

용액공정을 이용한 다중벽 탄소 나노튜브/폴리스티렌(MWCNT/PS) 복합체 합성 및 열적 거동

텅 다용 · 신영환 · 권영환[†]

대구대학교 공과대학 화학공학과
(2008년 5월 25일 접수, 2008년 7월 1일 채택)

Synthesis of Multi-Walled Carbon Nanotube/Polystyrene (MWCNT/PS) Composites by Solution Process and Their Thermal Behavior

Dayong Teng, Young Hwan Shin, and Younghwan Kwon[†]

Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk 712-714, Korea
(Received May 25, 2008; accepted July 1, 2008)

본 연구에서는 다양한 조성의 다중벽 탄소 나노튜브/폴리스티렌 복합체들을 유화제를 이용한 용액공정을 이용하여 제조하였다. 이때, 분자량이 다른 3종의 폴리스티렌(PS-1 : $\bar{M}_n = 101500$ g/mole, PS-2 : $\bar{M}_n = 89900$ g/mole, PS-3 : $\bar{M}_n = 85000$ g/mole)을 사용하였다. 복합체에서 매트릭스로 사용된 폴리스티렌의 임계흐름온도($T_{cr} \sim 195$ °C) 이상과 이하인 210 °C 및 180 °C에서의 열적 거동을 동적 유변측정기를 이용하여 측정하였다. 복합체의 저장 탄성률, 손실탄성률 및 용융점도는 복합체내에서 다중벽 탄소 나노튜브 함량이 증가함에 따라 증가하였으며, 용융점도의 경우에는 다중벽 탄소 나노튜브 함량이 2 wt%에서 5 wt% 사이에서 가장 큰 증가가 관찰되었다. 210 °C의 유변특성 거동에 의하면, 특정 다중벽 탄소 나노튜브 함량에서 복합체의 점성 특성이 탄성특성으로 전이되는 현상이 관찰되었으며, 이때 다중벽 탄소 나노튜브 함량은 MWCNT/PS-1, MWCNT/PS-2 및 MWCNT/PS-3 조성에 대해 각각 3.5 wt%, 3.2 wt 및 3.0 wt%를 나타내었다.

Multi-walled carbon nanotube/polystyrene (MWCNT/PS) composites with various MWCNT contents were prepared by using a solution process with an aid of surfactant. Particularly, PS's with 3 different molecular weights ($\bar{M}_n = 101500$ g/mole for PS-1, $\bar{M}_n = 89900$ g/mole for PS-2, and $\bar{M}_n = 85000$ g/mole for PS-3) were used in this study. Thermal behavior of these composites was examined by using an oscillator rheometer at 210 °C and 180 °C, of above and below the critical flow temperature ($T_{cr} \sim 195$ °C) of PS matrix, respectively. The storage and loss modulus, and the complex viscosity of these composites increased with increasing MWCNT content at both temperatures. Largest increases in the frequency-dependent moduli and complex viscosity were observed between 2 wt% and 5 wt% of MWCNTs at 210 °C and 180 °C. Only the composite at 210 °C showed the rheological phase transition from a viscous-dominant to an elastic-dominant behavior of the composites at a certain MWCNT content. The MWCNT content at the rheological phase transition of MWCNT/PS composites generally increased with decreasing molecular weight of PS, and was measured to be 3.5 wt% for MWCNT/PS-1, 3.2 wt% for MWCNT/PS-2, and 3.0 wt% for MWCNT/PS-3 composites.

Keywords: multi-walled carbon nanotube, composite, critical flow temperature, thermal behavior

1. Introduction

Polymer/carbon nanotube (CNT) composites have attracted considerable attention due to their unique mechanical, electrical, and thermal properties. CNTs usually have specific interactions with polymer matrices resulting from the nano-scale structure and extremely large interfacial area of CNTs[1-4]. It is well known, however, that CNTs are easy to agglomerate or entangle, limiting the effective utilization of CNTs in polymeric matrices[5]. Salvetat *et al.*[6] studied the effect of

dispersion of CNTs on mechanical properties of polymer/CNT composites, and found that poor dispersion and rope-like entanglement of CNTs led to drastic deterioration of the composites. Thus, dispersion of CNTs in polymer matrices has been considered to have a predominant role on mechanical and other functional properties of polymer/CNT composites[7,8].

