

Effect of Processing Parameters on the Surface Resistivity of Ethylene–Vinyl Acetate Copolymer/Multiwalled Carbon Nanotube Nanocomposites

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ABSTRACT: In this study, ethylene–vinyl acetate (EVA) copolymer was melt-mixed with multiwalled carbon nanotube (MWCNT). To realize full-scale application of MWCNT to the polymer industries, the effect of melt-processing parameters on the surface resistivity in the polymer/MWCNT nanocomposites should be well-understood. The effect of mixing time, rotor speed, compression molding time, and temperature on the surface resistivity was investigated. Increasing the rotor speed and longer mixing time lead to an improvement of dispersion of MWCNT in

polymer matrix, resulting in a decrease of surface resistivity. The surface resistivity of EVA/MWCNT nanocomposites is also sensitive to the press temperature and time. However, the dominant processing parameters to affect surface resistivity depend on the amount of MWCNT. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2962–2967, 2012

Key words: nanocomposites; compounding; carbon nanotube; processing; melt

INTRODUCTION

In recent years, the addition of conductive fillers into polymers has been commonly used for an electrostatic dissipative purpose. Carbon black is the most widely used filler, but its typical loading is 15–20 wt %, resulting in particulate sloughing and thus sacrificing other desirable properties of the host polymer such as lightweight and toughness. Recently, carbon nanotube (CNT)-based polymer nanocomposites have attracted considerable attention from both fundamental research and application points of view because of a unique combination of mechanical, electrical, and thermal properties of CNT. The excellent conductivity and very high aspect ratio of CNT provide polymers with electrical conductivity at 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 CNT into polymers, melt-compounding is the most compatible with current industrial practices. In polymer industries, large volumes of products are produced by melt processing. This method is also

environmentally safe, because it is free of solvents and contaminants, which are involved in solution blending and *in situ* polymerization method. In this aspect, many studies have recently employed melt-compounding method.^{1–27} Because multiwalled CNT (MWCNT) is competitive in cost, most melt-compounding methods have used MWCNT rather than single-walled CNT. Although the melt-compounding method has many advantages, uniform dispersion of CNTs in the polymer matrix is still the most challenging task.

Since electrical conductivity of composites is strongly influenced by filler's state of dispersion during processing, processing conditions are very important parameters. To realize full-scale application of MWCNT to the polymer industries, the effect of melt-processing parameters on the surface resistivity in the polymer/MWCNT composites should be well-understood. In this study, relatively large amounts (130 g) of ethylene–vinyl acetate (EVA) copolymer were melt-mixed with MWCNTs, and then the mixtures were compression molded. The effect of mixing time, rotor speed, compression molding time, and temperature on the surface resistivity of the EVA/MWCNT nanocomposites was investigated.

EXPERIMENTAL

Materials and nanocomposite preparation

EVA (vinyl acetate content: 22 wt %) was provided by Hanwha (Korea). MWCNTs were synthesized by

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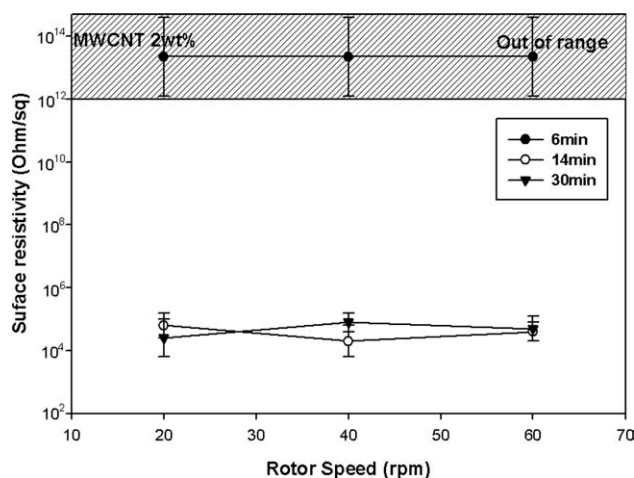


Figure 1 Effect of mixing time and rotor speed in the kneader on the surface resistivity of EVA/MWCNT nanocomposites with 2 wt % MWCNT.

thermal CVD. According to the provider (CNT Co., Korea), typical tube diameter is in the range 10–50 nm with tube lengths of 1–25 μm . MWCNTs (trade name: Ctube 100, purity: 95%) were used as-received. EVA and MWCNT were melt-mixed in a bench kneader PBV-03 (Irie Shokai, Japan) at various mixing times and rotor speeds. Mixing temperature was fixed at 110°C. 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 various temperatures and times. The compression-molded samples were naturally cooled to room temperature.

