

Effects of multi-walled carbon nanotubes on rheological and physical properties of polyamide-based thermoplastic elastomers

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(Received July 9, 2012; final revision received August 28, 2012; accepted August 30, 2012)

Abstract

The polyamide-based thermoplastic elastomers (Pebax[®]) were melt compounded with multi-walled carbon nanotubes (MWNTs: 0.25~5 wt%) and the variation of rheological and physical properties with MWNT contents was investigated. The crystallization temperature (T_c) of the nanocomposites with 0.5 wt% MWNTs was most increased by ca. 8°C, but it was decreased by further addition. In addition, the presence of MWNTs broadened the T_c peak with increasing nanotube contents. In contrast, the melting behavior was little influenced by the presence of MWNTs for all compositions. The incorporation of MWNTs increased the complex viscosity with MWNT contents and the abrupt increase was observed from 1 wt%. In addition, lower Newtonian flow region became disappearing with increasing MWNT contents, exhibiting notable shear thinning behavior from 1 wt% loading. Storage modulus was increased with MWNT contents in a similar manner to viscosity. Casson plot demonstrated a non-zero positive intercept for all the samples. In particular, the abrupt increase of yield stress was observed from 1 wt% loading. In the Cole-Cole plot, the nanocomposites gave a deviated curve from pure Pebax and the slope was decreased with increasing MWNT contents. The relaxation time calculated from viscoelastic parameters was increased with nanotube contents, but the increasing extents were reduced with increasing frequency. From 2 wt% MWNTs, the electrical conductivity was observed, indicating that the electrical percolation existed between 1.5 and 2 wt%. At 0.25 wt% loading the tensile strength was slightly increased, but it was gradually decreased by further addition. The introduction of MWNTs increased the tensile modulus with nanotube contents. In addition, ductile properties were reduced with increasing MWNT contents, resulting in low toughness.

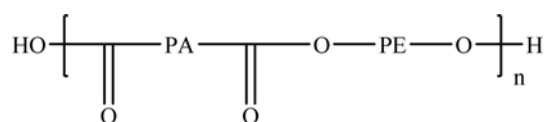
Keywords: thermoplastic elastomers, carbon nanotubes, rheology, nanocomposites

1. Introduction

The interest of thermoplastic elastomers (TPEs) is notably increased due to their wide applications in automotive parts, consumer goods, and medical products (Markarian, 2008). TPEs which consist of soft and hard chain segments possess both advantages of typical rubbery materials and plastic materials. Hard segments easily form physical crosslink sites due to their rigid morphology and dipolar structure. The crosslink domains maintain a three-dimensional network of polymeric system, providing TPEs with elastomeric properties at room temperature. However, they have their own melting temperature (T_m) where they flow like thermoplastics. Thus, TPEs are regarded as environmentally friendly materials unlike vulcanized rubbers (Rader and Stockel, 1995). In addition, they are suitable for the indus-

trial processes of large-processing load such as injection molding and melt extrusion (Spontak and Patel, 2000).

In the early of the 1980s, Atochem introduced thermoplastic polyether-block-amide copolymer (Deleens, 1981), commercially known as Pebax[®]. It is composed of aliphatic polyamide (PA) as hard block and polyether (PE) as soft block, and its general structural formula is as follows:



The hard segments form the rigid domain which acts as chemical crosslink and the hydrogen bonding between PA 12 produces a strong and durable domain unit, while the soft segments give flexibility to Pebax. Pebax finds various applications such as sport equipment, medical products, food packing, antistatic sheets or belts, and clothing (Fletcher, 1986). Recently its applications to membranes

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have been widely progressing because Pebax has extremely high polar/nonpolar gas selectivity (Kim and Lee, 2001; Bondar *et al.*, 1999). In order to enlarge the spectrum of novel properties of Pebax, it is hybridized with some fillers such as clay, titanium, and boron nitride (Yang and Tsai, 2006; Lyons *et al.*, 2010; Iyer *et al.*, 2006).

Carbon nanotubes (CNTs) which have high flexibility, low mass density, and large aspect ratio (ca. 300 – 1000) were first reported by Iijima (1991). They exhibit unique physical properties including high electrical and thermal conductivity and tensile strength. Some CNTs are stronger than steel or aluminum and more conductive than copper (Woo *et al.*, 2009; Kang and Lee, 2012; Oh *et al.*, 2010). When CNTs are introduced into polymer, these superior properties can be achieved even at very low contents in comparison with other carbon allotropes such as graphite and carbon black (Moniruzzaman and Winey, 2006). Therefore, many studies on CNTs/polymer composites have been actively done since they are first reported by Ajayan *et al.* (1994). Murali *et al.* (2010) and Yen *et al.* (2012) studied Pebax/CNTs composites membranes in terms of their gas permeation properties. Despite these studies, however, there are few studies on the rheological and physical properties of CNT-filled polyamide-based TPEs.