In order to disperse CNTs into the polymer homogeneously, the entanglement of CNTs inherited from their synthetic process and Van der Waals force between CNTs should be minimized. Three common methods to incorporate CNTs into polymeric matrices are solution process of mixing polymers and CNTs in solvents, *in-situ* polymer-

[†] 교신저자(e-mail: y_kwon@daegu.ac.kr)

ization of monomers in the presence of CNTs, and melt mixing of polymers with CNTs at elevated temperatures. High power mechanical methods such as ultrasonic and high speed stirring can be also used to improve the degree of dispersion of CNTs into polymers. In addition, surface treatment of CNTs by chemical functionalization or covalent attachment of polymer chains efficiently enhances the interfacial bonding between CNTs and the polymer matrix, resulting in better dispersion of CNTs into the polymer matrix[9-19]. However, the surface treatment of CNTs may introduce unsolicited defects on the surface of CNTs, reducing the efficiency of applied load in the composites. Although a number of studies have been conducted for a decade, the expected potential of CNTs as the reinforcement in polymer/CNT composites have not been fully realized[20,21]. It seems that the effective utilization of polymer/CNT composites strongly depends on the ability to disperse the CNTs homogeneously into the polymeric matrix without destroying the structural integrity of the CNTs.

In a previous paper[22], we measured rheological properties of multi-walled carbon nanotube (MWCNT)/polystyrene (PS) composites with various MWCNT contents in order to investigate the influence of various rheological parameters on MWCNT-filled polymeric composites. From these rheological results measured at 210 °C, which is above the critical flow temperature ($T_{cf} \sim 195$ °C)[23] of amorphous PS matrix, the rheological transition from a viscous-dominant to an elastic-dominant behavior was observed at 3.2 wt% of MWCNT content in MWCNT/PS composites. This transition might be related to a combination of interactions between MWCNTs and interactions between MWCNTs and PS chains, providing an alternative way to determine the degree of dispersion of MWCNTs in the composites.

In this article, we report the synthesis and thermal behavior of MWCNT/PS composites with various MWCNT contents and three different molecular weights of PS. An oscillatory rheometer was used to measure rheological properties above (at 210 °C) and below (at 180 °C) T_{cf} of amorphous PS matrix in MWCNT/PS composites. The influence of molecular weights of PS matrices on thermal behavior of the composites will be discussed.

2. Experimental

2.1. Materials and Methods

Commercial-grade polystyrenes (PS) with different molecular weights were obtained from LG Chemical Co. Characteristics of these polymers was summarized in Table 1. MWCNT (diameter: 10~15 nm, length: 10~20 μm) was purchased from Iljin Nanotech Co. All the materials were dried for 24 h at 80 °C in a vacuum oven prior to the experiments. MWCNT/PS composites with six different compositions between 0.1 wt% and 10 wt% of MWCNTs were prepared with the commercial-grade PS and a surfactant (Hypermer KD-15[®], Uniquema Co.) by using following solution process: After dissolving 5 g of PS in 100 mL of dichloroethane (Junsei Chemical Co.), 1 g of surfactant was subsequently added to the solution and stirred for 1 h. Then, a portion of the MWCNT powder was dispersed in the solution, followed by ultrasonification for 5 h with an ultrasonic generator operated at a nor-

Table 1. Results on Characterization of Polystyrenes

Polymers	M_n (g/mole)	M_w/M_n	MI (g/10 min.)	T_g (°C)
PS-1 (G 116 [®])	101,500	1.36	2.4	105.6
PS-2 (G126KS [®])	89,900	1.37	6.0	101.0
PS-3 (G 144 [®])	85,000	1.46	8.7	93.0

mal frequency of 40 kHz and a power of 400 W to make a homogeneous dispersion. The MWCNT-dispersed solution was poured into methanol (DC Chemical Co.). The precipitate was filtered and dried for 17 h at 80 °C in a vacuum oven.

2.2. Rheological Measurements

The rheological properties of the MWCNT/PS composite films prepared by using hot pressing were determined using an oscillatory rheometer (UDS-200, Paar Physica Co.). A frequency sweep experiment was performed at 210 °C or 180 °C in an oscillatory shear mode by using a parallel plate with a 25-mm diameter with a gap according to the disk thickness. To investigate the frequency dependence of the storage modulus (G') and the loss modulus (G'') of the MWCNT/PS composites, a constant value of the amplitude set was used at 0.1% of amplitude and a frequency range from 1×10^{-1} to 100 Hz.

2.3. Instruments

Differential scanning calorimetry (DSC) was performed with DSC (DSC 2010, TA Instruments) using a heating/cooling scan rate of 10 °C/min in the temperature range from room temperature to 250 °C. Each sample was first scanned from room temperature to 250 °C, maintained at that temperature for 1 min, and cooled down until room temperature. The glass transition temperature (T_g) of PS was taken as the midpoint of the specific heat jumps in the second heating scan. For morphological study, MWCNT/PS composites were immersed into liquid nitrogen and then fractured. Morphology of fractured surface of MWCNT/PS composites with 2 wt%, 5 wt%, and 10 wt% was observed by using field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi) with 15 kV of voltage. Morphology of MWCNT was observed after casting dilute solution of MWCNT in dichloromethane over thin aluminum plate.