Testing

The surface resistivity was measured on compression-molded samples (sample dimensions: 110 mm \times 180 mm \times 18 mm) using Worksurface tester ST-3 (SIMCO, Kobe, Japan). Model ST-3 Worksurface tester was used to measure surface resistivity in the range of 10^4 – 10^{12} Ω/square . Each sample was kept in a desiccator over anhydrous calcium chloride for 48 h before resistivity measurements. Surface resistivity measurements were conducted at 54% relative humidity and temperature of 20°C. Five measurements were made for the each sample and averaged to get the final result. To investigate the dispersion of MWCNT in EVA/MWCNT nanocomposites, the cross sections of EVA/MWCNT nanocomposites were cryogenically fractured and were examined with field emission gun scanning electron microscope (SEM, FEI Quanta 200, Hillsboro, Oregon).

RESULTS AND DISCUSSION

For viable electrostatic dissipative applications, the surface resistivity of the polymer/CNT nanocompo-

sites 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 . To investigate the effect of mixing time and rotor speed in the kneader on the surface resistivity, the EVA/MWCNT nanocomposites with 0.5, 1, 1.5, and 2 wt % MWCNT were prepared. Kneader temperature was fixed at 110°C. Press temperature and press time were fixed at 165°C and 5 min. Figure 1 shows the effect of mixing time and rotor speed in the kneader on the surface resistivity of EVA/MWCNT nanocomposites with 2 wt % MWCNT loading. The surface resistivity of EVA/MWCNT nanocomposites prepared at a mixing time of 6 min is above 10^{12} Ω/square . However, the surface resistivity of the nanocomposites prepared at a mixing time of 14 and 30 min and rotor speed of 20 rpm is around $10^{4.6}$ Ω/square . Increase of rotor speed does not change the surface resistivity much.

Figure 2 shows the surface resistivity of EVA/MWCNT nanocomposites with 1.5 wt % MWCNT loading. The surface resistivity of EVA/MWCNT nanocomposites prepared at a mixing time of 6 min is above 10^{12} Ω/square . However, the surface resistivity of the nanocomposites prepared at a mixing time of 14 min and rotor speed of 20 rpm is $10^{6.5}$ Ω/square . The surface resistivity decreases with increasing the rotor speed at a mixing time of 14 min. However, at a mixing time of 30 min, increasing the rotor speed from 40 to 60 rpm leads to a slight increase of surface resistivity. This increase of surface resistivity could be due to the reduction of MWCNT length.

For EVA/MWCNT nanocomposites with 1 wt % MWCNT loading (Fig. 3), the surface resistivity of EVA/MWCNT nanocomposites prepared at a mixing time of 6 min is above 10^{12} Ω/square . The

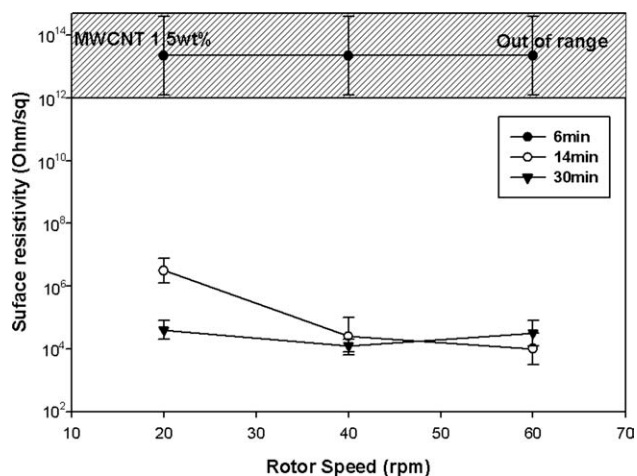


Figure 2 Effect of mixing time and rotor speed in the kneader on the surface resistivity of EVA/MWCNT nanocomposites with 1.5 wt % MWCNT.