There are several techniques to fabricate the nanocomposites such as solution blending, melt blending and in situ polymerization (Moniruzzaman and Winey, 2006; Hwang *et al.*, 2008; Kim and Lee, 2008; Hyun *et al.*, 2012). Among these methods, melt mixing is the most suitable and promising approach for the needs of industries because of its low cost, high productivity, and compatibility with current industrial practices (Liu *et al.*, 1999; Chae *et al.*, 2012). In this research, we prepared Pebax/multi-walled carbon nanotubes (MWNTs) composites by dry-mixing in a powder state and subsequent melt-compounding. The influences of MWNTs on the physical properties of Pebax such as thermal and rheological property and morphology were discussed varying nanotube contents.

2. Experimental

2.1. Materials

Polyamide-based thermoplastic elastomer (Pebax[®] 5533) composed of rigid polyamide 12 segments and flexible poly(tetramethylene glycol) segments was purchased from Arkema, France. MWNTs (95% < purity, diameter = 10 – 15 nm) produced by the thermal chemical vapor deposition process were purchased from Hanwha Nanotech, Korea.

2.2. Preparation of nanocomposites

Pebax which was grinded into powder was dry-mixed with MWNTs using a high speed blender. The premixture was then melt-compounded using an internal mixer (Haake PolyDrive, Thermo Electron Corp.) for 7 min at 200°C at

a rotor speed of 100 rpm. The loading levels (X) of MWNTs were 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 4, and 5, and the composites were coded PBX-X.

2.3. Measurement of physical properties

Field emission scanning electron microscopy (FESEM) images of fractured surface of the nanocomposites were obtained using a JEOL JSM-6340F to evaluate the dispersion state of MWNTs in the polymer matrix.

The rheological properties were measured using the universal dynamic spectrometer (UDS 200; Paar Physica). Parallel plate geometry with a diameter of 25 mm was employed. The plate gap and strain level were 1 mm and 5%, respectively. The specimen was melted between the plates in a nitrogen atmosphere at 200°C. The plate gap was adjusted at the melt state and the overflowed specimen was trimmed off. The specimen was then held at the temperature for 5 min to erase residual stress. The frequency sweep test was carried out over the angular frequency range of 0.05-300 rad/s. For the measurement a disk type specimen (thickness: 1 mm, diameter: 25 mm) was prepared by compression molding.

The thermal properties were measured with a differential scanning calorimeter (DSC 2010; TA instrument). All samples were kept at 200°C for 3 minutes to eliminate the thermal history. The cooling and subsequent heating scans were conducted at 10°C/min. About 7 mg samples were used for the examination.

The electrical conductivity was measured using the 4 point probe system (Jandel contact-probe) (Grossiord *et al.*, 2007). Sheet resistance and thickness of each sample were measured ten times. Their average values were used to compute the electrical conductivity (σ ; S/cm) by the following expression,

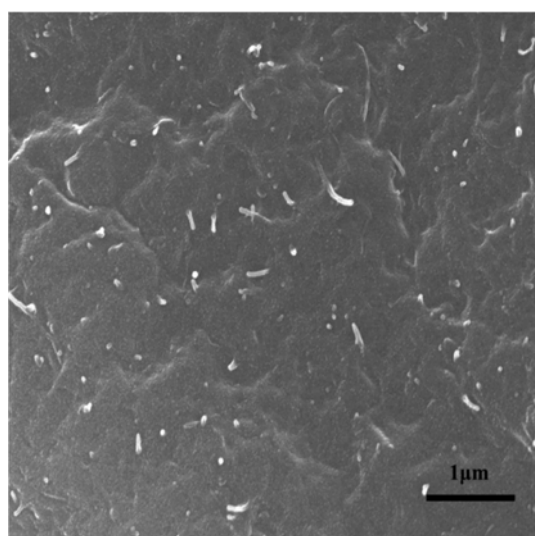
$$\sigma = 1/R_s \times d \quad (1)$$

where R_s is sheet resistance (ohm/sq) and d is sheet thickness (cm).

