

Effect of the Processing Parameters on the Surface Resistivity of Acrylonitrile–Butadiene Rubber/Multiwalled Carbon Nanotube Nanocomposites

Byung-Mook Cho, Gue-Hyun Kim

Division of Applied Bio Engineering, Dongseo University, Busan 617-716, South Korea

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ABSTRACT: In this study, acrylonitrile–butadiene rubber (NBR) was melt-mixed with multiwalled carbon nanotubes (MWCNTs). Because the electrical conductivity and mechanical properties of composites are strongly influenced by the filler's state of dispersion and the extent of filler breakage during processing, the processing conditions are very important parameters. The effects of the mixing time, rotor speed, cooling rate, and sulfur concentration on the surface resistivity were investigated. Increasing the rotor speed from 20 to 60 rpm at mixing times of 15 and 30 min led to an increase in the surface resistivity from around 10^4 to 10^{11} Ω /square. However, at a mixing

time of 7 min, the surface resistivity slightly decreased with increasing rotor speed. When slow cooling was applied, a surface resistivity of 10^4 Ω /square was obtained at around 2-phr MWCNTs. However, when the fast cooling was applied, a surface resistivity of 10^6 Ω /square was obtained at 5-phr MWCNTs. The tensile strength and tensile modulus at 300% elongation were improved with the addition of MWCNTs into NBR. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 555–561, 2010

Key words: compounding; crosslinking; dispersions; nanocomposites; rubber

INTRODUCTION

In recent years, the addition of conductive fillers into polymers has been commonly used for electrostatic dissipative purposes. Carbon black is the most widely used filler, but its typical loading is 15–20 wt %; this results in particulate sloughing and, thus, sacrifices other desirable properties of the host polymer, such as light weight and toughness. Recently, carbon nanotube (CNT)-based polymer nanocomposites have attracted considerable attention from both fundamental research and application points of view because of the unique combination of mechanical, electrical, and thermal properties of CNTs. The excellent conductivity and very high aspect ratio of CNTs provide polymers with electrical conductivity at a low CNT content. Therefore, CNT-based polymer nanocomposites can be manufactured into electrostatic dissipative parts with smoother surfaces, superior aesthetics, and better mechanical properties.

Although there are many methods to disperse CNTs into polymers, melt compounding is the most compatible with current industrial practices. This

method is also environmentally safe because it is free of solvents and contaminants, which are involved in the solution blending and *in situ* polymerization methods. Because of this aspect, many researchers have recently used the melt-compounding method.^{1–9} Because multiwalled carbon nanotubes (MWCNTs) are competitive in cost, most melt-compounding methods use MWCNTs rather than single-walled CNTs. Although the melt-compounding method has many advantages, the uniform dispersion of CNTs in the polymer matrix is still the most challenging task. Therefore, without modification of the surface of the CNTs, percolation has occurred above 3 wt % CNTs in most melt-compounding studies. However, unmodified CNTs are preferred for industrial applications. Until now, a 1 wt % percolation threshold has been achieved only for some special cases with the melt-compounding method. The percolation threshold of polymer blend/CNT nanocomposites was about 0.25–2 wt % CNTs with the concept of double percolation through the formation of a cocontinuous morphology.^{10,11} Also, some researchers, using a masterbatch provided by Hyperion, found a percolation threshold of about 1 wt % CNTs.^{4–6} However, in those studies, the masterbatch was prepared with a specific kneader (a Buss kneader), and melt mixing was conducted in a microcompounder (capacity = 4.5 cm³). Moreover, the resistivity was measured on thin films (~ 350 μ m).^{4–6} When an epoxy prepolymer

Correspondence to: G.-H. Kim (guehyun@gdsu.dongseo.ac.kr).

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(a viscous liquid) was mixed with CNTs with special rolls, the percolation threshold was also less than 1 wt %.¹² Mechanical tests of poly(styrene-*b*-butadiene-*co*-butylene-*b*-styrene)/MWCNT nanocomposites showed that the tensile modulus, tensile strength, and elasticity of nanocomposites prepared at a high shear rate (2000 rpm) were much higher than those of nanocomposites prepared at a low shear rate.¹³

Although a lot of studies have been conducted on polymer/CNT nanocomposites, there have been few studies on rubber/CNT nanocomposites. Because the electrical conductivity and mechanical properties of composites are strongly influenced by the filler's state of dispersion and the extent of filler breakage during processing, the processing conditions are very important parameters. It has been reported that the processing/molding parameters, such as melt temperature and injection velocity, significantly affect the dispersion of CNTs and the electrical resistivity of polymer/CNT nanocomposites.^{4,14–18} In addition, vulcanization may have a considerable effect on the electrical properties of rubber/CNT nanocomposites. In this study, relatively large amounts of acrylonitrile-butadiene rubber (NBR; 120 g) were melt-mixed with MWCNTs, and the effects of mixing time, rotor speed, cooling rate, and sulfur concentration on the surface resistivity were investigated. Also, the tensile properties of the NBR/MWCNT nanocomposites were investigated.

