

Ethylene Vinyl Acetate Copolymer (EVA)/Multiwalled Carbon Nanotube (MWCNT) Nanocomposite Foams

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ABSTRACT: In this study, multiwalled carbon nanotube (MWCNT) and ethylene vinyl acetate copolymer (EVA) nanocomposite bulk foams were prepared for static dissipative applications by using melt compounding method, the most compatible with current industrial applications. Closed-cell structure was verified with Scanning Electron Microscope. All the mechanical properties investigated improved with increasing content of MWCNT except elongation at break. At 5 phr of MWCNT, significant improvement of

mechanical properties and compression set were observed. Also, the surface resistivity begins to decrease at 5 phr of MWCNT. Interestingly, the increase of surface resistivity of nanocomposite foams with 8 and 10 phr MWCNT were observed with increasing thickness of removed surface layers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1845–1849, 2009

Key words: nanocomposites; melt; TEM; compounding; surfaces

INTRODUCTION

In the recent years, the addition of conductive fillers into the polymer has been commonly used for the static dissipative purpose. Carbon black is the most widely used filler and typical carbon black loading is in the range 15–20 wt %, resulting in particulate sloughing and sacrificing other desirable properties of polymers such as their light weight and good toughness. Recently, carbon nanotube (CNT)-based polymer nanocomposites have attracted considerable attention from both fundamental research and application point of view, due to the unique combination of mechanical, electrical, and thermal properties of CNT. The excellent conductivity and very high aspect ratio of CNT provide electrical conductivity to the polymers even at low CNT contents. Therefore, CNT-based polymer nanocomposites produce static dissipative parts with smoother surfaces, superior esthetics, and better mechanical properties.

Many applications requiring static electrical dissipation such as electronic devices, computer housings, and exterior automotive parts prefer light weight materials. There are some reports about clay-based polymer nanocomposite foams^{1–10} but there are few studies about CNT-based polymer nanocomposite foams for the static dissipative application. Even the

studies about electrical conductivity of polymer composite foams are rare.^{11–13} Recently, a study about the preparation of polymer foams filled with carbon nanofiber has been reported for the electronic applications. In the study, carbon nanofiber was dispersed into a PS/toluene solution under ultrasonication, and the resulting solution was sprayed onto flat plate via a microsyringe.¹ A chemical foaming agent was added to the carbon nanofiber/PS solution. And in the final hot-compression molding process, the melted PS matrix filled with carbon nanofibers was expanded by the nitrogen gas originated by the chemical foaming agent.¹⁴

Although there are many methods to disperse CNT into the polymers, melt compounding method is the most compatible with current industrial practices. This method is also environmentally benign because it is free of solvents and contaminants, which are present in solution blending and *in situ* polymerization method. In this aspect, many studies have recently employed melt compounding method.^{15–23} As melt compounding is the most compatible with current industrial practices and the foams made by microsyringe method are the thin film, the aim of the present work is to use melt compounding CNT and polymers, and develop bulk foams containing CNT for static dissipative applications.

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EXPERIMENTAL

Materials and foam preparation

EVA having 15% vinyl acetate content was provided by Hanwha, Korea. MWCNTs were synthesized by

thermal chemical vapor deposition (CVD) method. According to the provider (CNT Co., Korea), typical tube diameters were in the range 10–50 nm with tube lengths of 1–25 μm . MWCNTs (purity: 95%) were used as received because MWCNTs without surface modification were competitive in cost for industrial applications. Dicumyl peroxide (DCP) provided by Akzo Nobel (Netherlands) was used as a crosslinking agent. The chemical blowing agent used was azodicarbonamide-based blowing gas release system (JTR-M, Kum Yang, Korea). Azodicarbonamide is odorless and easily dispersed. It is activated by organic acids, bases, and metal compounds.

EVA and MWCNT were melt-mixed in a bench kneader PBV-03 (Irie Shokai, Japan) at 110°C for 20 min (20 rpm). There was no surface treatment for MWCNT and various contents (phr) of MWCNT were used based on the amount of EVA. Then, the obtained EVA/MWCNT nanocomposites were mixed with chemical blowing agent and crosslinking agent in a two roll-mill at 105°C. After mixing in a two roll-mill the mixture was put in a mold and the foams were obtained by compression-molding at 14.7 MPa, in a hydraulic press at 155°C for 40 min. After removal of the pressure, expansion takes place immediately. For comparison purpose, EVA foam without MWCNT was also prepared by the same method.

