Effect of Processing Parameters on the Surface Resistivity of Ethylene Propylene Diene Terpolymer/Multiwalled Carbon Nanotube Nanocomposites

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ABSTRACT: In this study, ethylene propylene diene terpolymer (EPDM) is melt-mixed with multiwalled carbon nanotube (MWCNT). To realize full-scale application of MWCNT to the rubber industries, the effect of melt-processing parameters on the surface resistivity in the rubber/MWCNT nanocomposites should be well understood. The effect of rotor speed, mixing temperature, and annealing time on the surface resistivity of the EPDM/MWCNT nanocomposites has been investigated. The surface resistivity of EPDM/MWCNT nanocomposites with 3 phr MWCNT increases with increasing the rotor speed and decreasing the mixing temperature. Tensile strength and tensile modulus of EPDM/MWCNT (3 phr) nanocomposites are higher than those of EPDM, respectively. For the nanocomposite with 3 phr MWCNT loadings, surface resistivity increases as the annealing time at room temperature increases. This is the first report that surface resistivity of rubber/MWCNT nanocomposites increases significantly on annealing at room temperature. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40129.

INTRODUCTION

In recent years, the addition of conductive fillers into polymers has been commonly used for static dissipative purposes. The most widely used filler for the purpose is carbon black. High carbon black loadings are typically necessary, which results in particulate sloughing and making polymer/carbon black composites brittle. Because of the excellent conductivity and very high aspect ratio of carbon nanotube (CNT), polymer/CNT nanocomposites can exhibit electrical conductivity at low CNT loadings. Therefore, CNT-based polymer nanocomposites can be manufactured into static dissipative parts with smoother surfaces, superior aesthetics, and better mechanical properties.

Depending on the preparation method and polymer, a wide range of values has been reported for surface resistivity of polymer/CNT nanocomposites. According to literature,[1] each surface resistivity of polypropylene/MWCNT (0.25 vol %) and polystyrene/MWCNT (0.25 vol %) nanocomposites was 10^5 Ω/square. However, much higher surface resistivity ($10^{11}-10^{12}$ Ω/square) was reported for acrylonitrile-butadiene-styrene/MWCNT (0.25 vol %) nanocomposite.[1] The surface resistivity, 10^6 Ω/square, was reported for UV cured epoxy nanocomposites with addition of significantly low content of MWCNT (0.1 wt %).[2]

Melt-compounding is the most cost-effective method to disperse CNTs into polymers with current industrial practices. Many studies about polymer/CNT nanocomposites prepared by melt-compounding have shown that the electrical conductivity of these nanocomposites is significantly affected by processing parameters such as rotor speed, mixing temperature, and annealing time.[1,3–19] However, few reports are available about the effect of processing parameters on the electrical conductivity of rubber/CNT nanocomposites, even though they could display different behaviors because of high viscosity and lower T_g of rubbers.[20]

Especially, many studies have shown that the electrical conductivity of polymer/CNT nanocomposites is significantly enhanced by annealing above the melting temperature of polymer matrix as a result of formation of secondary CNT agglomerates.[7–12] This indicates that polymer/CNT nanocomposites are thermodynamic nonequilibrium systems under usual polymer processing operations. Because the T_g of rubbers is lower than room temperature, the rubbers can relax to more thermodynamically stable conformation during annealing at room temperature. As a result, the surface resistivity of rubber/CNT nanocomposites could be changed. However, to the best of our knowledge no study has been carried out about the effect of annealing at room temperature on the surface resistivity of rubber/CNT nanocomposites.

Ethylene propylene diene terpolymer (EPDM) was melt-mixed with MWCNTs and then the mixtures were compression-molded in this study. The effect of rotor speed and mixing temperature on the surface resistivity of the compression-molded samples of EPDM/MWCNT nanocomposites has been investigated. Also, the change in the surface resistivity of the compression-molded samples with annealing time at room temperature was examined. For the nanocomposite with 3 phr MWCNT loadings, surface resistivity increases as the annealing time at room temperature increases.

