples, the conductivity continues to increase above 8% CNT. In the case of freeze-dried samples, the fine dispersion of CNT generated during solution mixing almost remains intact, while for the samples prepared by thermal drying, there is much greater chance to displacement and/or rotation of CNT. It seems that in the freeze-dried samples, the network structure responsible for low-frequency nonterminal behavior is formed through CNT/matrix interaction, the structure which could not necessarily lead to the CNT interconnectivity and therefore appreciable conductivity.

Moreover, it was found that the conductivity of the samples prepared by melt mixing was too low to be measured by the device used in this study.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis results in terms of damping as a function of temperature for the melt-mixed and thermal-dried samples as are shown in Figure 10. As can be observed for both samples, the glass-transition temperature of SAN is increased from 94.5°C to about 115°C in the presence of CNTs. These results could be due to the chain mobility restriction as a result of effective interactions between nanotubes and polymer chains. A similar result was also achieved for the freeze-dried samples and it had to be noted that the nanotube content has no significant effect on the Tg of SAN phase for all the nanocomposite samples.

Increasing CNT concentration, the amount of damping for both samples is decreased due to the rubber phase (Fig. 11). It indicates that a fraction of

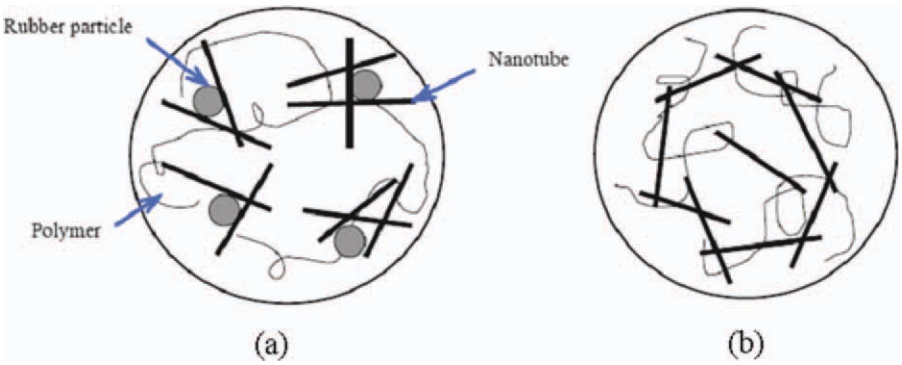

Figure 9 Different structures formed: (a) in the ABS/MWNT nanocomposites and (b) other containing polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

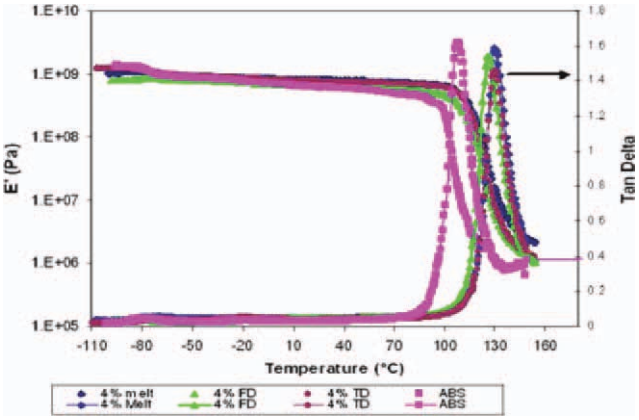

Figure 10 Tan δ variations in ABS and nanocomposite samples prepared by melt mixing and solution methods (FD, TD). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

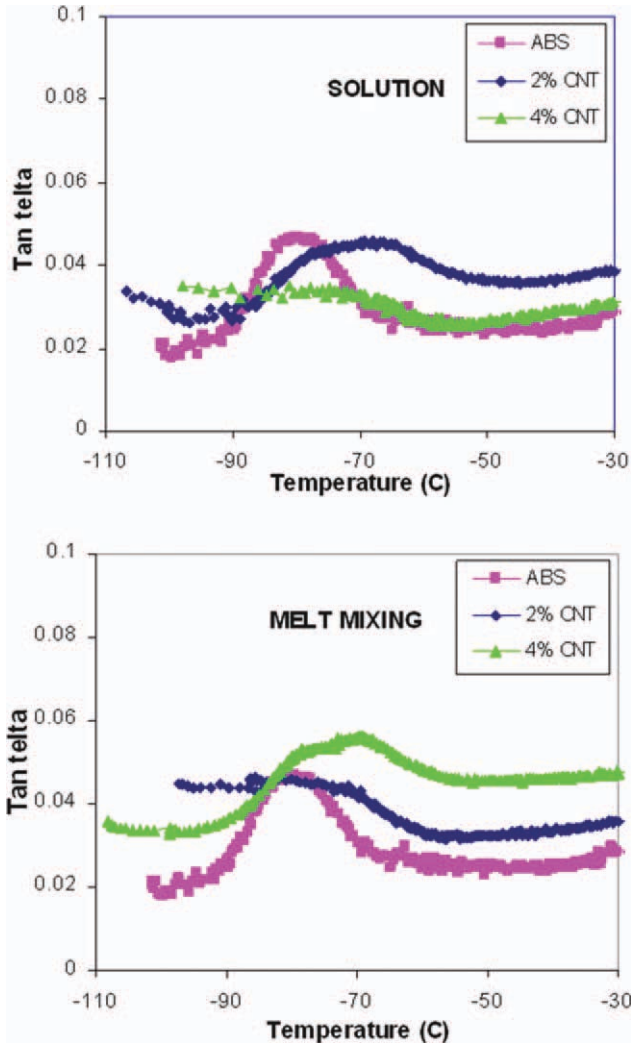

Figure 11 Cole–cole plots for the samples prepared by two different methods: melt mixing and solution method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