Foam testing

The surface resistivity was measured on compression molded foams (sample dimensions: 110 \times 180 \times 18 mm³) using a MAXCON MAX-812 m (Maxcone, Korea). To investigate the cell structure of foams, the cross sections of the EVA/MWCNT nanocomposite foams were cryogenically microtomed and were examined with FE-Scanning Electron Microscope

(HITACHI S-4200, Japan). To investigate the dispersion of MWCNT, Transmission electron microscopy (TEM) images were taken from cryogenically microtomed ultra thin sections using EF-TEM (EM 912 Omega, Carl Zeiss, Germany).

A Universal Testing Machine (Model 4466, Instron Co., USA) was used to obtain the tensile properties of the foams at room temperature. The crosshead speed was 500 mm/min. Also the tear strength was measured using unnicked 90° angle test pieces at a cross head speed of 500 mm/min in the Universal Testing Machine. All measurements were performed for five replicates of dog-bone shaped specimens and averaged to get the final result. The density of the foam was measured by a buoyancy method using a gravimeter (Ueshima MS-2150, Japan). Compressions set measurements were performed according to ASTM D395. The foams were compressed by 50% for 6 h at 50°C and then the pressure was removed and the foam was allowed to recover for 30 min at ambient temperature. The final sample thickness was measured and the compression set was calculated using the following equation.

$$\text{Compression set (\%)} = [(T_o - T_f)/(T_o - T_s)] \times 100 \quad (1)$$

T_o = Original sample thickness; T_f = Final sample thickness; T_s = spacer thickness.

Compression set is the reduction in thickness after a material is aged in compression. The lower the compression set is, the better the elastic recovery of the foam. Compression set is a very important property for the application of foams.

RESULTS AND DISCUSSION

Figure 1 shows typical SEM images of the cellular structure of the EVA foam and EVA/MWCNT

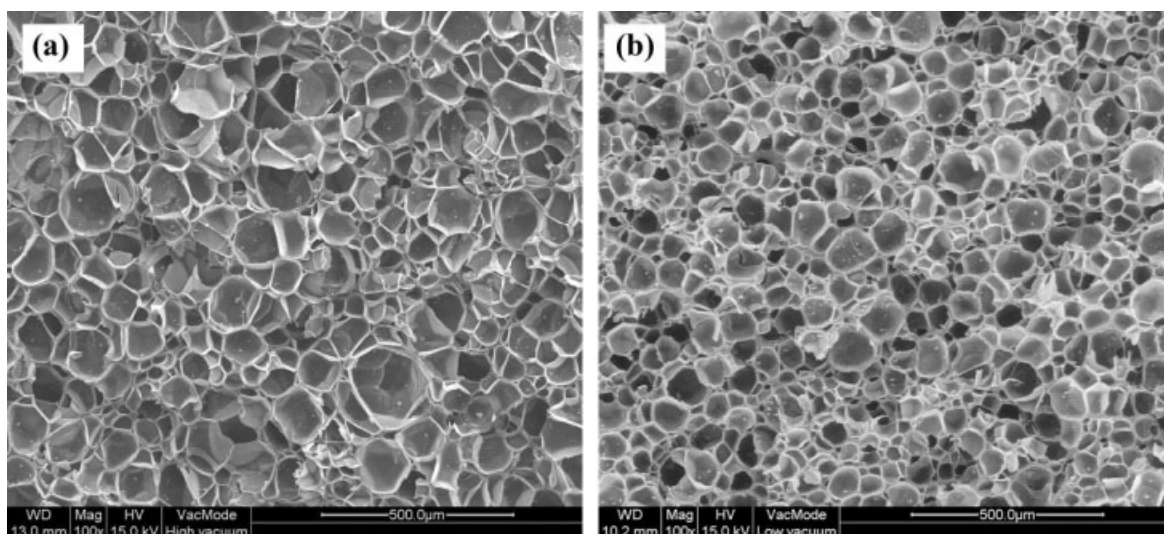


Figure 1 SEM photographs: (a) EVA foam, (b) EVA/MWCNT nanocomposite foam.