EXPERIMENTAL

Materials and nanocomposite preparation

NBR (acrylonitrile content = 40%) was provided by Kumho Petrochemical (Seoul, Korea). The MWCNTs were synthesized by thermal chemical vapor deposition. According to the provider, the typical tube diameter was in the range 10–50 nm with tube lengths of 1–25 μm . The MWCNTs (purity = 95%) were used as received. NBR and the MWCNTs were melt-mixed in a bench kneader PBV-03 (Irie Shokai, Ltd., Japan) for various times and at various rotor speeds. The mixing temperature was fixed at 60°C. Then, the obtained NBR/MWCNT nanocomposites were mixed with sulfur in a two-roll mill at 45°C. After mixing in the two-roll mill, the nanocomposites were compression-molded at 165°C.

Testing

The surface resistivity was measured on the compression-molded samples (sample dimensions = 110 \times 180 \times 18 mm³) with a MAXCON MAX-812 meter. A universal testing machine (model UL25, Hounsfield Co., Kobe, Japan) was used to determine the tensile properties of the nanocomposites at room

temperature. The crosshead speed was 10 mm/min. All measurements were performed for five replicates of dog-bone-shaped specimens and averaged to get the final result. To investigate the dispersion and length of the MWCNTs in the NBR/MWCNT nanocomposites, transmission electron microscopy (TEM) images were taken from cryomicrotomed ultrathin sections with an energy-filtered transmission electron microscope (EM 912 Omega, Zeiss).

RESULTS AND DISCUSSION

For viable electrostatic dissipative applications, the surface resistivity of the polymer/CNT nanocomposites should be in the range 10^5 – 10^{12} Ω /square (preferably, 10^8 Ω /square). The surface resistivity range in our experimental setup was limited to values below 10^{12} Ω /square. The NBR and MWCNTs were melt-mixed in a kneader for various mixing times and at various rotor speeds, and the obtained NBR/MWCNT nanocomposites were mixed with sulfur (2 phr on the basis of the amount of NBR) in a two-roll mill for a fixed time (6 min). The compression-molded samples were naturally cooled to room temperature. Figure 1 shows the effect of the mixing time and rotor speed in the kneader on the surface resistivity of the NBR/MWCNT nanocomposites with 2-phr MWCNT loading. At a mixing time of 7 min, the surface resistivity slightly decreased with increasing rotor speed. However, at mixing times of 15 and 30 min, increasing the rotor speed from 20 to 60 rpm led to an increase in the surface resistivity from around 10^4 to 10^{11} Ω /square. This was a significant difference and a very important result. It has been reported that screw speed and mixing time have a significant influence on the electrical resistivity of polymer/CNT nanocomposites.^{4,14–16}

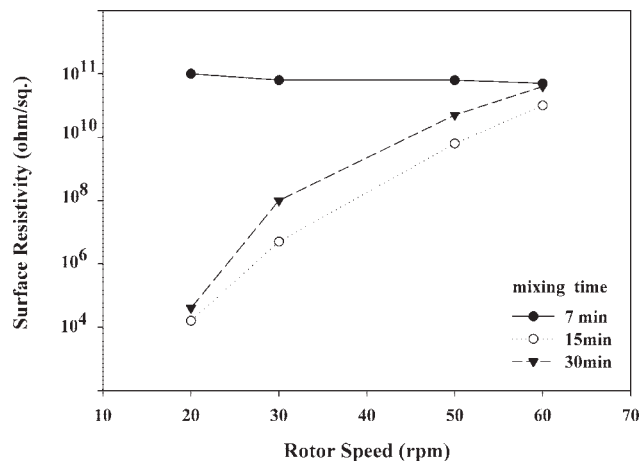


Figure 1 Effects of the mixing time and rotor speed in the kneader on the surface resistivity of NBR/MWCNT nanocomposites with 2 phr MWCNTs.