EXPERIMENTAL

Materials and Nanocomposite Preparation

Two commercial EPDMs, KEP-435 (Mooney viscosity ML (1+4) 100°C: 33, ethylene content: 56.5 wt %) and KEP-240 (Mooney viscosity ML (1+4) 100°C: 42, ethylene content: 56.5 wt %) were provided by Kumho Polychemical, Korea. The EPDMs are amorphous polymers. MWCNTs were synthesized by thermal CVD (Chemical Vapor Deposition). According to the provider, typical tube diameter is in the range 10–50 nm with tube lengths of 1–25 μm. MWCNTs (purity: 95%) were used as received. EPDM and MWCNT were melt-mixed in a bench kneader (Irie Shokai Ltd., Japan) at various rotor speeds and mixing temperatures. Mixing time was fixed at 14 min. Then, the mixture was put in a mold and the nanocomposites were obtained by compression-molding at 14.7 MPa, in a hydraulic press at 185°C for 10 min. The compression-molded samples were naturally cooled to room temperature.

Testing

The surface resistivity was measured on compression-molded samples (sample dimensions: 110 $\times$ 180 $\times$ 18 mm^3) using Worksurface tester ST-3 (SIMCO, Kobe, Japan). Each sample was kept in a desiccator over anhydrous calcium chloride at room temperature before resistivity measurements. Surface resistivity measurements were conducted at 54% relative humidity and temperature of 20°C. The cross sections of EPDM/MWCNT nanocomposites were cryogenically fractured and were examined with field emission gun-Scanning Electron Microscope (SEM, FEI Quanta 200, USA).

A Universal Testing Machine (Model UL25, Hounsfield Co.) was used to obtain the tensile properties of the nanocomposites at room temperature. The crosshead speed was 500 mm/min. All measurements were performed for five replicates of dog-bone shaped specimens and averaged to get the final result.

RESULTS AND DISCUSSION

For viable electrostatic dissipative applications, the surface resistivity of the polymer/CNT nanocomposites should be in the range 10^5 to 10^{12} Ω/square and preferably at the low end of this range.[1] The surface resistivity range in our experimental set-up is limited to values below 10^{12} Ω/square. With addition of 1 and 2 phr MWCNT, the surface resistivity of EPDM/WMWN nanocomposites is above 10^{12} Ω/square. The surface resistivity of the nanocomposites begins to decrease with addition of 3 phr MWCNT. Therefore, 3 phr is used for the content of MWCNT in this study.
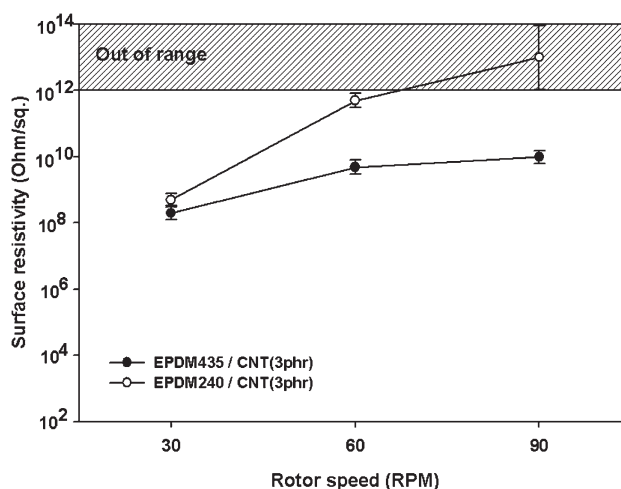

Figure 1. Effect of rotor speed in the kneader on the surface resistivity of EPDM/MWCNT nanocomposites with 3 phr MWCNT loadings.