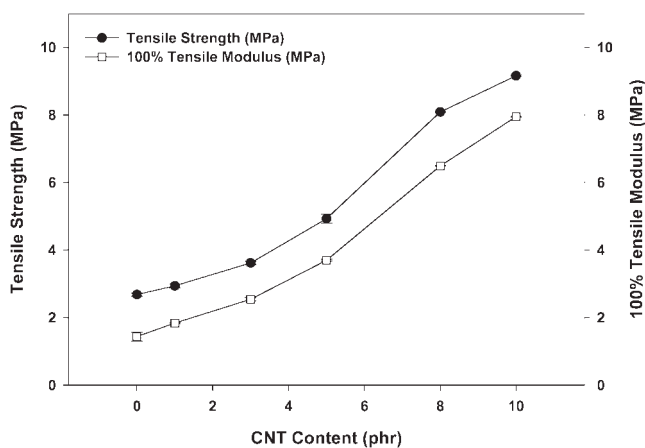


Figure 2 Tensile strength and 100% tensile modulus of EVA/MWCNT nanocomposite foam with MWCNT content.

nanocomposite foam. The EVA foams and nanocomposite foams have a closed-cell structure. Generally the residues of chemical blowing agent act as nucleating agents. Similarly, MWCNT can provide nucleating sites in the heterogeneous nucleating process. More nucleation sites are available in EVA/MWCNT nanocomposite foams than in EVA foams. As a result, EVA/MWCNT nanocomposite foams have smaller cell size than EVA foams.

The mechanical properties of EVA/MWCNT nanocomposite foams are shown in Figures 2–4. A remarkable increase in the mechanical properties is observed for the EVA/MWCNT foams. With increasing content of MWCNT, all the mechanical properties investigated improve except elongation at break. There is a significant increase in the mechanical properties at 5 phr of MWCNT. The tensile and tear strength of EVA/MWCNT foams at 5 phr is 1.7 times and 2.5 times greater than those of EVA foam, respectively. An improvement of 260% is observed in 100% tensile modulus over that of EVA foam. There is a decrease in elongation at break. Generally, improve-

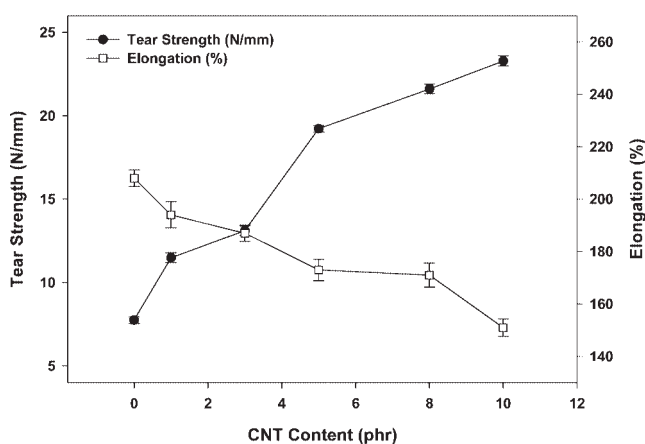


Figure 3 Tear strength and elongation at break of EVA/MWCNT nanocomposite foam with MWCNT content.

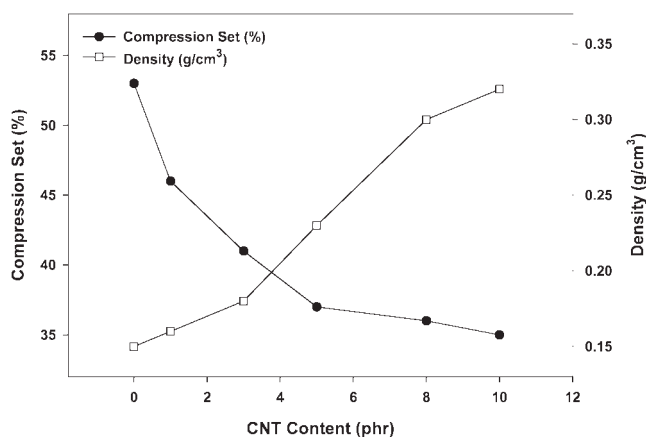


Figure 4 Compression set and density of EVA/MWCNT nanocomposite foam with MWCNT content.

ments in tensile strength and modulus are coupled with a reduction in elastic recovery in composites. This is also true for clay/elastomer nanocomposites.^{24,25} This is particularly problematic for the elastomer applications such as tire, seals, O-rings, etc. However, in this study, the addition of MWCNT in EVA nanocomposite foams leads to the improved elastic recovery of the EVA/MWCNT foams deduced from the compression set measurements in addition to the reinforcing effect. The compression set of EVA/MWCNT foams at 5 phr of MWCNT is improved by 30% compared with EVA foams. This mechanical enhancement may be due to the strong and (resilient) flexible MWCNT and/or the increased density. As the addition of MWCNT leads to the higher melt viscosity during foam processing, density of EVA/MWCNT foams increases with addition of MWCNT. Several researchers have reported reversible bending of CNT.^{14,26–28} However, as far as we know, this work is the first observation of improvement of elastic recovery of polymer nanocomposite foams by addition