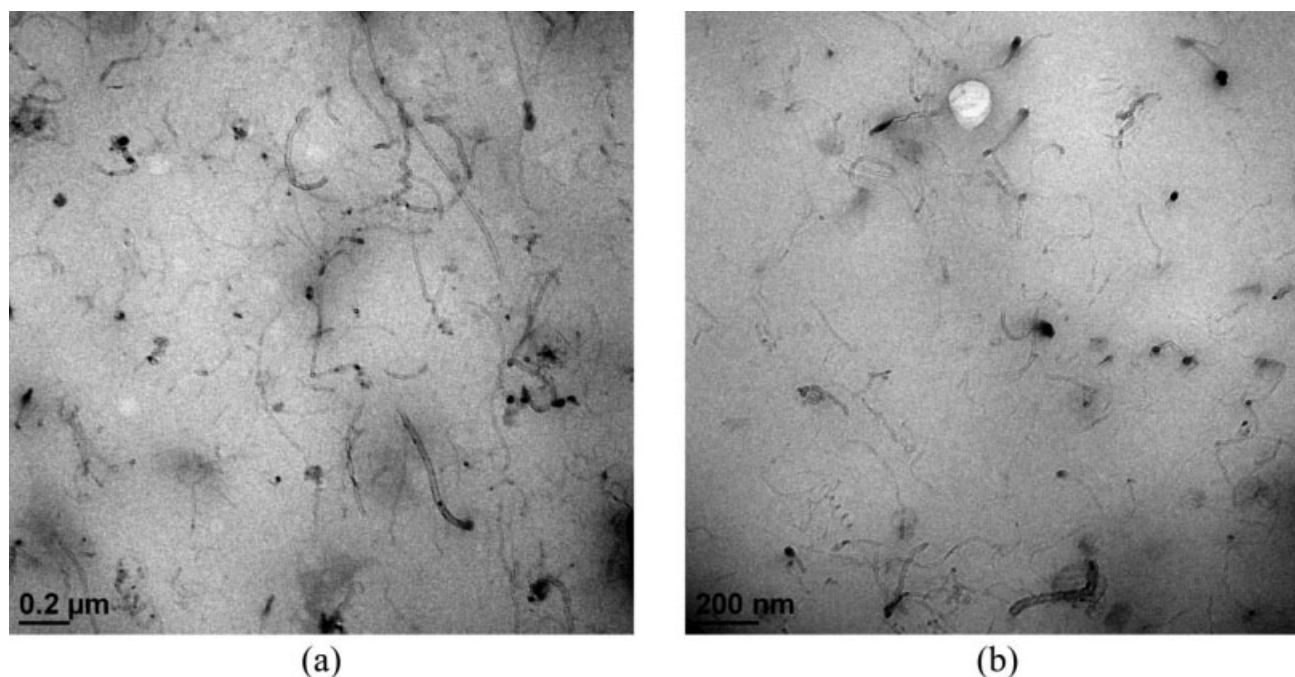


Figure 2 TEM micrographs of MWCNTs in the NBR matrix: (a) the NBR/MWCNT nanocomposite prepared at 20 rpm for 15 min and (b) the NBR/MWCNT nanocomposite prepared at 60 rpm for 15 min.

In the MWCNT/polymer nanocomposites, increasing the rotor speed led to an improvement in the dispersion of the MWCNTs in the polymer matrix and a decrease in the MWCNT length. The improvement in the dispersion of the MWCNTs resulted in a decrease in the surface resistivity, but a decrease in the MWCNT length led to an increase in the inter-CNT gap, which resulted in an increase in the surface resistivity. Therefore, increasing the rotor speed at fixed mixing time produced opposing effects on the surface resistivity.

With increasing rotor speed for a short mixing time (7 min), the effect of the improved dispersion of the MWCNTs on the surface resistivity may have overwhelmed the effect of the decreased MWCNT length on the surface resistivity. As a result, a slightly lower surface resistivity was obtained with increasing rotor speed. However, with increasing rotor speed for long mixing times (15 and 30 min), the effect of the decreased MWCNT length on the surface resistivity may have overwhelmed the effect of the improved dispersion of the MWCNTs. As a result, a higher surface resistivity was obtained with increasing rotor speed.

Figure 2 shows the TEM micrographs of the MWCNTs in the NBR matrix. In the TEM images, one can observe a better dispersion of the MWCNTs [Fig. 2(b), cf. Fig. 2(a)]. This may have been due to the increasing rotor speed. However, with increasing rotor speed, although a better dispersion was achieved, it was done so at the expense of decreased length, as shown in Figure 2(b). This led to an

increase in the surface resistivity at a mixing time of 15 min.

According to our previous research, the effect of mixing time and rotor speed on the surface resistivity of ethylene vinyl acetate (EVA)/MWCNT nanocomposites was similar.¹⁹ For the EVA/MWCNT nanocomposites, increasing the rotor speed from 60 to 150 rpm at a mixing time of 30 min led to an increase in the surface resistivity from around 10^5 to 10^6 Ω /square. However, the NBR/MWCNT nanocomposites displayed a faster increase in the surface resistivity with increasing rotor speed for a mixing time of 30 min. This might have been due to the higher viscosity of NBR than EVA, which led to a higher shear stress on the MWCNTs during mixing.