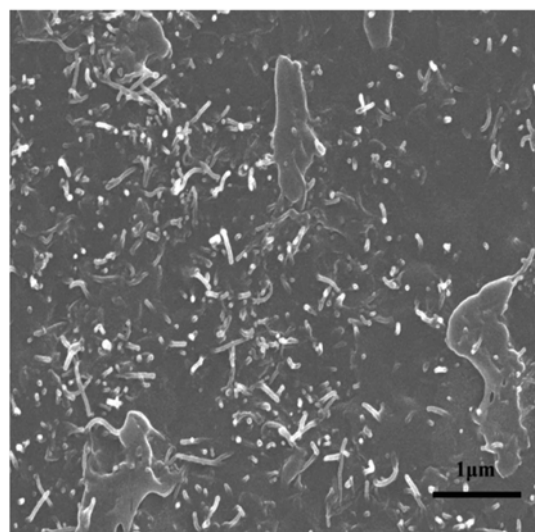
The tensile test was conducted on a universal testing machine (Instron tensile tester model 4465) at room temperature. The crosshead speed and gauge length were 10 mm/min and 25 mm, respectively. Tensile samples were prepared according to ASTM D 638 Type V. All measurements were repeated 10 times and average values were taken as data.

3. Results and Discussion

Fig. 1(a) and (b) show FESEM images of fractured surface of the nanocomposites with 2 and 5 wt% MWNTs, respectively. On the whole, MWNTs are well dispersed in the Pebax matrix without large agglomerates. This suggests that melt-compounding of powdered Pebax and MWNTs is quite effective to obtain good dispersion. The spatial inter-



(a)

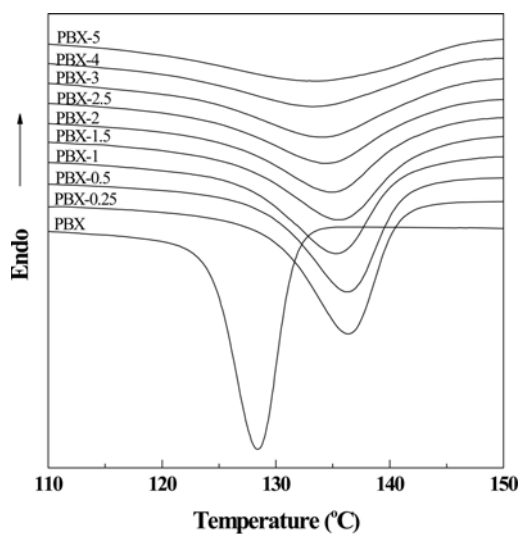


(b)

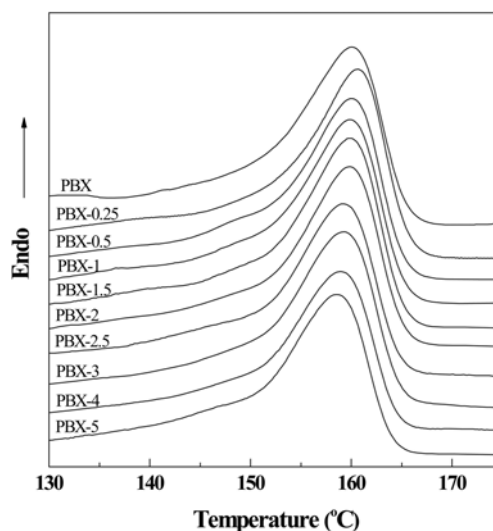
Fig. 1. FESEM images of (a) Pebax composites with 2 wt% MWNTs and (b) Pebax composites with 5 wt% MWNTs.

vals between nanotubes decrease with increasing MWNT contents, which might lead to the formation of physical associations above a critical concentration. These MWNT morphologies are expected to significantly affect the rheological, electrical, and mechanical properties of the composites.

The DSC cooling and subsequent heating scan of Pebax and Pebax/MWNTs composites are shown in Fig. 2. The introduction of 0.5 wt% MWNTs increases the crystallization temperature (T_c) by ca. 8°C, resulting from their nucleation effects. However, further addition slightly decreases T_c with increasing MWNT contents. This suggests that above some critical loading level, MWNTs in the polymer matrix retard the crystallization



(a)



(b)

Fig. 2. DSC (a) cooling and (b) subsequent heating scan thermograms of Pebax and Pebax/MWNTs composites.

by decreasing the chain mobility because of the physical hindrance effects (Chae *et al.*, 2006). Moreover, the crystallization peak is broadened by the incorporation of MWNTs, indicating that longer crystallization time is required at greater nanotube contents. However, the addition of MWNTs does not seem to influence the melting behavior of the Pebax/MWNTs composites (Manchado *et al.*, 2005; Chae *et al.*, 2006). The melting temperature (T_m) of the samples is little affected by the presence of MWNTs, giving the T_m ca. 160°C. In addition, the melting peaks show similar shape and intensity regardless of nanotube contents.