Figure 1 shows the effect of rotor speed in the kneader on the surface resistivity of EPDM/MWCNT nanocomposites with 3 phr MWCNT loadings. EPDM was not cross-linked and mixing temperature was fixed at 185°C in this study. The surface resistivity increases with increasing the rotor speed. According to our previous research,[21] the effect of rotor speed on the surface resistivity of ethylene-vinyl acetate copolymer (EVA)/MWCNT nanocomposites with 1 and 1.5 wt % MWCNT loadings displayed different behavior. The surface resistivity of the EVA/MWCNT nanocomposites (mixing time: 14 min) decreases with increasing the rotor speed. Kasaliwal et al.[5] have also shown that the volume resistivity of polycarbonate/MWCNT decreases with increasing the rotor speed.

In polymer/CNT nanocomposites, increasing the rotor speed leads to an improvement of dispersion of CNTs in polymer matrix[5,7] and a decrease of the CNT length.[6,7] Improvement of dispersion of CNT results in a decrease in resistivity[5,21] but decrease of CNT length leads to an increase in inter-CNT gap, resulting in an increase in resistivity.[6] Therefore, increasing the rotor speed can lead to a decrease or an increase in resistivity depending on the many factors such as the polymers used.

With increasing rotor speed for EVA/MWCNT nanocomposites, the effect of improved dispersion of MWCNT may predominate over the effect of the decreased MWCNT length on surface resistivity. As a result, lower surface resistivity was obtained by increasing the rotor speed in our previous study.[21] However, with increasing rotor speed for EPDM/MWCNT nanocomposites, the effect of the decreased MWCNT length may predominate over the effect of improved dispersion of MWCNT. As a result, higher surface resistivity is obtained by increasing the rotor speed. This difference might be due to the higher viscosity of EPDM than that of EVA, leading to higher shear stress on the MWCNT during melt-mixing. As a result, more severe MWCNT breakage may occur. According to fiber-level simulations together with a resister network model for sheared CNT/polymer nanocomposites,[22] increasing the shear rate decreases electrical conductivity of the nanocomposites. The surface
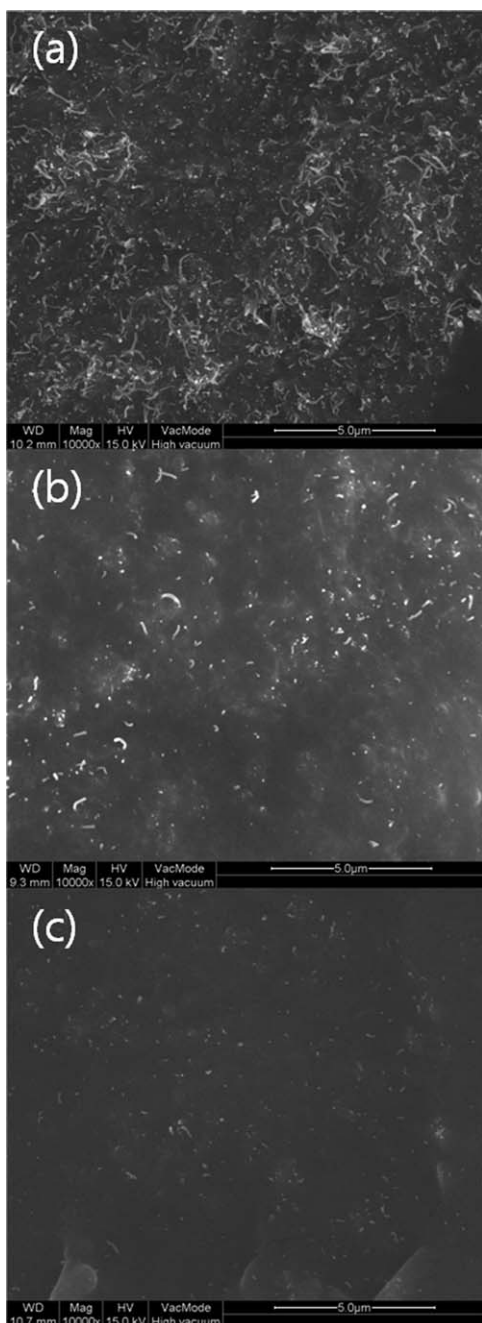
Figure 2. SEM micrographs of cryofractured surface of EPDM 240/MWCNT (5 phr) nanocomposites melt-mixed at (a) 30 rpm, (b) 60 rpm, and (c) 90 rpm.

resistivity of EPDM435/MWCNT nanocomposites is lower than that of EPDM240/MWCNT nanocomposites at the same rotor speed. This may be due to the higher viscosity of EPDM240 (Mooney viscosity: 42) than that of EPDM435 (Mooney viscosity: 33).