3. Results and Discussion

Figure 1 presents the dependence of complex viscosity (η^*) on frequency for PS1, PS2, and PS3 at 210 °C. It showed a general trend that complex viscosity of PS increased with increasing molecular weights of PS, and decreased with increasing frequency from 1×10^{-1} to 100 Hz.

Figure 2 presents FE-SEM photographs of MWCNT and MWCNT/PS-3 composites with different MWCNT contents. FE-SEM photographs of MWCNT/PS-3 composites showed dispersed MWCNTs wrapped by PS matrix. With increasing MWCNT contents in the composites, interactions between MWCNTs began to form. In Figure 2(c), 5 wt% of MWCNT content in the composite eventually led to the for-

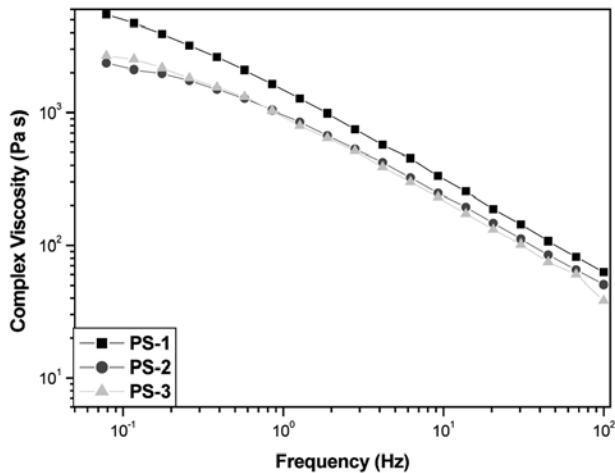


Figure 1. Complex viscosity of PS-1, PS-2, and PS-3 with different molecular weight as a function of the frequency at 210 °C.

mation of interconnected structures of MWCNTs with relatively reasonable dispersion in PS matrix. The connectivity between MWCNTs in PS matrix became more pronounced at 10 wt% of MWCNT content, as presented in Figure 2(d).

In order to investigate thermal behavior of MWCNT/PS composites, complex viscosity (η^*), storage modulus (G') and loss modulus (G'') of 3 different types of composites (MWCNT/PS-1, MWCNT/PS-2 and MWCNT/PS-3) with various MWCNT contents were measured as a function of frequency at 210 °C and 180 °C, respectively. Since all MWCNT/PS composites showed similar trends in the rheological measurement, the rheological properties of MWCNT/PS-3 composite were mainly discussed in this article. The complex viscosity of MWCNT/PS-3 composites with different MWCNT contents was measured as a function of frequency at 210 °C and 180 °C, as can be seen in Figure 3(a) and (b), respectively. At both temperatures, the complex viscosity (η^*) of MWCNT/PS-3 composite increased with increasing MWCNT contents, and the composite with 10 wt% of MWCNT was more viscous by an order of magnitude than the one with 0 wt% of MWCNT even at high frequency region. The effect of MWCNT contents on the complex viscosity was more prominent at low frequency region, and decreased with increasing frequency due to well-known shear thinning of polymers[24,25]. MWCNT/PS-3 composites between 2 wt% and 5 wt% of MWCNT exhibited a significant change in the frequency dependence of their complex viscosity at both 210 °C and 180 °C.