Fig. 3 presents the variation of complex viscosity (η^*) of Pebax/MWNTs composites with nanotube contents. Pebax

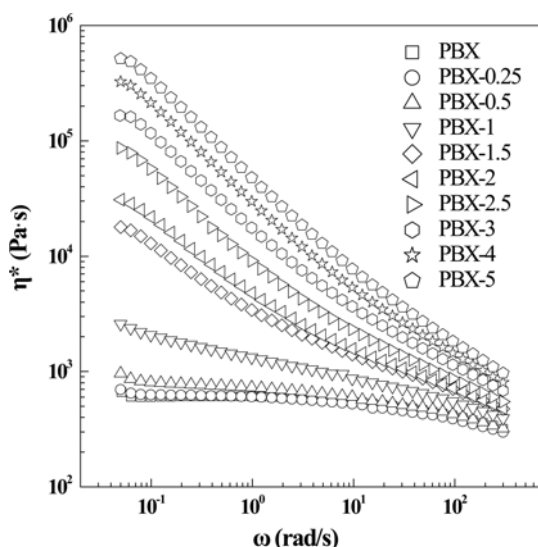


Fig. 3. Complex viscosity curve of Pebax and Pebax/MWNTs composites at 200°C.

and its nanocomposites containing up to 0.5 wt% MWNTs show little dependence of η^* on the frequency over most of the frequency range examined. Further addition causes lower Newtonian flow region to disappear, exhibiting the yield behavior. The incorporation of MWNTs increases the η^* with nanotube contents. In particular, there is an abrupt increase in η^* from 1 wt% MWNTs at the low frequency range. This can be explained that the network structure of MWNTs is formed from the critical loading level and restricts the mobility of polymer chain considerably. At the high frequency range, however, the viscosity difference with regard to nanotube contents is reduced. This indicates that the interceptive effects of the nanotubes are diminished, which might be attributed to the breakdown of the network structure under high shear force. In addition, MWNTs with large aspect ratio accelerate the orientation of polymer chains along the shear direction, giving rise to a high degree of shear thinning for highly concentrated nanocomposites.

The storage modulus (G') of Pebax and Pebax/MWNTs composites at 200°C is plotted against frequency in Fig. 4. The introduction of MWNTs increases G' notably in the low frequency range in a similar manner to viscosity. The solid-like character becomes greater with increasing nanotube contents. In particular, between 0.5 and 1 wt% a noticeable increase in G' is observed, suggesting that the development of MWNT networks begins from 1 wt%. As the frequency increases, the differences of G' between Pebax and its nanocomposites become smaller because the nanotube network in the composites is hardly sustained under high shear rate.

The yield behavior of heterogeneous system is well expressed by the following Casson plot

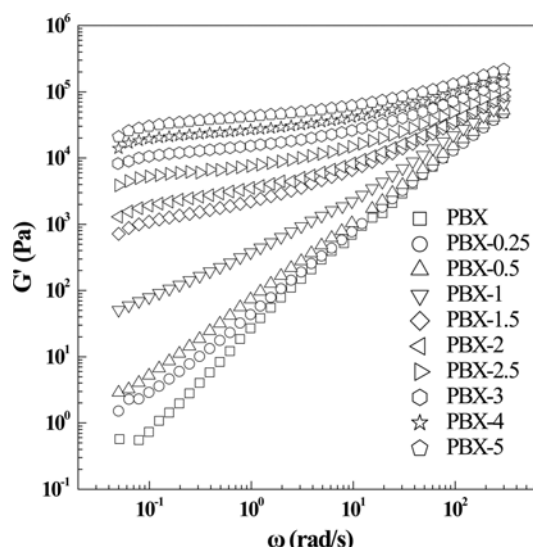


Fig. 4. Storage modulus curve of Pebax and Pebax/MWNTs composites at 200°C.

$$G''^{1/2} = G_y''^{1/2} + K\omega^{1/2} \quad (2)$$

where G_y'' stands for yield stress and K is constant. In Fig. 5, the Casson plot demonstrates a non-zero positive intercept for all the samples and their intercepts are tabulated in Table 1. Between 0.5 and 1 wt% MWNTs, abrupt increase of G_y'' more than 5 times is observed, which is in a good agreement with the aforementioned rheological data. On the other hand, the presence of MWNTs up to 0.5 wt% has little effect on the yield stress, meaning that no structural change in the polymeric systems occurs by the addition of nanotubes.