applied stress is concentrated on the CNTs, which leads to less contribution of the rubber phase in mechanical response of nanotube containing samples compared with neat ABS. This can be attributed to the reduced contribution of the rubber particles as a result of stress concentration on the nanotubes in the nanocomposite samples compared with ABS. That is why damping of the rubber phase for the solution-processed samples with greater degree of dispersion is lower than the melt-mixed samples.

CONCLUSIONS

The microstructure development and the linear melt viscoelastic properties of ABS/MWNT nanocomposites were investigated. Comparing the results of two preparation methods, one can conclude that the microstructure development in the samples prepared by solution method is more complete and significant than in the samples produced by the melt-compounding method. It is due to good dispersion of CNTs as a result of ultrasonication confirmed by SEM micrographs. Furthermore, at higher extent of CNT dispersion and/or greater amount of CNT, besides polymer–nanotube network, a 3D network is formed between nanotubes that made a percolation behavior in storage modulus and electrical conductivity versus CNT concentration. In addition, glass-transition temperature for all samples was affected by CNT incorporation and increased about 20°C as a result of interaction between SAN chains and nanotubes.

References

1. Pötschke, P.; Dudkin, S. M.; Alig, I. Polymer 2003, 44, 5023.
2. Sung, Y. T.; Han, M. S.; Song, K. H.; Jung, J. W.; Lee, H. S.; Kum, C. K.; Joo, J.; Kim, W. N.;Polymer 2006, 47, 4434.
3. Kim, J. Y.; Park, H. S.; Kim, S. H.;J Appl Polym Sci 2007, 103, 1450.
4. Andrews, R.; Jaques, D.; Minot, M.; Rantell, T. Macromol Mater Eng 2002, 287, 395.
5. Chen, G. X.; Li, Y.; Shimizu, H. Carbon 2007, 45, 2334.
6. Kim, J. A.; Seong, D. G.; Kang, T. J.; Youn, J. R. Carbon 2006, 44, 1898.
7. Shin, D. H.; Yoon, K. H.; Kwon, O. H.; Min, B. G.; Hwang, C. I. J Appl Polym Sci 2006, 99, 900.
8. Kumar, S.; Dang, T. D.; Arnold, F. E.; Battacharyya, A. R.; Min, B. G.; Zhang, X. Macromolecules 2002, 35, 9039.
9. Tang, B. Z.; Xu, H. Macromolecules 1999, 32, 2569.
10. Qian, D.; Dickey, E. C.; Andrews, R.; Rantell, T. Appl Phys Lett 2000, 76, 2868.
11. Star, A.; Stoddart, J. F.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X. Angew Chem Int 2002, 40, 1721.
12. Barrera, E. V. JOM 2000, 52, 38.
13. Shofner, M. L.; Rodriguez-Macias, F. J.; Vaidyanathan, R.; Barrera, E. V. Compos A Appl Sci Manuf 2003, 34, 1207.
14. Yang, S.; Castilleja, J. R.; Barrera, E. V.; Lozano, K. Polym Degrad Stab 2004, 83, 383.

15. Pötschke, P.; Bhattacharyya, A. R.; Janke, A. Eur Polym J 2004, 40, 137.
16. Lin, B.; Sundararaj, U.; Pötschke, P. Macromol Mater Eng 2006, 291, 227.
17. Abdel-Goad, M.; Pötschke, P. J Non-Newtonian Fluid Mech 2005, 128, 2.
18. Pötschke, P.; Abdel-Goad, M.; Alig, I.; Dudkin, S.; Lellinger, D. Polymer 2004, 45, 8863.
19. Boyaud, M. F.; Ait-Kadi, A.; Bousmina, M.; Michel, A.; Cassagnau, Ph. Polymer 2001, 42, 6515.
20. Kalgaonkar, R. A.; Jog, J. P. Polym Int 2008, 57, 114.
21. Wu, D.; Wu, L.; Zhang, M. J Polym Sci B Polym Phys 2007, 45, 2239.
22. Khare, R. A.; Bhattacharyya, A. R.; Kulkarni, A. R.; Saroop, M.; Biswas, A. J Polym Sci Polym Phys 2008, 46, 2286.
23. Du, F.; Scogna, R. C.; Zhou, W.; Brand, S.; Fisher, J. E.; Winey, K. I. Macromolecules 2004, 37, 9048.
24. Pötschke, P.; Fornes, T. D.; Paul, D. R. Polymer 2002, 43, 3247.
25. Chen, L.; Pang, X. J.; Yu, Z. L.;Mater Sci Eng A 2007, 457, 287.