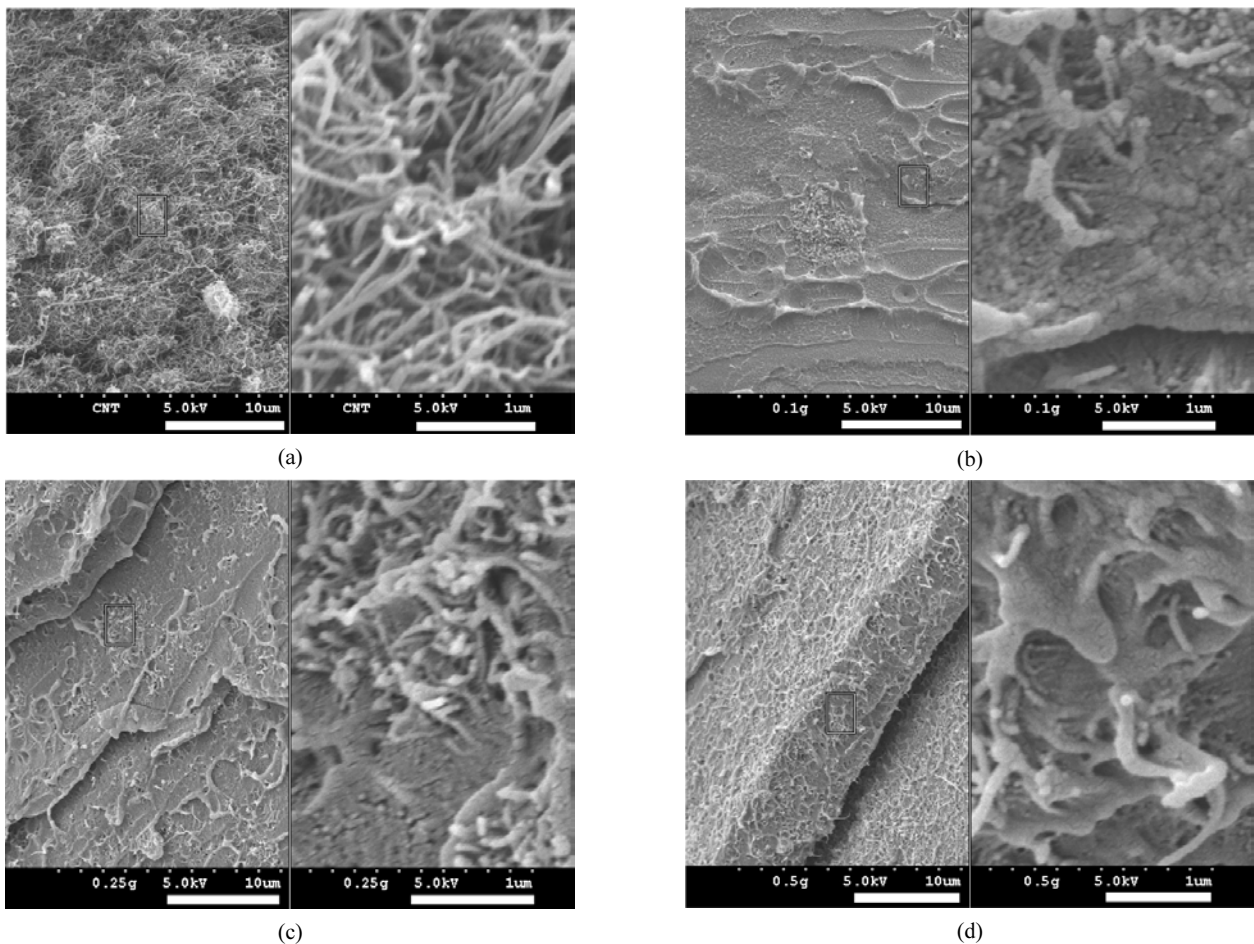
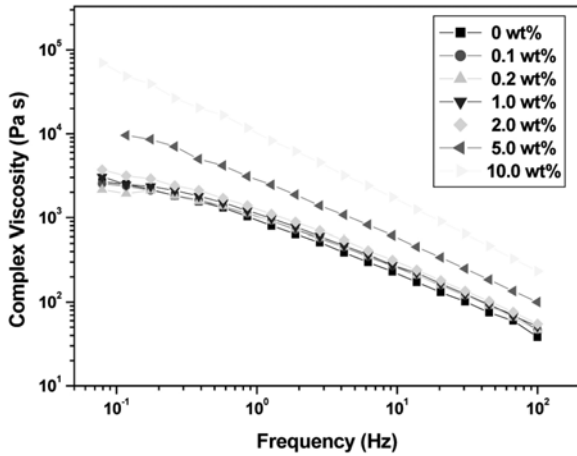
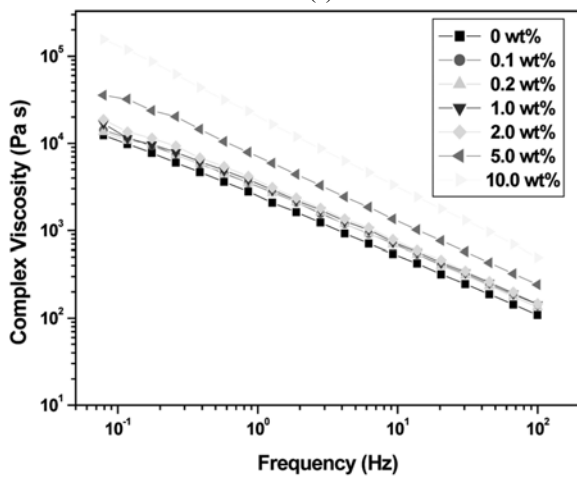


Figure 2. FE-SEM photographs of (a) MWCNT, (b) 2 wt%, (c) 5 wt%, and (d) 10 wt% of MWCNT contents in MWCNT/PS-3 (scale bar; left = 5 μm, right = 0.5 μm).