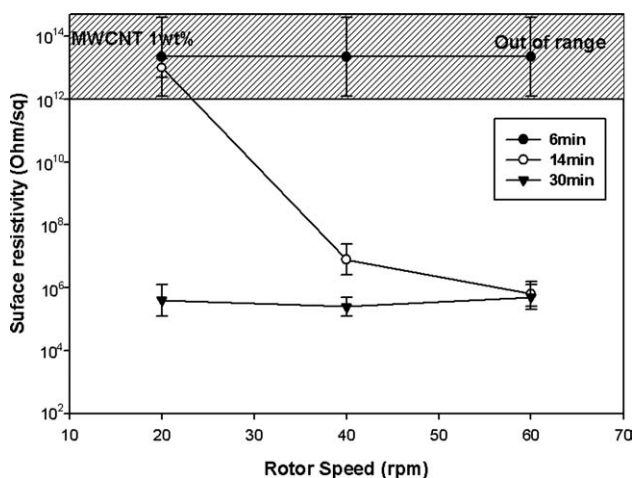


Figure 3 Effect of mixing time and rotor speed in the kneader on the surface resistivity of EVA/MWCNT nanocomposites with 1 wt % MWCNT.

surface resistivity of the nanocomposites prepared at a mixing time of 14 min significantly decreases with increasing the rotor speed from above 10^{12} to $10^{5.8}$ Ω /square. Therefore, rotor speed is a very important parameter at a mixing time of 14 min for the nanocomposites with 1 wt % MWCNT loading. At a mixing time of 30 min, the surface resistivity remains around $10^{5.6}$ Ω /square.

Figure 4 shows the SEM images of EVA/MWCNT nanocomposites with 1 wt % MWCNT prepared at a mixing time of 14 min. Aggregates of MWCNTs are observed in the nanocomposites prepared at rotor speed 20 rpm [Fig. 4 (a)]. With increasing the rotor speed, the dispersion of MWCNTs is much improved as shown in Figure 4(b,c). The improvement of dispersion of MWCNTs with increasing rotor speed results in a decrease in surface resistivity as shown in Figure 3. Longer mixing time also shows the improvement of dispersion of MWCNTs according to the SEM images (not shown in this article).

Figure 5 shows the surface resistivity of EVA/MWCNT nanocomposites with 0.5 wt % MWCNT loading. The surface resistivity of EVA/MWCNT nanocomposites prepared at a mixing time of 6 and 14 min is above 10^{12} Ω /square. However, the surface resistivity of the nanocomposites prepared at a mixing time of 30 min and rotor speed of 20 rpm is $10^{10.5}$ Ω /square. With only 0.5 wt % MWCNT, longer mixing time leads to the electrical percolation. Therefore, it can be concluded that mixing time is a very important parameter.

In summary, for the EVA/MWCNT nanocomposites prepared at press temperature of 165°C and press time of 5 min, the surface resistivity of all the EVA/MWCNT nanocomposites prepared at mixing time of 6 min in the kneader is above 10^{12} Ω /square

irrespective of rotor speed. The surface resistivity of EVA/MWCNT nanocomposites with 1.5 and 2 wt % MWCNT is not as sensitive to the mixing time and rotor speed as the surface resistivity of EVA/MWCNT nanocomposites with 1 wt % MWCNT. For