Figure 2 shows the SEM micrographs of cryofractured surface of EPDM 240/MWCNT (5 phr) nanocomposites melt-mixed at different rotor speed. The white dots and lines are MWCNTs. In the SEM images, one can observe better dispersion of MWCNTs in EPDM matrix with increasing rotor speed. However, on
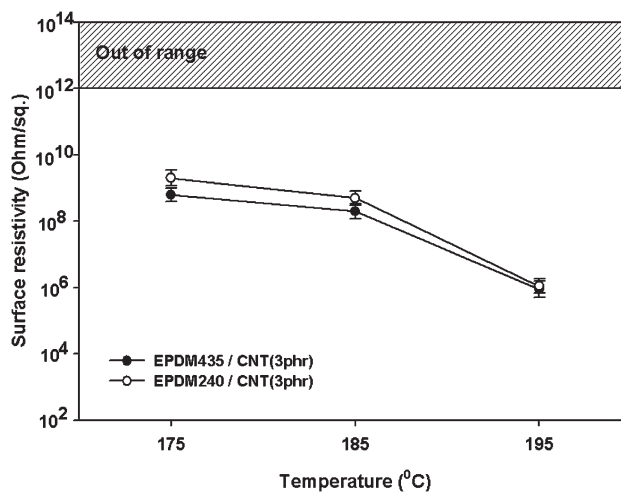

Figure 3. Effect of mixing temperature in the kneader on the surface resistivity of EPDM/MWCNT nanocomposites with 3phr MWCNT loadings.

increasing rotor speed, better dispersion is achieved at the expense of decreased length. This leads to increase in surface resistivity with increasing rotor speed.

Figure 3 shows the effect of mixing temperature in the kneader on the surface resistivity of EPDM/MWCNT nanocomposites with 3 phr MWCNT loadings. Rotor speed was fixed at 30 rpm because 30 rpm produced the lowest surface resistivity as shown in Figure 1. The surface resistivity increases with decreasing the mixing temperature. Decreasing mixing temperature leads to a higher viscosity and a higher shear stress, resulting in more breakage of the MWCNT. The surface resistivity of EPDM435/MWCNT nanocomposites is lower than that of EPDM240/MWCNT nanocomposites at the same mixing temperature. High shear stress induced by high rotor speed and low melt temperature is not preferred processing condition for the lower surface resistivity of EPDM/MWCNT nanocomposites with 3 phr MWCNT.

Figures 4–6 show the tensile strength, elongation at break, and tensile modulus of EPDM and EPDM/MWCNT
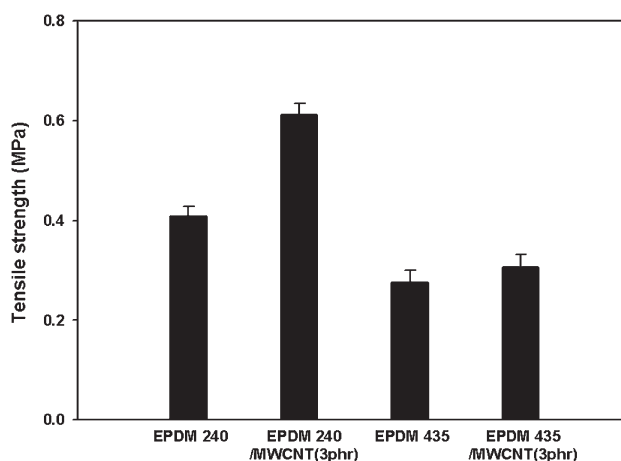