(a)



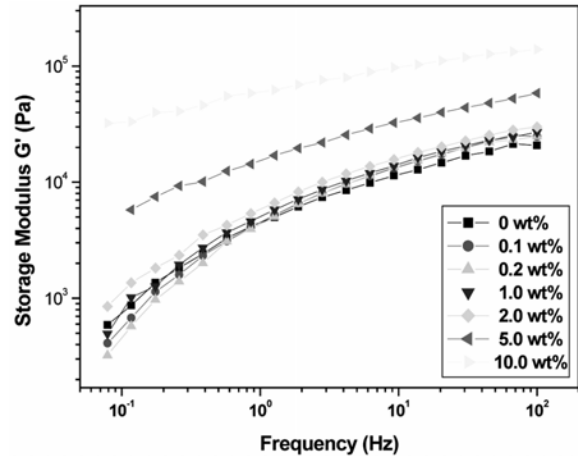
(b)

Figure 3. Complex viscosity (η^*) of MWCNT/PS-3 composites as a function of frequency at (a) 210 °C and (b) 180 °C.

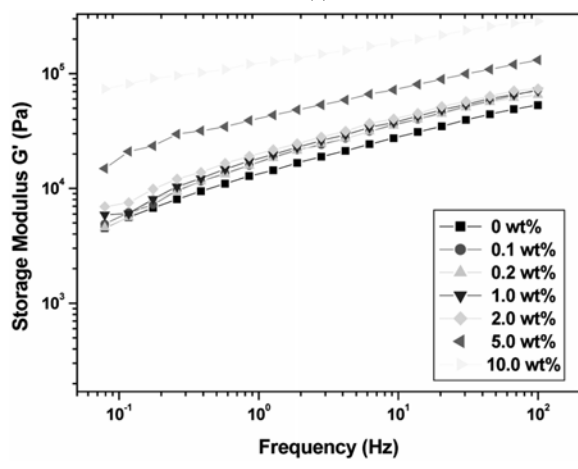
The storage modulus (G') and loss modulus (G'') of the MWCNT/PS-3 composites with various MWCNT contents, measured at 210 °C and 180 °C, are logarithmically plotted as a function of frequency in Figure 4 and Figure 5, respectively. The storage and loss moduli generally increased with increasing frequency. Particularly, this increase was prominent at low frequency region, and the increase in the storage modulus was more pronounced than in the loss modulus. It also appeared that a noticeable qualitative change in the moduli vs. frequency curves was observed as the MWCNT content was increased from 2 wt% to 5 wt%.

Figure 6 presents a plot of the storage modulus (G') vs. the loss modulus (G'') of MWCNT/PS-3 composites as a function of frequency, which are so-called Cole-Cole plots[26,27]. In general, these plots have been used to study the viscoelastic behavior of bulk polymers[28-31]. On the line at $\log G' = \log G''$ in Figure 6, the composites show a viscoelastic behavior with a combination of elastic and viscous properties. However, the composites will exhibit either elastic-dominant property above the line, or viscous-dominant behavior below the line, respectively.

In Figure 6(b), the storage modulus of MWCNT/PS-3 composites at



(a)

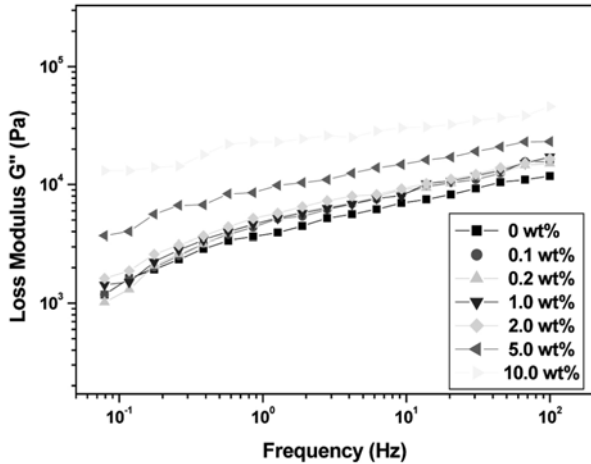


(b)

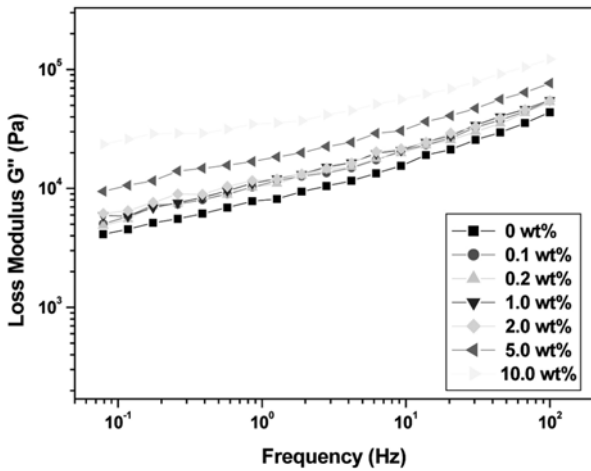
Figure 4. Storage modulus (G') of MWCNT/PS-3 composites as a function of frequency at (a) 210 °C and (b) 180 °C.