The existence of MWNT networks is expected to affect the relaxation behavior of polymeric systems. In other words, if there are some hindrances in the mobility of polymer chain, the response to the stimulation will be delayed. The relaxation time (λ) of polymers is computed by the following equation.

$$\lambda = G' / (|\eta^*| \times \omega^2) \quad (3)$$

To clarify the effects of MWNTs on the relaxation time at several frequencies, the normalized relaxation time ($\Delta\lambda$) is defined by the ratio of λ of nanocomposites to that of pure Pebax at the corresponding frequency. The variation of $\Delta\lambda$ with MWNT contents at four different frequencies is shown in Fig. 6. The $\Delta\lambda$ of the nanocomposites is proportional to MWNT contents but inversely proportional to frequency. MWNTs restrict the mobility of polymer chains by decreasing the polymeric free-volume, resulting in long relaxation time. At frequency as low as 0.5 rad/s, the $\Delta\lambda$ is considerably increased from 1 wt% content. At a high frequency of 120 rad/s, the dependence of $\Delta\lambda$ on MWNT contents is extremely low, suggesting that the restricting

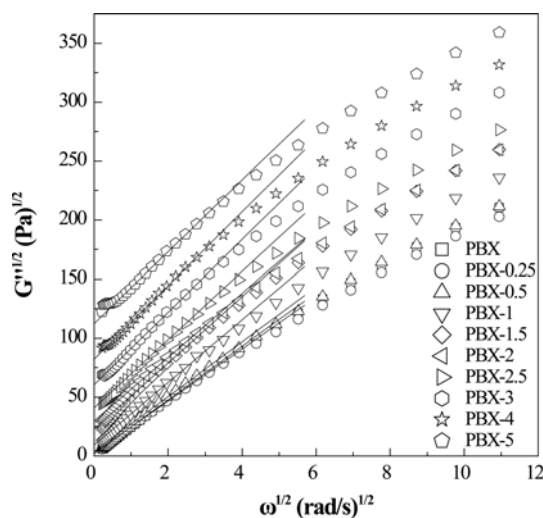


Fig. 5. Casson plot of Pebax and Pebax/MWNTs composites at 200°C.

Table 1. Yield stress (G_y'') of Casson plot and slope of Cole-Cole plot.

Sample	G_y'' of Casson plot (Pa)	Slope of Cole-Cole plot
PBX	4.54	1.43
PBX-0.25	7.56	1.40
PBX-0.5	16.84	1.34
PBX-1	88	1.15
PBX-1.5	531	0.89
PBX-2	889	0.84
PBX-2.5	1680	0.73
PBX-3	3676	0.67
PBX-4	6773	0.63
PBX-5	12663	0.63

effects on chain mobility by the MWNT networks are negligible under the high shear force.

A log-log plot of G' versus loss modulus (G''), so called Cole-Cole plot, is shown in Fig. 7, and its slopes are summarized in Table 1. It is well known fact that the homogeneous and isotropic polymer melts/solutions give the slope of 2. The introduction of MWNTs decreases the slope with MWNT contents, indicative of an increased heterogeneity. In particular, the inflection points above which the slope is increased are clearly observed from the 1 wt% loading level. The reason for this phenomenon is that the heterogeneity in the polymeric systems is changed with frequency. The reduced heterogeneity of the composites is attributed to the breakdown of MWNT networks over a critical shear force.

Fig. 8 shows the electrical conductivity of Pebax and Pebax/MWNTs composites at room temperature. The electrical conductivity of 2.12×10^{-6} S/cm is observed at 2 wt% MWNTs, above which it increases with MWNT contents.

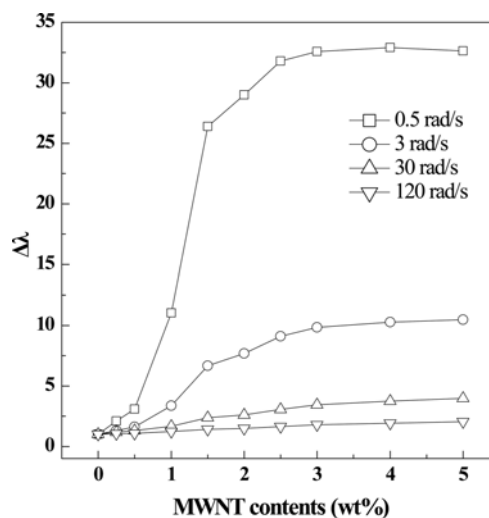


Fig. 6. Variation of $\Delta\lambda$ with MWNT contents at four different frequencies.