To investigate the effect of the mixing time in the two-roll mill on the surface resistivity, the NBR and MWCNTs were melt-mixed in a kneader for a fixed mixing time (15 min), and the obtained NBR/MWCNT nanocomposites were mixed with sulfur (2 phr) in a two-roll mill for various mixing times. Figure 3 shows the effect of mixing time in two-roll mill on the surface resistivity. For the NBR/MWCNT nanocomposites prepared in a kneader at 20 rpm, the surface resistivity was the highest (10^{11} Ω /square) without mixing in the two-roll mill (mixing time = 0 min). This may indicate that the dispersion of the MWCNTs in the NBR matrix was poor in the NBR/MWCNT nanocomposites prepared in a kneader at 20 rpm before two-roll mill mixing. With increasing mixing time in the two-roll mill from 0 to 6 min, the surface resistivity decreased from 10^{11} to

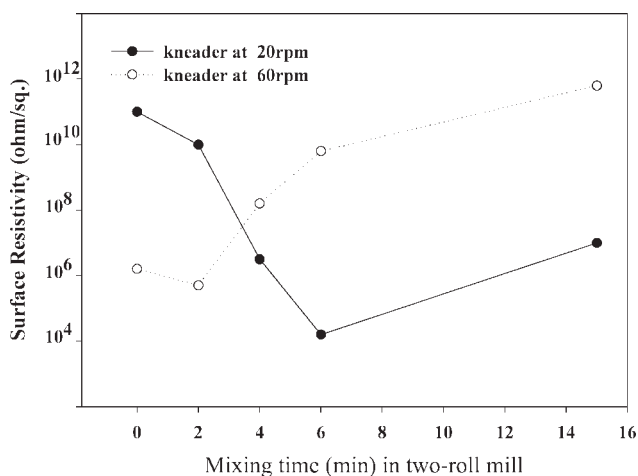


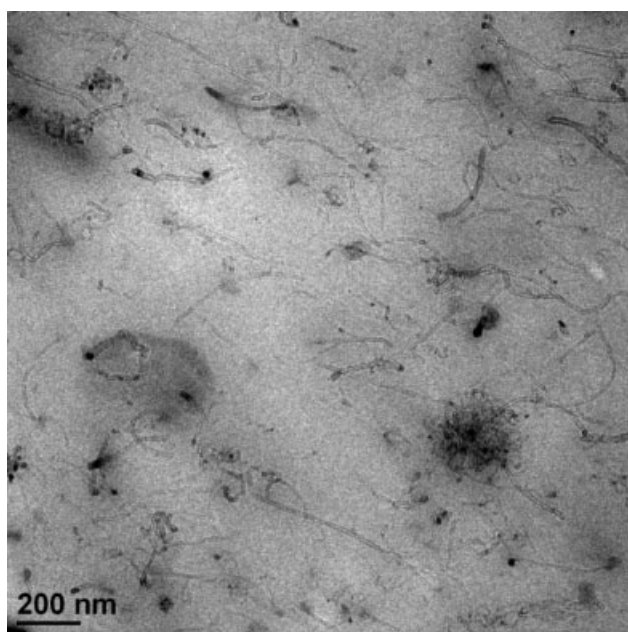
Figure 3 Effect of the mixing time in the two-roll mill on the surface resistivity of the NBR/MWCNT nanocomposites with 2 phr MWCNTs.

10^4 Ω /square. However, a further increase in the mixing time in the two-roll mill led to an increase in the surface resistivity. Therefore, up to 6 min, with increasing mixing time in two-roll mill, the effect of the improved dispersion of MWCNTs on the surface resistivity may have overwhelmed the effect of the decreased MWCNT length. However, further increases in the mixing time led to a decreased nanotube length, which manifested as a higher surface resistivity. For the NBR/MWCNT nanocomposite prepared in a kneader at 60 rpm, the surface re-

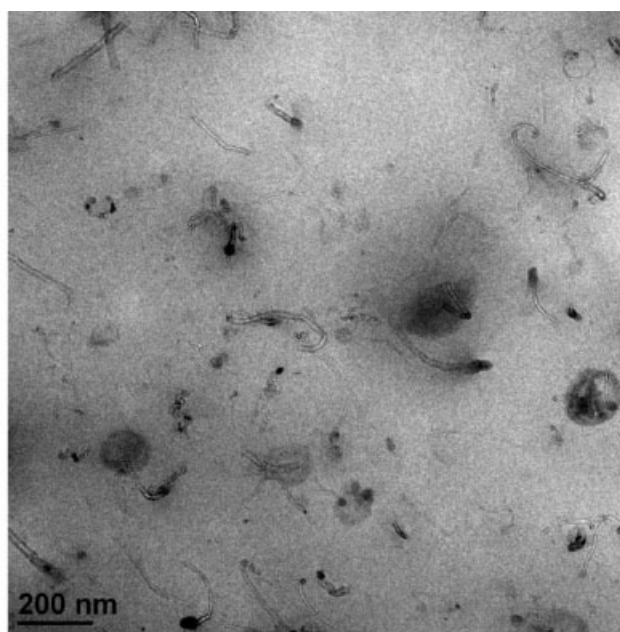
sistivity was around 10^6 Ω /square at mixing times of 0 and 2 min in the two-roll mill. This may indicate that the dispersion of the MWCNTs in the NBR matrix was good in the NBR/MWCNT nanocomposites prepared in a kneader at 60 rpm before two-roll mill mixing. Further increases in the mixing time in the two-roll mill led to significant increases in the surface resistivity.