180 °C was always larger than the loss modulus, implying an elastic-dominant property of MWCNT/PS-3 composites regardless of the compositions. This could be originated from rheological measurement at such a low temperature (at 180 °C), which was lower than the critical flow temperature (T_{cf}) of amorphous PS matrix in the composites. Since an isorheological state of amorphous polymers could be obtained above T_{cf} , the amorphous PS could be only regarded as a viscous polymer melt above T_{cf} . In the above experimental condition below T_{cf} , therefore, a solid-like elastic behavior of the amorphous PS could be dominated at 180 °C.

On the other hand, MWCNT/PS-3 composites with below 2 wt% of MWCNT contents at 210 °C exhibited a transition from viscous-dominant to elastic-dominant behavior with increasing frequency, as seen in Figure 6(a). Above 5 wt% of MWCNT, the storage modulus was larger than the loss modulus, indicating an elastic-dominant behavior of the MWCNT/PS-3 composites over the whole frequency region. It has been generally known that amorphous polymers show a viscous-dominant behavior above their T_{cf} . From Figure 6(a) it is clearly revealed that a transition from viscous-dominant to elastic-dominant behavior between 2 wt% and 5 wt% of MWCNT contents occurred above the



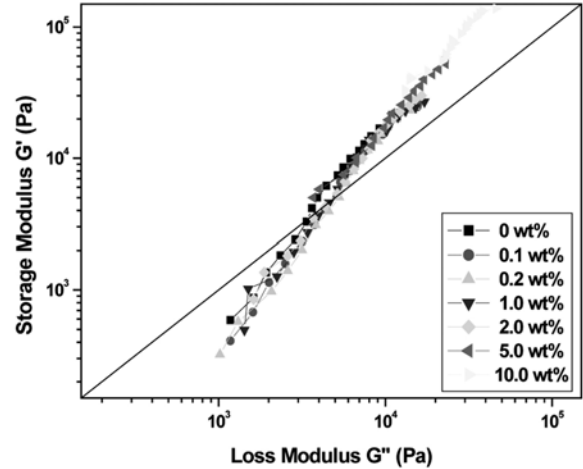
(a)



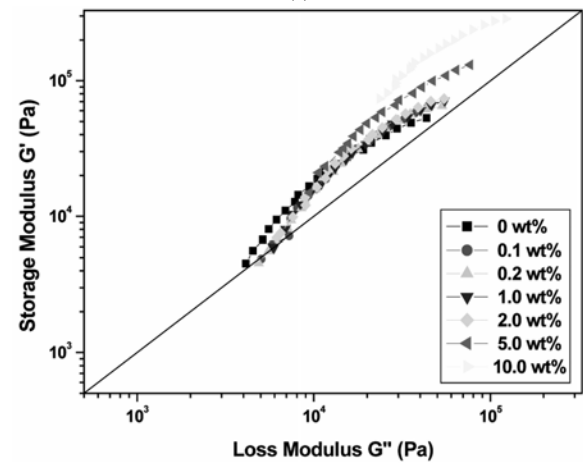
(b)

Figure 5. Loss modulus (G'') of MWCNT/PS-3 composites as a function of frequency at (a) 210 °C and (b) 180 °C.

T_{cf} of the amorphous PS matrix even at low frequencies. This phenomenon of MWCNT/PS composites has been observed at a certain content of MWCNTs, and similar phenomena were already reported to be related to physical gelation of the filler-reinforced composites[32,33]. It was also reported[34] that the rheological transition mentioned above



(a)

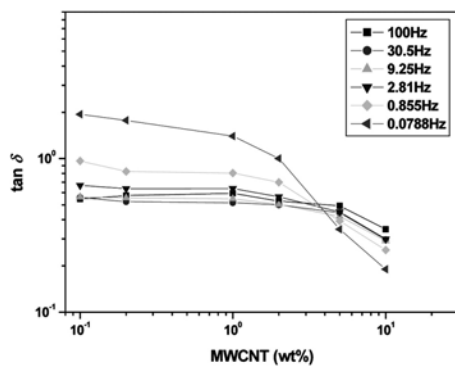


(b)