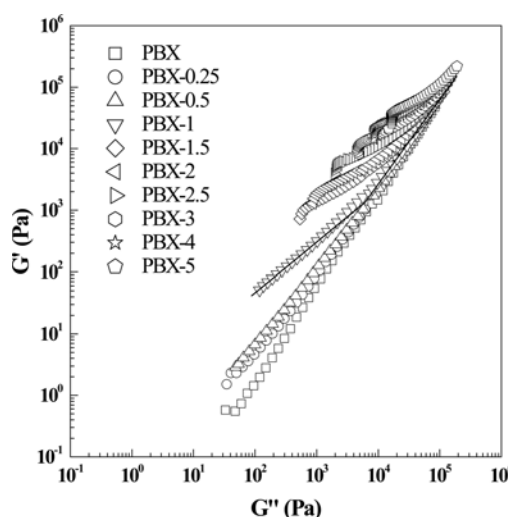


Fig. 7. Logarithmic plot of storage modulus versus loss modulus of Pebax and Pebax/MWNTs composites.

This indicates that at least 2 wt% loading of MWNTs is necessary to construct electrical path via the MWNT network in the polymer matrix. It is worth noting that the electrical percolation threshold is greater than rheological one where notable changes in the rheological properties occur. The electrical conductivity of nanocomposites is rapidly increased from 3 wt% with MWNT contents. The absence of the level-off value within nanotube concentrations examined implies that the improvement of electrical conductivity can still be achieved by further addition of MWNTs.

Fig. 9 shows the variation of stress-strain (SS) curve of Pebax and Pebax/MWNTs composites with nanotube contents and their tensile properties are summarized in Table 2. As MWNT contents increase, the yield behavior of the

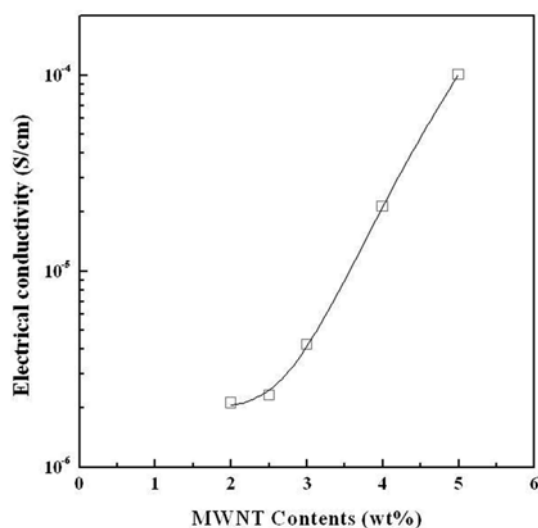


Fig. 8. Electrical conductivity of Pebax and Pebax/MWNTs composites at room temperature.

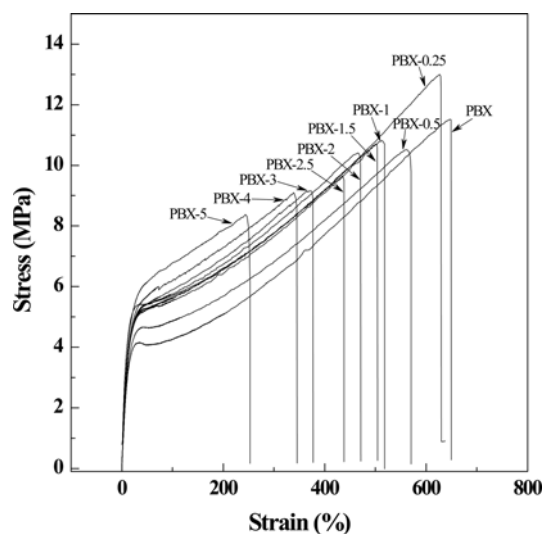


Fig. 9. Stress-strain curve of Pebax and Pebax/MWNTs composites at room temperature.

Table 2. Tensile properties of Pebax and Pebax/MWNTs composites.