Figure 4 shows the TEM micrographs of the MWCNTs in the NBR matrix. In the TEM images, one can observe small clusters of MWCNTs [Fig. 4(a), cf. Fig. 4(b)]. However, with further increasing mixing time, a uniform dispersion was achieved but at the expense of decreased length, as shown in Figure 4(b). This led to an increase in the surface resistivity in the NBR/MWCNT nanocomposites prepared in a kneader at 60 rpm.

To investigate the effect of gap distance between the rolls on the surface resistivity, the NBR and MWCNTs were melt-mixed in a kneader for a fixed mixing time (15 min), and the obtained NBR/MWCNT nanocomposites were mixed with sulfur (2 phr) in a two-roll mill with various gap distances for a fixed time (6 min). For the NBR/MWCNT nanocomposites prepared in a kneader at 20 rpm, the surface resistivity decreased with decreasing gap distance (Fig. 5). As shown in Figure 3, the surface resistivity was 10^{11} Ω /square without two-roll mill mixing (0 min). Because the dispersion of MWCNTs in the NBR/MWCNT nanocomposites prepared at 20 rpm was poor before two-roll mill mixing, with



(a)



(b)

Figure 4 TEM micrographs of MWCNTs in the NBR/MWCNT nanocomposites: (a) a mixing time of 2 min in the two-roll mill and a rotor speed at the kneader of 60 rpm and (b) a mixing time of 14 min in the two-roll mill and a rotor speed at the kneader of 60 rpm.

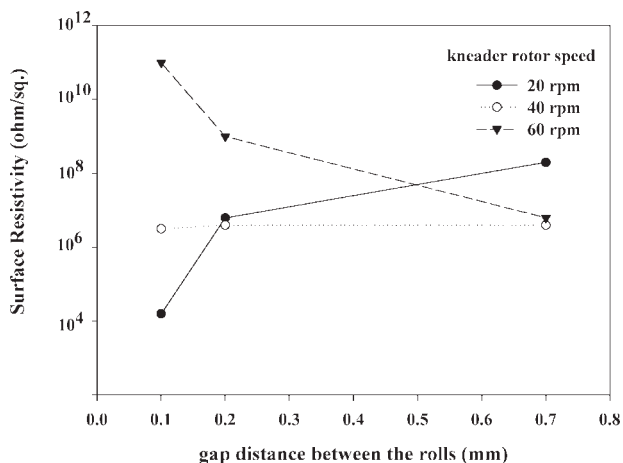


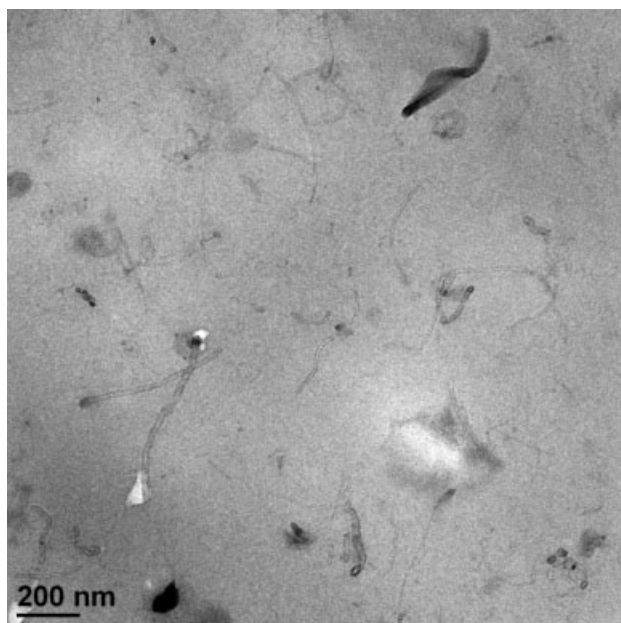
Figure 5 Effect of the gap distance between the rolls on the surface resistivity of the NBR/MWCNT nanocomposites with 2 phr MWCNTs.

high shear force by two-roll mill mixing, the effect of the improved dispersion of the MWCNTs on the surface resistivity may have overwhelmed the effect of the decreased MWCNT length. Therefore, a higher shear force with decreasing gap distance led to a lower surface resistivity. For the NBR/MWCNT nanocomposites prepared in a kneader at 60 rpm, the surface resistivity decreased with increasing gap distance. As observed in Figure 3, the surface resistivity was 10⁶ Ω/square without two-roll mill mixing (0 min). Because the dispersion of the MWCNTs in the NBR/MWCNT nanocomposites prepared at 60