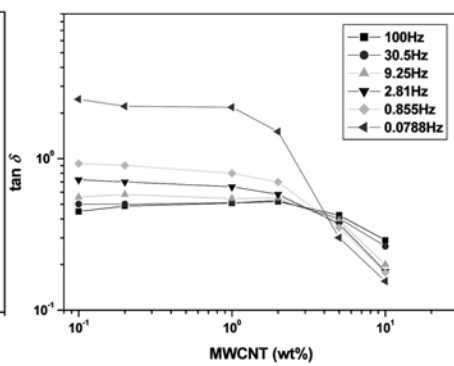
Figure 6. Storage modulus (G') vs. loss modulus (G'') plots of MWCNT/PS-3 composites at (a) 210 °C and (b) 180 °C.

was sensitive to the interconnectivity of the nanotubes in polymeric matrix.

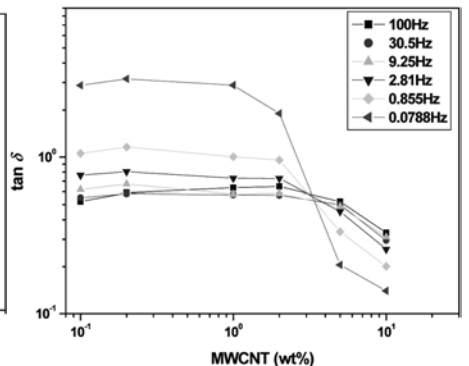
Along this line, the interconnectivity of all MWCNT/PS composites was studied by using a multifrequency plot of $\tan \delta$ vs. MWCNT contents, as presented in Figure 7(a), (b) and (c)[34]. This is based on



(a)



(b)



(c)

Figure 7. The $\tan \delta$ vs. MWCNT content in MWCNT/PS composites at 210 °C in terms of the frequency; (a) MWCNT/PS-1, (b) MWCNT/PS-2, and (c) MWCNT/PS-3.

the frequency-independent value of $\tan \delta$ obtained at 210 °C. The general trend is a steady decrease in the $\tan \delta$ ($= G''/G'$) values with increasing MWCNT contents due to the relatively dominant contribution of the storage modulus to the loss modulus. After crossover point observed in Figure 7, a value of $\tan \delta$ showed frequency-independent behavior at a particular MWCNT content. The MWCNT content at the crossover point was estimated to be 3.5 wt% for MWCNT/PS-1 (Figure 7(a)), 3.2 wt% for MWCNT/PS-2 (Figure 7(b)), and 3.0 wt% for MWCNT/PS-3 (Figure 7(c)), where the interconnected MWCNT content of MWCNT/PS composites increased with increasing molecular weights of PS matrix. This results might be effected by following three intermolecular force; MWCNT-MWCNT interaction in a highly dispersed state, MWCNT-polymer interaction, and polymer-polymer chains interaction. It is initially expected that the polymer-polymer interaction increases with molecular weight of PS so that the MWCNT content at the crossover point of the composites decreases. It appears, however, that contribution of increased molecular weight of PS weakly affects on the polymer-polymer interaction, resulting in increased MWCNT content with increasing molecular weight of PS. It can be assumed that, therefore, this rheological transition at a particular MWCNT content is largely related to a combination of interactions between MWCNTs as well as interactions between MWCNTs and PS chains. In the case of MWCNT/PS composites measured at 180 °C, however, it could not be obtained by using the frequency-independent value of $\tan \delta$, due to absence of the rheological transition of the composites from Figure 6(b).

4. Conclusions

The thermal behavior of MWCNT/PS composites with various MWCNT contents was characterized by using a frequency sweep experiment with an oscillatory rheometer at 210 °C and 180 °C, where three kinds of PS with different molecular weights were used for preparing MWCNT/PS composites by a solution process assisted with a surfactant. At 210 °C, rheological phase transition from a viscous-dominant to an elastic-dominant behavior of the MWCNT/PS composites was observed at a certain MWCNT content. Generally, the MWCNT content at the transition increased with decreasing molecular weight of PS matrix. This rheological transition at a particular MWCNT content could be related to a combination of interactions between MWCNTs as well as interactions between MWCNTs and PS chains.

Acknowledgment

This work is the outcome of a Manpower Development Program for Energy & Resources supported by the Ministry of Knowledge and Economy (MKE).

References

1. H. C. Zeng, in Handbook of Organic-Inorganic Hybrid Materials and Nanocomposites Vol. 2, H. S. Nalwa Ed., pp.151, American Scientific Publisher, Los Angeles (2003).