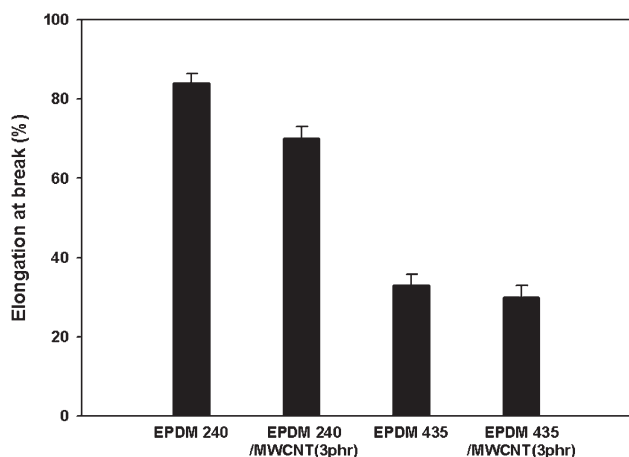**Figure 4.** Tensile strength of EPDM and EPDM/MWCNT (3 phr) nanocomposites.

Figure 5. Elongation at break of EPDM and EPDM/MWCNT (3 phr) nanocomposites.

nanocomposites, respectively. For the measurement of tensile properties, EPDM and MWCNT were melt-mixed in a kneader at fixed mixing temperature (185°C) and rotor speed (30 rpm). Tensile strength and tensile modulus of EPDM240/MWCNT (3 phr) and EPDM435/MWCNT (3 phr) nanocomposites are higher than those of EPDM240 and EPDM435, respectively. Elongation at break of EPDM240/MWCNT (3 phr) and EPDM435/MWCNT (3 phr) nanocomposites is lower than that of EPDM 240 and EPDM 435, respectively.

Figures 7 and 8 show the dependence of surface resistivity on the annealing time at room temperature for EPDM435/ MWCNT nanocomposite with 3 and 5 phr MWCNT loadings, respectively. Compression molded samples were annealed at room temperature without pressure. For the nanocomposites with 3 phr MWCNT loadings, surface resistivity increases slightly over the annealing time at the early stage, and sharp increase in the surface resistivity is observed, as the annealing time increases. The surface resistivity of EPDM435/MWCNT nanocomposite with 3 phr MWCNT annealed at room temperature for 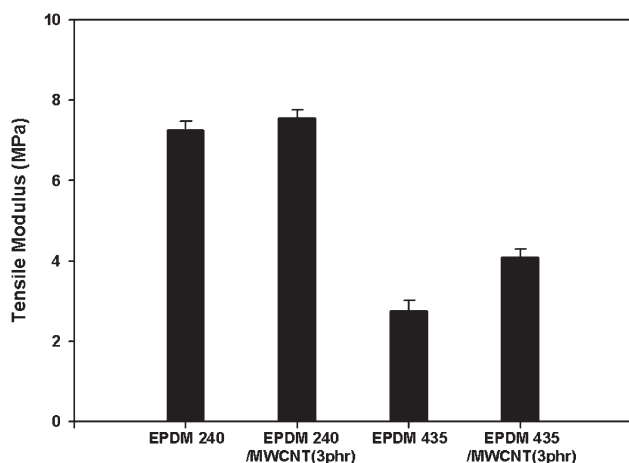6 days is above 10^{12}. For the nanocomposites with 5 phr MWCNT loadings, surface resistivity almost does not change over the observed annealing time.

Because the T_g of EPDM is lower than room temperature, the polymers can relax to more thermodynamically stable conformation during annealing at room temperature. As a result, the conductive networks of EPDM/MWCNT nanocomposite with 3 phr MWCNT may be in the process of breaking down during annealing at room temperature. However, the nanocomposite with 5 phr MWCNT, due to high MWCNT content, the conductive networks may not break down during annealing at room temperature. High MWCNT content in the matrix results in strong networks. Hence, annealing at room temperature has less effect on the surface resistivity.