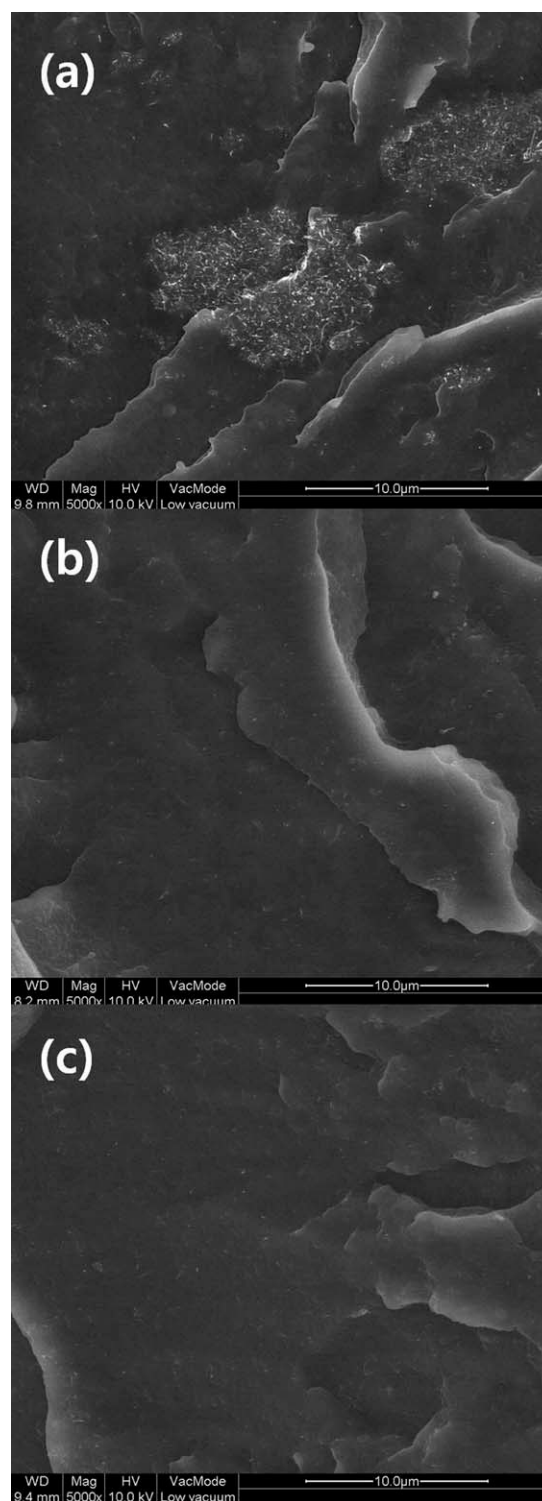


Figure 4 SEM images of EVA/MWCNT nanocomposites with 1 wt % MWCNT prepared at a mixing time of 14 min and (a) rotor speed: 20 rpm, (b) rotor speed: 40 rpm, and (c) rotor speed: 60 rpm.

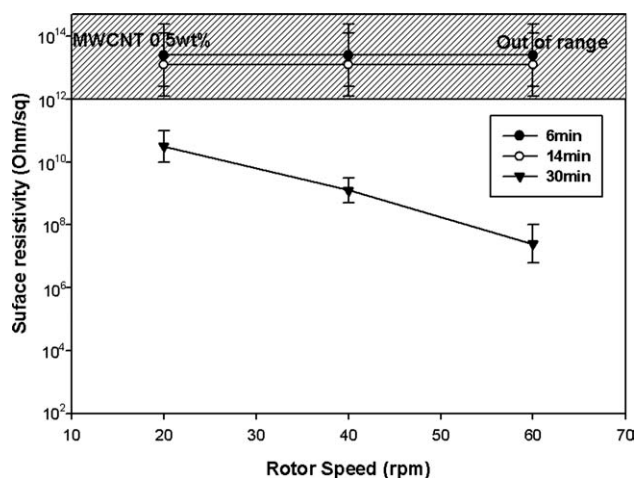


Figure 5 Effect of mixing time and rotor speed in the kneader on the surface resistivity of EVA/MWCNT nanocomposites with 0.5 wt % MWCNT.

the EVA/MWCNT nanocomposites prepared at press temperature of 185°C and press time of 5 min, the effect of mixing time and rotor speed on the surface resistivity had the same trend (not shown in this article) as observed in Figures 2, 3, and 5.

To investigate the effect of compression molding parameters on the surface resistivity, the EVA/MWCNT nanocomposites with 0.5, 1, and 1.5 wt % MWCNT were prepared. Kneader temperature was fixed at 110°C. Mixing time and rotor speed in the kneader were fixed at 14 min and 20 rpm for the results as shown in Figures 6(a), 8(a), and 9(a) and 14 min and 60 rpm for the results as shown in Figures 6(b), 8(b), and 9(b). Figure 6(a) shows the effect of press time and press temperature on the surface resistivity of EVA/MWCNT nanocomposites with 1.5 wt % MWCNT loading. At a press temperature of 140°C, the surface resistivity of EVA/MWCNT

nanocomposites is above 10^{12} Ω /square. However, the surface resistivity decreases to about $10^{6.3}$ Ω /square at a press temperature of 165°C. Further increase of press temperature does not lead to the change of surface resistivity much. Similar surface resistivity values are observed for press time of 5 and 12 min. The similar trend was observed in Figure 6(b) although the surface resistivity of EVA/MWCNT nanocomposites in Figure 6(b) is lower than that of the nanocomposites in Figure 6(a) at the same press time and temperature.