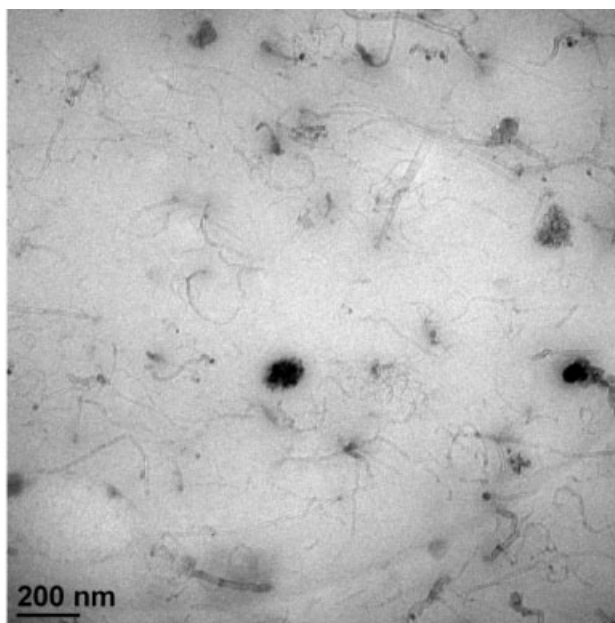
rpm was good before two-roll mill mixing, with high shear force by two-roll mill mixing, the effect of the decreased MWCNT length on the surface resistivity may have overwhelmed the effect of the improved dispersion of the MWCNTs. Therefore, the higher shear force with decreasing gap distance led to the higher surface resistivity.

Figure 6 shows TEM micrographs of the MWCNTs in the NBR matrix. In the TEM images, one can observe a better dispersion of MWCNTs [Fig. 6(a), cf. Fig. 6(b)]. This may have been due to the decreasing gap distance. However, with decreasing gap distance, a better dispersion was achieved but at the expense of decreased length, as shown in Figure 6(a). Decreasing the gap distance led to a decrease in the average length of the MWCNTs. This led to an increase in the surface resistivity in the NBR/MWCNT nanocomposites prepared in a kneader at 60 rpm.

We also investigated the effect of fast and slow cooling on the surface resistivity of the NBR/MWCNT nanocomposites. For fast cooling, the compression-molded samples were immediately moved to a cold molder under minimal pressure. For slow cooling, the compression-molded samples were naturally cooled to room temperature. For this experiment, the NBR and MWCNTs were melt-mixed in a kneader at 20 rpm for 15 min, and the obtained NBR/MWCNT nanocomposites were mixed with sulfur (2 phr) in a two-roll mill for 6 min. The surface resistivity of the NBR/MWCNT nanocomposites with



(a)



(b)

Figure 6 TEM micrographs of MWCNTs in the NBR/MWCNT nanocomposite: (a) a gap distance between the rolls of 0.1 mm and a rotor speed at the kneader of 60 rpm and (b) a gap distance between the rolls of 0.7 mm and a rotor speed at the kneader of 60 rpm.

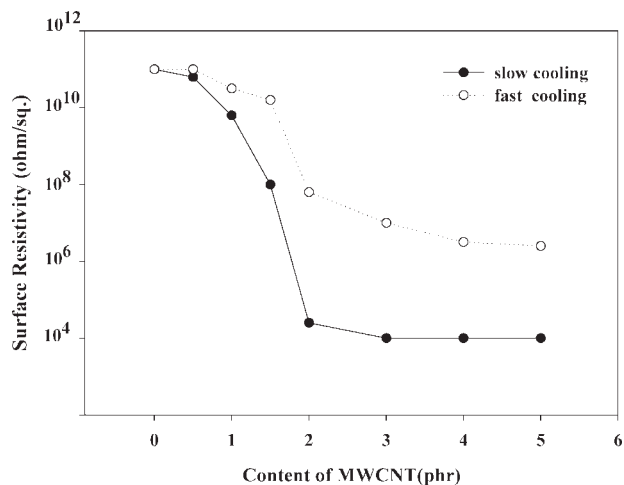


Figure 7 Surface resistivity of the NBR/MWCNT nanocomposites with different MWCNT contents.

different MWCNT contents is shown in Figure 7 for slow cooling and fast cooling. When slow cooling was applied, a surface resistivity of $10^4 \Omega/\text{square}$ was obtained at around 2-phr MWCNTs. However, when fast cooling was applied, a surface resistivity of $10^6 \Omega/\text{square}$ was obtained at around 5-phr MWCNTs. This was a significant difference, and to the best of our knowledge, this is the first report that recognizes the importance of different cooling rates on the surface resistivity of rubber/MWCNT nanocomposites. It is well known that the degree of volume shrinkage depends on the cooling rate. A slow cooling rate leads to larger volume shrinkages. Therefore, larger volume shrinkages by slow cooling may lead to smaller distances between neighboring MWCNTs in the NBR matrices. It was reported that the orientation of nanotubes in the plate direction or the formation of a frozen-oriented skin layer (as shown for the injection-