The surface resistivity of EPDM435/MWCNT nanocomposite with 3 phr MWCNT annealed at room temperature for 6 days is above 10^{12}. To investigate the reversibility, the EPDM435/ MWCNT nanocomposite with 3 phr MWCNT annealed at
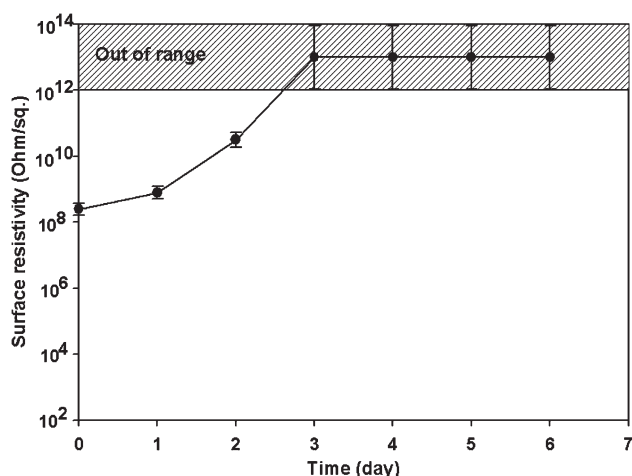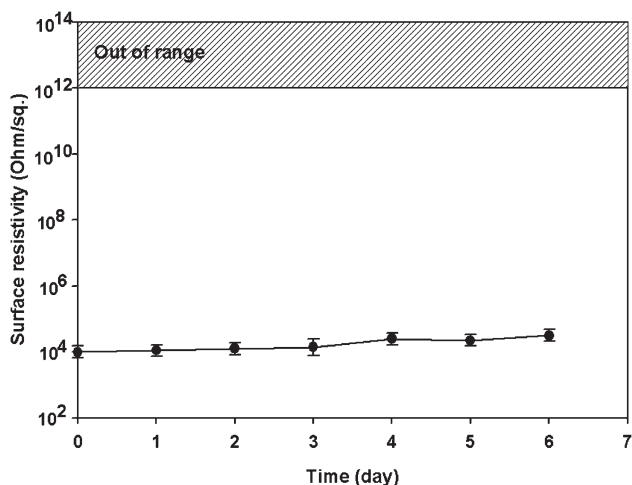

Figure 7. Dependence of surface resistivity on the annealing time at room temperature for EPDM435/MWCNT nanocomposite with 3 phr MWCNT loadings.

Figure 6. Tensile modulus of EPDM and EPDM/MWCNT (3 phr) nanocomposites.

Figure 8. Dependence of surface resistivity on the annealing time at room temperature for EPDM435/MWCNT nanocomposite with 5 phr MWCNT loadings.
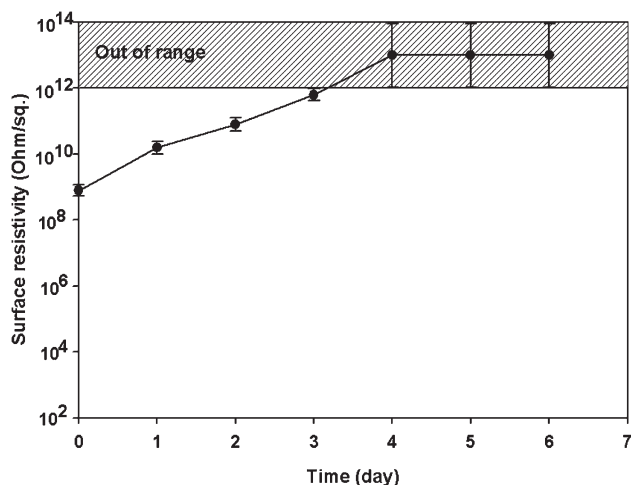
Figure 9. Dependence of surface resistivity on the annealing time at room temperature for EPDM435/MWCNT nanocomposite with 3 phr MWCNT loadings. The nanocomposite was compression molded again after being annealed at room temperature for 6 days.

room temperature for 6 days was compression molded again, and its measured surface resistivity is around 10^9. Then, the nanocomposite was annealed at room temperature again, and the increase of surface resistivity is observed as shown in Figure 9. The behavior is very similar to Figure 7.