Figure 7 shows the SEM images of EVA/MWCNT nanocomposites with 1.5 wt % MWCNT prepared at a press time of 5 min. Aggregates of MWCNTs are easily observed in the nanocomposites prepared at a press temperature of 140°C [Fig. 7(a)]. However, the dispersion of MWCNTs is much improved for the nanocomposites prepared at a press temperature of 185°C [Fig. 7(b)]. This improvement of dispersion of MWCNTs with increasing the press temperature is attributed to the decrease of surface resistivity as shown in Figure 6.

Figure 8(a) shows the effect of press time and press temperature on the surface resistivity of EVA/MWCNT nanocomposites with 1.0 wt % MWCNT loading. At a press time of 5 min, the surface resistivity is above 10^{12} Ω /square at press temperature of 140°C and 165°C. However, the surface resistivity decreases to $10^{9.5}$ Ω /square at 185°C. Longer press time, 12 min, leads to the lower surface resistivity except 140°C. Figure 8(b) shows the decrease of surface resistivity of the nanocomposites with increasing the press temperature. Based on these results, it can be concluded that press temperature and time are also very important parameters to affect the surface resistivity of EVA/MWCNT nanocomposites. However, for EVA/MWCNT nanocomposites with

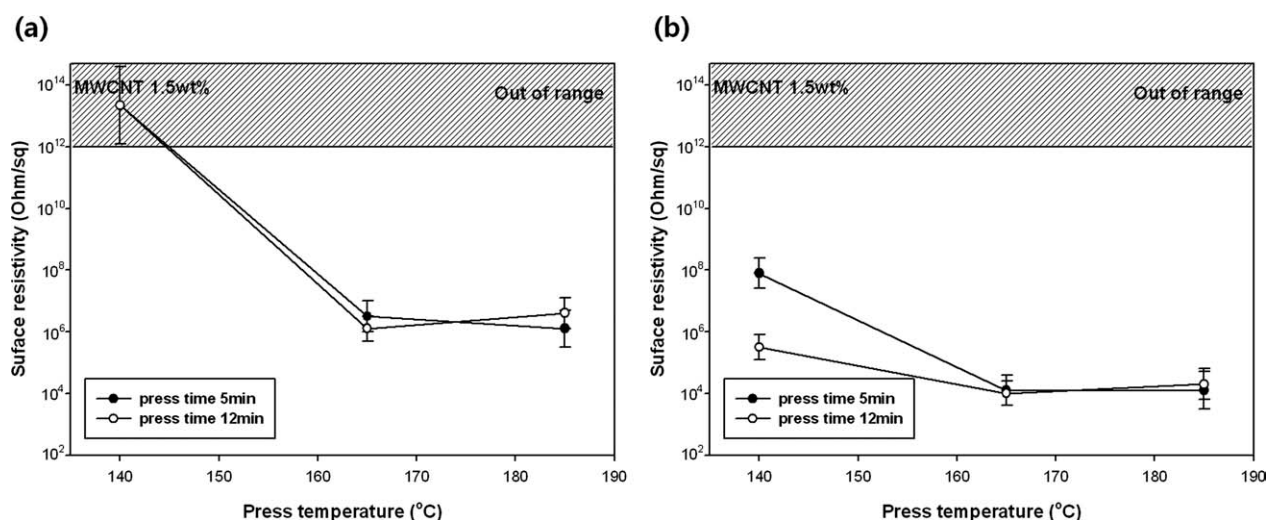


Figure 6 Effect of press time and press temperature on the surface resistivity of EVA/MWCNT nanocomposites with 1.5 wt % MWCNT prepared at a mixing time of 14 min and (a) rotor speed: 20 rpm and (b) rotor speed: 60 rpm.