Sample	Tensile properties			
	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation to break (%)	Toughness (MPa)
PBX	11.5	32.8	648.7	46.2
PBX-0.25	13	38.3	627.4	52.6
PBX-0.5	10.5	38.8	560.6	39.3
PBX-1	10.8	39	511.5	38
PBX-1.5	10.7	39.3	500.2	36.7
PBX-2	10.4	39.4	465.5	34.3
PBX-2.5	9.7	39.6	434.8	30.2
PBX-3	9.2	40.2	370.9	25.6
PBX-4	9.1	41.6	338.6	23.8
PBX-5	8.4	43	243.5	17.1

samples is changed. Pebax and its composites containing up to 0.5 wt% MWNTs show a yield point at which slope falls to zero and then upturns to a high stress. However, further addition gives a yield point where the slope of the curve is just decreased in comparison with the initial slope. This can be explained that the network structure of MWNTs over a critical concentration plays a role in preventing the molecular slip of Pebax under stress. The tensile strength slightly increases only at 0.25 wt% loading level, and further addition decreases it with MWNT contents. A small amount of MWNTs retard the disentanglement of polymer chain under extension. Thus, much energy is necessary to the fracture of the specimens. As MWNT contents increase, however, the stress concentrated polymer parts increase, causing the defects in the matrix. Thus, the specimen with higher filler contents is fractured under less stress (Chae and Kim, 2005). However, tensile modulus increases with nanotube

contents, indicating that the presence of MWNTs increases the chain rigidity. The incorporation of MWNTs decreases the elongation to break with MWNT contents. This reduction of the ductility suggests that the polymer chains surrounded by MWNTs are immobilized, resulting in limited deformation. The low elongation to break also leads to low toughness calculated from the area under the SS curve.

4. Conclusions

The introduction of MWNTs to Pebax matrix increased both crystallization temperature and crystallization time, indicating that not only did the nanotubes act as a nucleating agent but they retarded the mobility of the polymer chain. However, it had little effect on melting temperature regardless of MWNT contents. In rheological properties, the first sudden increase of complex viscosity and storage modulus

in low frequency range were observed at 1 wt% MWNTs, which might be regarded as a rheological percolation. At the nanotube content and above, the MWNT network began to develop in Pebax matrix. However, in high frequency range, the increasing extents of the viscosity with nanotube contents were reduced, resulting from a notable shear thinning behavior. The electrical conductivities were observed from 2 wt% MWNTs, which might be another evidence of the existence of MWNT network. The tensile strength and elongation to break were decreased with MWNT contents, except for 0.25 wt% filled nanocomposites which presented a little increased tensile strength. However, the presence of MWNTs increased the tensile modulus with nanotube contents. Therefore, the appropriate amount of MWNTs as filler should be decided carefully in service purpose.

Acknowledgements

This work was supported by the Kyungpook National University Research Grant, 2009.