To investigate the origin of the increase in the surface resistivity of the EPDM/MWCNT nanocomposite on the annealing at room temperature, the thickness of the sample was examined by using SEM. Figure 10 shows the SEM image of EPDM435/MWCNT nanocomposite with 3 phr MWCNT annealed at room temperature for 1 day. The thickness of the sample measured with SIS Scandium Image Software is about 1938 μm. After the measurement, the sample was kept for 5 days in the sample holder at room temperature, and its thickness was measured at the same position. The thickness of the sample is about 1952 μm as shown in Figure 11. During compression molding, the polymers were under pressure, and the polymers can relax
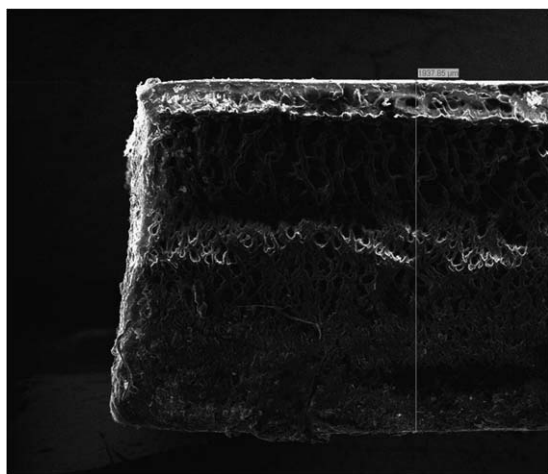

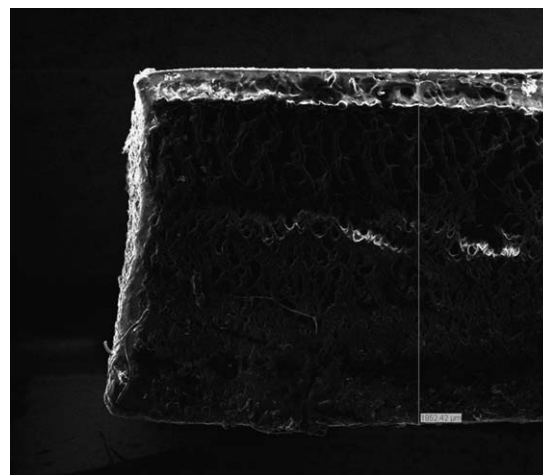Figure 10. SEM image of EPDM435/MWCNT nanocomposite with 3 phr MWCNT annealed at room temperature for 1 day.

Figure 11. SEM image of EPDM435/MWCNT nanocomposite with 3 phr MWCNT annealed at room temperature for 6 days.

to more thermodynamically stable conformation during annealing at room temperature. As a result, the thickness of sample increases. Because of poor interfacial interactions between EPDM and MWCNT, MWCNTs may be at the original positions without movement while the thickness of sample increases due to relaxation of polymers during annealing. As a result, the concentration of MWCNT may decrease around surface and surface resistivity increases. The increase in thickness of the sample may be also accompanied by increase in void volume. The presence of air in the voids may be also responsible for the increase in surface resistivity. Therefore, the sample thickness is a very important parameter for EPDM/MWCNT nanocomposites.

CONCLUSIONS

Eventhough the surface resistivity of EPDM435/MWCNT nanocomposite with 5 phr MWCNT loadings almost does not change over the observed annealing time, the surface resistivity of EPDM435/MWCNT nanocomposite with 3 phr MWCNT loadings increases significantly on annealing at room temperature. This is the first report that surface resistivity of rubber/MWCNT nanocomposite increases significantly on annealing at room temperature. The possible origin of this behavior is the increase in the sample thickness during annealing at room temperature.