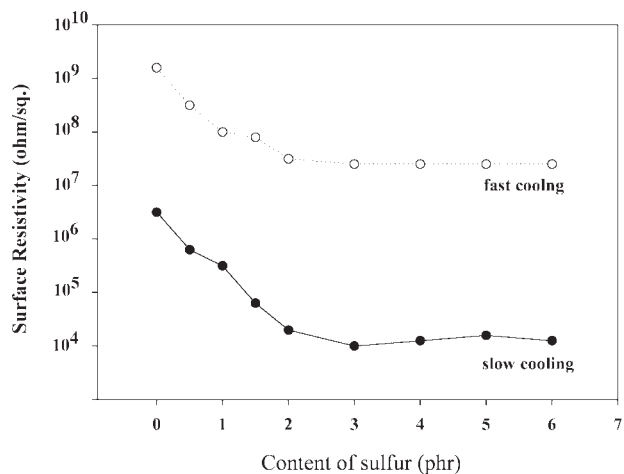


Figure 8 Effect of the concentration of sulfur on the surface resistivity of the NBR/MWCNT nanocomposites with 2 phr MWCNTs.

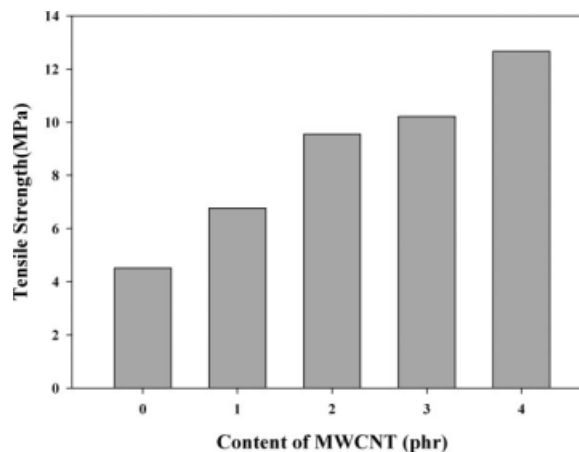


Figure 9 Tensile strength of the NBR/MWCNT nanocomposites.

molded samples¹⁷) are not dominant effects in compression molding.¹⁶

Figure 8 shows the effect of the concentration of sulfur on surface resistivity. With increasing sulfur concentration, the surface resistivity decreased. During crosslinking, the polymer chains were linked by covalent bonds, and a three-dimensional network was formed. It is well known that an increase in the sulfur concentration leads to an increase in the crosslinking density. Increasing crosslinking density may have decreased the free volume of the NBR matrix, which may have caused a decreased inter-CNT gap in the MWCNTs.

For the measurement of tensile properties, the NBR and MWCNTs were melt-mixed in a kneader for a fixed mixing time (15 min) and rotor speed (20 rpm), and the obtained NBR/MWCNT nanocomposites were mixed with sulfur (2 phr) in a two-roll mill for a fixed time (6 min). With increasing content of MWCNTs, the tensile strength (Fig. 9) and tensile modulus at 300% elongation (Fig. 10) of the NBR/

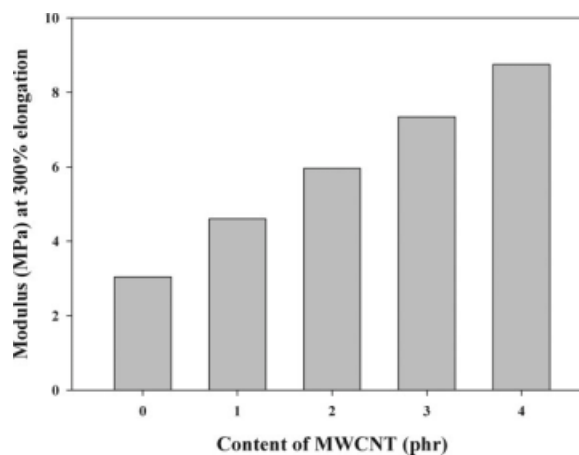


Figure 10 Tensile modulus at 300% elongation of the NBR/MWCNT nanocomposites.

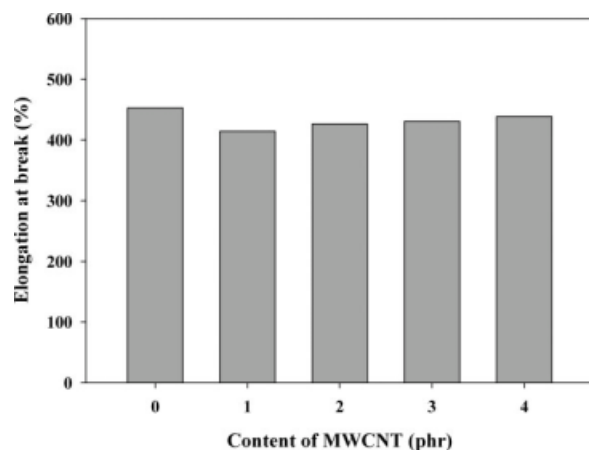


Figure 11 Elongation at break of the NBR/MWCNT nanocomposites.