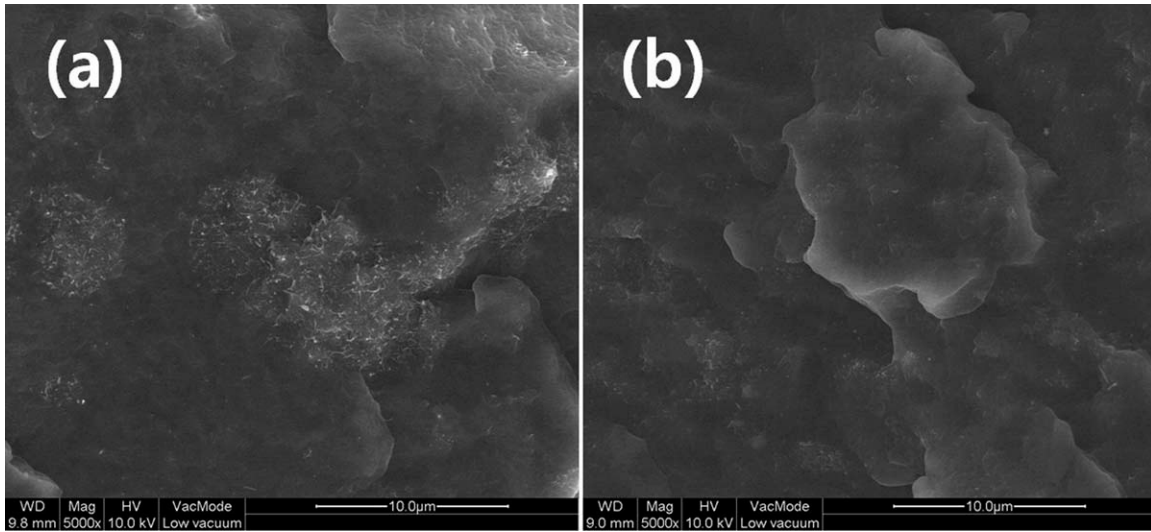


Figure 7 SEM images of EVA/MWCNT nanocomposites with 1.5 wt % MWCNT prepared at a press time of 5 min and (a) press temperature: 140°C and (b) press temperature: 185°C.

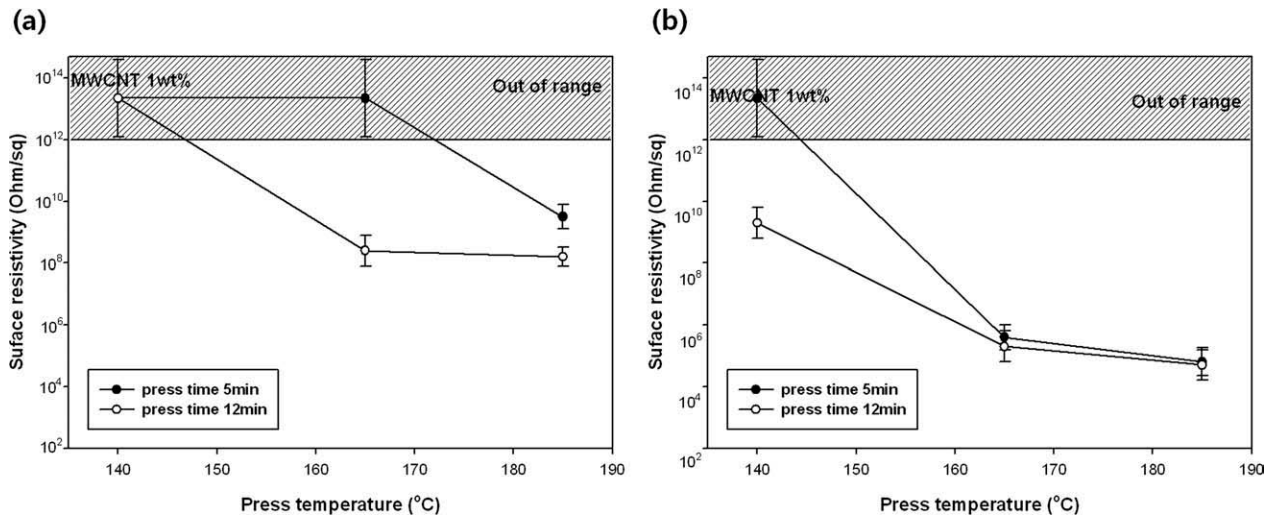


Figure 8 Effect of press time and press temperature on the surface resistivity of EVA/MWCNT nanocomposites with 1 wt % MWCNT prepared at a mixing time of 14 min and (a) rotor speed: 20 rpm and (b) rotor speed: 60 rpm.