Also, rotor speed and mixing temperature significantly affect the surface resistivity of EPDM/MWCNT nanocomposites with 3 phr MWCNT loadings. Because the breakage of MWCNT is severe for EPDM/MWCNT nanocompsites during melt-mixing, high shear stress induced by high rotor speed and low melt temperature is not preferred processing condition for the lower surface resistivity. Surface resistivity of EPDM/MWCNT nanocomposites with 3 phr MWCNT loadings depends on the dispersion state of MWCNT in the matrix. Because the dispersion state of MWCNT including MWCNT length is dependent on the process parameters, surface resistivity of EPDM/MWCNT nanocomposites changes with the process parameters. Based on this result, for rubber/CNT nanocomposites to be

commercialized, the effect of processing parameters on the surface resistivity of rubber/CNT nanocomposites should be well understood.

ACKNOWLEDGMENTS

REFERENCES

1. Andrews, R.; Jacques, D.; Minot, M.; Rantell, T. *Macromol. Mater. Eng.* **2002**, *287*, 395.

2. Sangermano, M.; Pegel, S.; Pötschke, P.; Voit, B. *Macromol. Rapid Commun.* **2008**, *29*, 396.

3. Pegel, S.; Pötschke, P.; Petzold, G.; Alig, I.; Dudkin, S. M.; Lellinger, S. *Polymer* **2008**, *49*, 974.

4. Villmow, T.; Pötschke, P.; Pegel, S.; Haussler, L.; Kretzschmar, B. *Polymer* **2008**, *49*, 3500.

5. Kasaliwal, G.; Göldel, A.; Pötschke, P. *J. Appl. Polym. Sci.* **2009**, *112*, 3494.

6. Krause, B.; Pötschke, P.; Häußler, L. *Compos. Sci. Technol.* **2009**, *69*, 1505.

7. Alig, I.; Pötschke, P.; Lellinger, D.; Engel, M.; Skipa, T.; Pegel, S.; Kasaliwal, G.; Villmow, T. *Polymer* **2012**, *53*, 4.

8. Pötschke, P.; Fornes, T. D.; Paul, D. R. *Polymer* **2002**, *43*, 3247.

9. Pötschke, P.; Dudkin, S. M.; Alig, I. *Polymer* **2003**, *44*, 5023.

10. Alig, I.; Skipa, T.; Lellinger, D.; Pötschke, P. *Polymer* **2008**, *49*, 3524.

11. Alig, I.; Lellinger, D.; Engel, M.; Skipa, T.; Pötschke, P. *Polymer* **2008**, *49*, 1902.

12. Su, C.; Xu, L.; Zhang, C.; Zhu, J. *Compos. Sci. Technol.* **2011**, *71*, 1016.

13. Villmow, T.; Pegel, S.; Pötschke, P.; Wagenknecht, U. *Compos. Sci. Technol.* **2008**, *68*, 777.

14. Bose, S.; Bhattacharyya, A. R.; Kodgire, P. V.; Kulkarni, A. R.; Misara, A. *J. Nanosci. Nano. Technol.* **2008**, *8*, 1867.

15. Jamali, S.; Paiva, M. C.; Covas, J. A. *Polym. Test.* **2013**, *32*, 701.

16. Tiusanen, J.; Vlasveld, D.; Vuorinen, J. *Compos. Sci. Technol.* **2012**, *72*, 1741.

17. Zhang, Y. C.; Zheng, D.; Pang, H.; Tang, J. H.; Li, Z. M. *Compos. Sci. Technol.* **2012**, *72*, 1875.

18. Göldel, A.; Kasaliwal, G. R.; Pötschke, P.; Heinrich, G. *Polymer* **2012**, *53*, 411.

19. Socher, R.; Krause, B.; Müller, M. T.; Boldt, R.; Pötschke, P. *Polymer* **2012**, *53*, 495.

20. Kummerlöwe, C.; Vennemann, N.; Yankova, E.; Wanitschek, M.; Größ, C.; Heider, T.; Haberkorn, F.; Siebert, A. *Polym. Eng. Sci.* **2013**, *53*, 849.

21. Yu, D. R.; Kim, G. H. *J. Appl. Polym. Sci.* **2012**, *124*, 2962.

22. Eken, A. E.; Tozzi, E. J.; Klingenberg, D. J.; Bauhofer, W. *Polymer* **2012**, *53*, 4493.