CNT nanocomposites increased. The tensile strength and 300% modulus of the NBR/MWCNT nanocomposites with a 2-phr MWCNT loading were around two times higher than those of NBR. The elongation at break (Fig. 11) of the NBR/MWCNT nanocomposites was slightly lower than that of NBR.

CONCLUSIONS

A strong dependence of the surface resistivity on the processing parameters was observed. Increasing the rotor speed and mixing time resulted in an improvement in the dispersion of the MWCNTs in NBR and a decrease in the MWCNT length. These results produced opposing effects on the surface resistivity. An improvement in the dispersion of MWCNTs led to a decrease in the surface resistivity, but a decrease in the MWCNT length led to an increase in the surface resistivity. With increasing rotor speed at long mixing times (15 and 30 min), the effect of the decreased MWCNT length on the surface resistivity may have overwhelmed the effect of improved dispersion of the MWCNTs, which resulted in a higher surface resistivity.

The mixing time in the two-roll mill was also an important parameter for the surface resistivity. With increasing mixing time in the two-roll mill from 0 to 6 min for the NBR/MWCNT nanocomposites prepared in a kneader at 20 rpm, the surface resistivity decreased from 10^{11} to 10^4 Ω /square. However, a

further increase in the mixing time in the two-roll mill led to an increase in the surface resistivity.

It is well known that the gap distance in a roll mill is also an important parameter for CNT dispersion and CNT length. Interestingly, an opposing effect of gap distance on the surface resistivity was observed, which depended on the processing parameters of the nanocomposites in this study. The surface resistivity decreased with decreasing gap distance for the NBR/MWCNT nanocomposites prepared in the kneader at 20 rpm, but the surface resistivity decreased with increasing gap distance for NBR/MWCNT at 60 rpm. The cooling rate of the compression-molded samples and sulfur concentration also influenced the surface resistivity for the NBR/MWCNT nanocomposites.

References

- Xiao, K. Q.; Zhang, L. C.; Zarudi, I. *Compos Sci Technol* 2007, 67, 177.
- McNally, T.; Potschke, P.; Halley, P.; Murphy, M.; Martin, D.; Bell, S. E. J.; Brennan, G. P.; Bein, D.; Lemoine, P.; Quinn, J. P. *Polymer* 2005, 46, 8222.
- Kodgire, P. V.; Bhattacharyya, A. R.; Bose, S.; Gupta, N.; Kulkarni, A. R.; Misra, A. *Chem Phys Lett* 2006, 432, 480.
- Potschke, P.; Dudkin, S. M.; Alig, I. *Polymer* 2003, 44, 5023.
- Potschke, P.; Abdel-Goad, M.; Alig, I.; Dudkin, S.; Lellinger, D. *Polymer* 2004, 45, 8863.
- Potschke, P.; Fornes, T. D.; Paul, D. R. *Polymer* 2002, 43, 3247.
- Andrews, R.; Jacques, D.; Minot, M.; Rantell, T. *Macromol Mater Eng* 2002, 287, 395.
- Grossiord, N.; Loos, J.; Regev, O. O.; Koning, C. E. *Chem Mater* 2006, 18, 1089.
- Coleman, J. N.; Khan, U.; Gun'ko, Y. K. *Adv Mater* 2006, 18, 689.
- Potschke, P.; Bhattacharyya, A. R.; Janke, A. *Polymer* 2003, 44, 8061.
- Bose, S.; Bhattacharyya, A. R.; Kulkarni, A. R.; Potschke, P. *Compos Sci Technol* 2009, 69, 365.
- Thostenson, E. T.; Chou, T. W. *Carbon* 2006, 44, 3022.
- Li, Y.; Shimizu, H. *Polymer* 2007, 48, 2203.
- Pegel, S.; Potschke, P.; Petzold, G.; Alig, I.; Dudkin, S. M.; Lellinger, S. *Polymer* 2008, 49, 974.
- Villmow, T.; Potschke, P.; Pegel, S.; Haussler, L.; Kretschmar, B. *Polymer* 2008, 49, 3500.
- Kasaliwal, G.; Goldel, A.; Potschke, P. *J Appl Polym Sci* 2009, 112, 3494.
- Villmow, T.; Pegel, S.; Potschke, P.; Wagenknecht, U. *Compos Sci Technol* 2008, 68, 777.
- Bose, S.; Bhattacharyya, A. R.; Kodgire, P. V.; Kulkarni, A. R.; Misra, A. *J Nanosci Nanotechnol* 2008, 8, 1867.
- Lim, G. O.; Min, K. T.; Kim, G. H. *Polym Eng Sci*, to appear.