2. C. P. Poole, Jr. and F. J. Owens, Introduction to Nanotechnology, p. 114, Wiley, New Jersey (2003).
3. J. W. Kang and H. J. Hwang, *J. Korean Phys. Soc.*, **46**, 875 (2005).
4. J. W. Jang, S. H. Kim, C. E. Lee, T. J. Lee, C. J. Lee, H. S. Kim, E. H. Kim, and S. J. Noh, *J. Korean Phys. Soc.*, **42**, S985 (2003).
5. D. Qian, E. C. Dickey, R. Andrews, and T. Rantell, *Appl Phys. Lett.*, **76**, 2868 (2000).
6. J. P. Salvétat, A. D. Briggs, J. M. Bonard, R. R. Bacsá, A. J. Kulik, T. Stockli, N. A. Burnham, and L. Forro, *Phys. Rev. Lett.*, **82**, 944 (1999).
7. L. Jin, C. Bower, and O. Zhou, *Appl. Phys. Lett.*, **73**, 1197 (1998).
8. E. S. Choi, J. S. Brooks, D. J. Eaton, M. S. Al-Haik, M. Y. Hussaini, H. Garmestani, D. Li, and K. Dahmen, *J. Appl. Phys.*, **94**, 6034 (2003).
9. M. S. P. Shaffer, X. Fan, and A. H. Windle, *Carbon*, **36**, 1603 (1998).
10. P. Potschke, A. R. Bhattacharyya, and A. Janke, *Eur. Polym. J.*, **40**, 137 (2004).
11. S. J. Park, M. S. Cho, S. T. Lim, H. J. Choi, and M. S. Jhon, *Macromol. Rapid Commun.*, **24**, 1070 (2003).
12. A. Eitan, K. Jiang, D. Dukes, R. Andrews, and L. S. Schadler, *Chem. Mater.*, **15**, 3198 (2003).
13. Y. Lin, A. M. Rao, B. Sadanadan, E. A. Kenik, and Y. P. Sun, *J. Phys. Chem. B*, **106**, 1294 (2002).
14. S. Cui, R. Canet, A. Derre, M. Couzi, and P. Delhaes, *Carbon*, **41**, 797 (2003).
15. J. L. Bahr and J. M. Tour, *J. Mater. Chem.*, **12**, 1952 (2002).
16. E. T. Thostenson and T. W. Chou, *J. Phys. D: Appl. Phys.*, **35**, L77 (2002).
17. T. Satio, K. Matsushige, and K. Tanake, *Physica B*, **323**, 208 (2002).
18. F. H. Gojny, J. Nastalczyk, Z. Roslaniec, and K. Schelte, *Chem. Phys. Lett.*, **370**, 820 (2003).
19. P. Poulin, B. Vigolo, and P. Launois, *Carbon*, **40**, 1741 (2002).
20. L. S. Schadler, S. C. Giannaris, and P. M. Ajayan, *Appl. Phys. Lett.*, **73**, 3842 (1998).
21. S. J. V. Frankland and V. M. Harik, *Surf. Sci.*, **86**, 2079 (2002).
22. S.-D. Park, D.-H. Han, D. Teng, Y. Kwon, and G.-Y. Choi, *J. Korean Phys. Soc.*, **48**, 476 (2006).
23. G.-Y. Choi, H.-G. Kim, Y.-H. Kim, C.-W. Seo, J.-H. Choi, D.-H. Han, D.-H. Oh, and K.-E. Min, *J. Appl. Polym. Sci.*, **86**, 917 (2002).
24. A. T. Mutel and M. R. Kamal, in Two Phase Polymer Systems, A. Utracki Ed. pp. 305, Carl Hanser, New York (1991).
25. T. Kitano, T. Kataoka, and Y. Nagatsuka, *Rheol. Acta.*, **23**, 20 (1984).
26. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).
27. N. Nakayama and E. R. Harrell, in Current Topics in Polymer Science, vol. II: Rheology and Polymer Processing/Multiphase Systems, R. M. Ottenbrite, L. A. Utracki, and S. Inoue Eds. pp. 149, Carl Hanser, New York (1987).
28. C. D. Han and K. W. Lem, *Polym. Eng. Rev.*, **2**, 135 (1983).
29. H. K. Chuang and C. D. Han, *J. Appl. Polym. Sci.*, **29**, 2205 (1984).
30. C. D. Han and J. K. Kim, *Macromolecules*, **22**, 383 (1989).
31. D. U. Ahn and S.-Y. Kwak, *Macromol. Mater. Eng.*, **286**, 17 (2001).
32. C. Liu, J. Zhang, J. He, and G. Hu, *Polymer*, **44**, 7529 (2003).
33. M. Abdel-Goad and P. Pötschke, *J. Non-Newtonian Fluid Mech.*, **128**, 2 (2005).
34. P. Pötschke, T. D. Fomes, and D. R. Paul, *Polymer*, **43**, 3247 (2002).