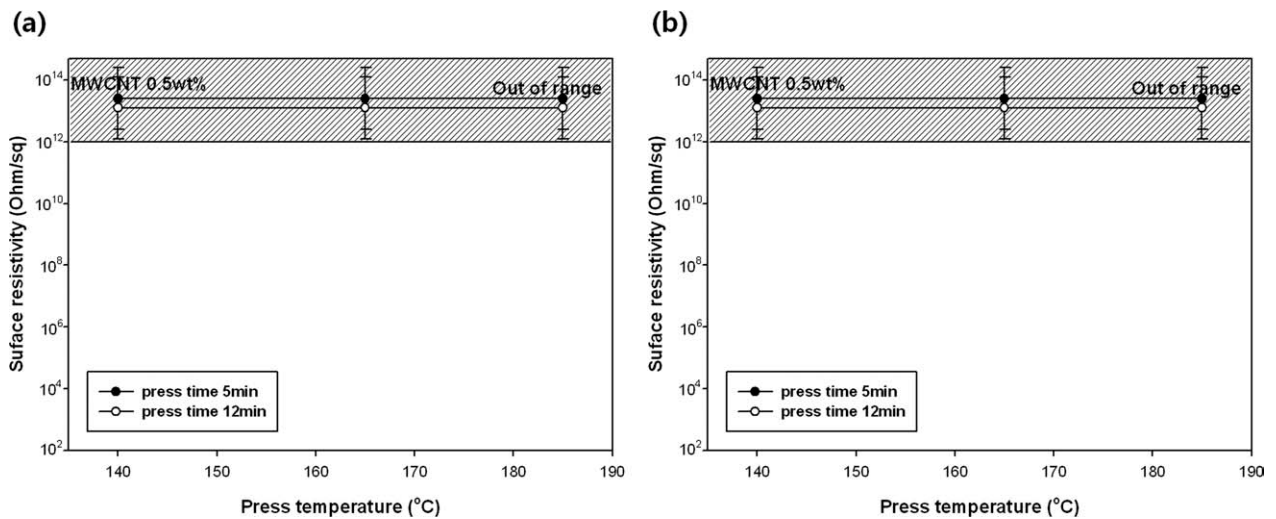


Figure 9 Effect of press time and press temperature on the surface resistivity of EVA/MWCNT nanocomposites with 0.5 wt % MWCNT prepared at a mixing time of 14 min and (a) rotor speed: 20 rpm and (b) rotor speed: 60 rpm.

0.5 wt % MWCNT, press temperature and time do not affect the surface resistivity (Fig. 9).

In summary, for the EVA/MWCNT nanocomposites prepared at mixing time of 14 min and rotor speed of 20 rpm in the kneader, the surface resistivity of the nanocomposites with 1.5 wt % MWCNT is sensitive to the press temperature. The surface resistivity of the nanocomposites with 1 wt % MWCNT is sensitive to the press time and temperature. However, the surface resistivity of the nanocomposites with 0.5 wt % MWCNT is not sensitive to both the press time and temperature. However, the dominant compression molding parameters to affect surface resistivity could be changed for different kneading parameters since the change of kneading parameters also affect the surface resistivity of EVA/MWCNT nanocomposites as observed in Figures 6(b), 8(b), and 9(b).

CONCLUSIONS

The strong dependence of surface resistivity on processing parameters was observed. The surface resistivity of all the EVA/MWCNT nanocomposites prepared at mixing time of 6 min in this study is above 10^{12} Ω /square irrespective of rotor speed. Increasing rotor speed and longer mixing time result in an improvement of dispersion of MWCNTs in EVA matrix. Generally, improvement of dispersion of MWCNT leads to a decrease in surface resistivity. However, the surface resistivity of EVA/MWCNT nanocomposites with 1.5 and 2 wt % MWCNT is not as sensitive to the mixing time and rotor speed as the surface resistivity of EVA/MWCNT nanocomposites with 1 wt % MWCNT.

The surface resistivity of EVA/MWCNT nanocomposites is also sensitive to the press temperature and time. The improvement of dispersion of MWCNTs with increasing the press temperature is attributed to the decrease of surface resistivity. However, the surface resistivity of the nanocomposites with 0.5 wt % MWCNT is not sensitive to both the press time and temperature. Based on these results, it can be concluded that depending on the amount of

MWCNT, the dominant processing parameters to affect surface resistivity are different.

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