References

- Ajayan, P.M., O. Stephan, C. Colliex, and D. Trauth, 1994, Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite, *Science* **265**, 1212-1214.
- Bondar, V.I., B.D. Freeman, and I. Pinnau, 1999, Gas sorption and characterization of poly(ether-b-amide) segmented block copolymer, *J. Polym. Sci. Part B: Polym. Phys.* **37**, 2463-2475.
- Chae, D.W. and B.C. Kim, 2005, Physical properties of isotactic poly(propylene)/silver nanocomposites: Dynamic crystallization behavior and resultant morphology, *Macromol. Mater. Eng.* **290**, 1149-1156.
- Chae, D.W., J.H. Lim, J.S. Seo, and B.C. Kim, 2012, Variation of physical properties of nylon-66/clay nanocomposites with preparation conditions, *Korea-Aust. Rheol. J.* **24**, 45-52.
- Chae, D.W., K.J. Kim, and B.C. Kim, 2006, Effects of silicalite-1 nanoparticles on rheological and physical properties of HDPE, *Polymer* **47**, 3609-3615.
- Chae, D.W., K.H. Lee, and B.C. Kim, 2006, Rheological properties of ferrite nanocomposites based on nylon-66, *J. Polym. Sci. Part B: Polym. Phys.* **44**, 371-377.
- Deleens, G., 1981, A new generation of thermoplastic elastomers the polyether block amide (PEBA), Presented at 39th Ann. Tech. Conf. of SPE, Boston, May 4-7.
- Flesher, J.R., 1986, Pebax polyether block amide – a new family of engineering thermoplastic elastomers, Abstracts of Papers of the American Chemical Society **191**, 64.
- Grossiord, N., H.E. Miltner, J. Loos, J. Meuldijk, B.V. Mele, and C.E. Koning, 2007, On the crucial role of wetting in the preparation of conductive polystyrene-carbon nanotube composites, *Chem. Mater.* **19**, 3787-3792.
- Hwang, T.Y., S.M. Lee, Y.J. Ahn, and J.W. Lee, 2008, Development of polypropylene-clay nanocomposite with supercritical CO₂ assisted twin screw extrusion, *Korea-Aust. Rheol. J.* **20**, 235-243.
- Hyun, K., H.T. Lim, and K.H. Ahn, 2012, Nonlinear response of polypropylene (PP)/Clay nanocomposites under dynamic oscillatory shear flow, *Korea-Aust. Rheol. J.* **24**, 113-120.
- Iijima, S., 1991, Helical microtubules of graphitic carbon, *Nature* **354**, 56-58.
- Iyer, S., A. Detwiler, S. Patel, and D.A. Schiraldi, 2006, Control of coefficient of thermal expansion in elastomers using boron nitride, *J. Appl. Polym. Sci.* **102**, 5153-5161.
- Kang, M.H. and S.J. Lee, 2012, Rheological and electrical properties of polystyrene/multi-walled carbon nanotube nanocomposites prepared by latex technology, *Korea-Aust. Rheol. J.* **24**, 97-103.
- Kim, B.C. and S.J. Lee, 2008, Silicate dispersion and rheological properties of high impact polystyrene/organoclay nanocomposites via in situ polymerization, *Korea-Aust. Rheol. J.* **20**, 227-233.
- Kim, J.H. and Y.M. Lee, 2001, Gas permeation properties of poly(amide-6-b-ethylene oxide)-silica hybrid membranes, *J. Membrane. Sci.* **193**, 209-225.
- Liu, L., Z. Qi, and X. Zhu, 1999, Studies on nylon 6/clay nanocomposites by melt-intercalation process, *J. Appl. Polym. Sci.* **71**, 1133-1138.
- Lyons, J.G., J.E. Kennedy, S. Lordan, L.M. Geever, and C.L. Higginbotham, 2010, Characterisation of the effects of a titanium micro particle filler on a polyether-block-amide host matrix, *J. Mater. Sci.* **45**, 3204-3214.
- Manchado, M.A.L., L. Valentini, J. Biagiotti, and J.M. Kenny, Thermal and mechanical properties of single-walled carbon nanotubes-polypropylene composites prepared by melt processing, *Carbon* **43**, 1499-1505.
- Markarian, J., 2008, Thermoplastic elastomer compounds continue upward trend, *Plast. Addit. Compound.* **10**, 38-40, 42-43.
- Moniruzzaman, M. and K.I. Winey, 2006, Polymer nanocomposites containing carbon nanotubes, *Macromolecules* **39**, 5194-5205.
- Murali, R.S., S. Sridhar, T. Sankarshana, and Y.V.L. Ravikumar, 2010, Gas permeation behavior of Pebax-1657 nanocomposite membrane incorporated with multiwalled carbon nanotubes, *Ind. Eng. Chem. Res.* **49**, 6530-6538.
- Oh, J.S., K.H. Ahn, and J.S. Hong, 2010, Dispersion of entangled carbon nanotube by melt extrusion, *Korea-Aust. Rheol. J.* **22**, 89-94.
- Rader, C.P. and R.F. Stockel, 1995, Polymer recycling: an overview, *Plastics, Rubber, and Paper Recycling*, ACS Symposium Series **609**, 2-10.
- Spontak, R.J. and N.P. Patel, 2000, Thermoplastic elastomers: fundamentals and applications, *Curr Opin. Colloid. In.* **5**, 333-340.
- Woo, D.K., B.C. Kim, and S.J. Lee, 2009, Preparation and rheological behavior of polystyrene/multi-walled carbon nanotube composites by latex technology, *Korea-Aust. Rheol. J.* **21**, 185-191.
- Yang, I.K. and P.H. Tsai, 2006, Intercalation and viscoelasticity of poly(ether-block-amide) copolymer/montmorillonite nanocomposites: Effect of surfactant, *Polymer* **47**, 5131-5140.
- Yen, H.W., Z.H. Chen, and I.K. Yang, 2012, Use of the composite membrane of poly(ether-block-amide) and carbon nanotubes (CNTs) in a pervaporation system incorporated with fermentation for butanol production by *Clostridium acetobutylicum*, *Bioresource. Technol.* **109**, 105-109.