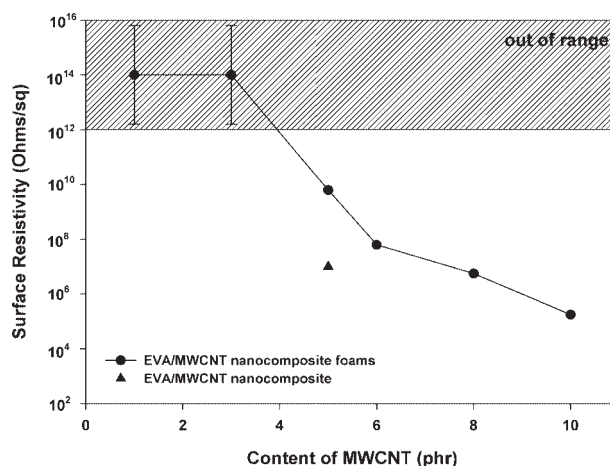


Figure 5 Surface resistivity of EVA/MWCNT nanocomposite foam with MWCNT content.

of MWCNT. This result may have significant implications toward the elastomer applications of polymer/MWCNT nanocomposites.

To be used for static dissipative applications, the surface resistivity of the polymer/MWCNT nanocomposites is in the range 10^5 – 10^{12} Ω /square, and preferably 10^8 Ω /square. The surface resistivity was measured on the compression molded foams (sample dimensions: $110 \times 180 \times 18$ mm³). Figure 5 shows the effect of MWCNT content on the surface resistivity of foams. The surface resistivity range in our experimental set-up is limited to values below 10^{12} Ω /square. At 1 and 3 phr of MWCNT, the surface resistivity of EVA/MWCNT nanocomposite is out of our measurement range (above 10^{12} Ω /square). At 5 phr, the surface resistivity begins to decrease and the mechanical properties improve significantly. EVA/MWCNT nanocomposites with 5 phr MWCNT displays slightly lower surface resistivity than the nanocomposite foams.

To investigate the surface effect on the surface resistivity of EVA/MWCNT foams with 5 phr MWCNT, 1-mm surface layer was removed from the sample using skiving machine. Then, the surface resistivity of the sample was measured and its surface resistivity is out of our measurement range (above 10^{12} Ω /square). However, for the foams with 8 and 10 phr MWCNT, when 1-mm surface layer was removed using skiving machine, the surface resistivity of sample is within our measurement range. Figure 6 shows the increase of surface resistivity of nanocomposite foams (8 and 10 phr MWCNT) with increasing thickness of removed surface layers. According to TEM images (Fig. 7), the length of MWCNT in the surface layer (thickness: 1 mm) which was removed from sample by skiving machine is much longer than the length of MWCNT in the remaining sample. Short MWCNTs are indicated by circles in Figure 7. This might contribute to

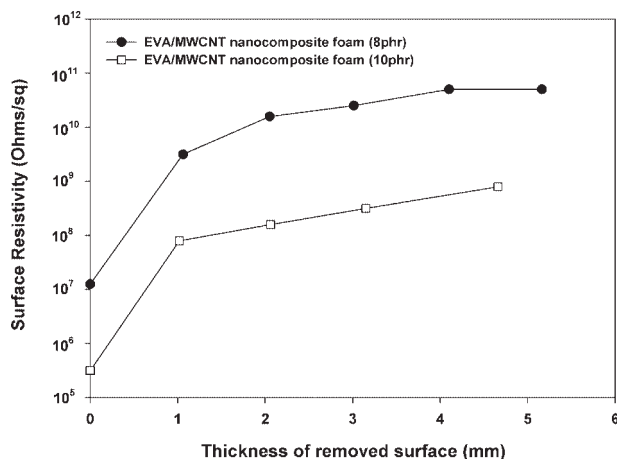


Figure 6 Surface resistivity of EVA/MWCNT nanocomposite foam (8 and 10 phr MWCNT) with increasing thickness of removed surface layers.

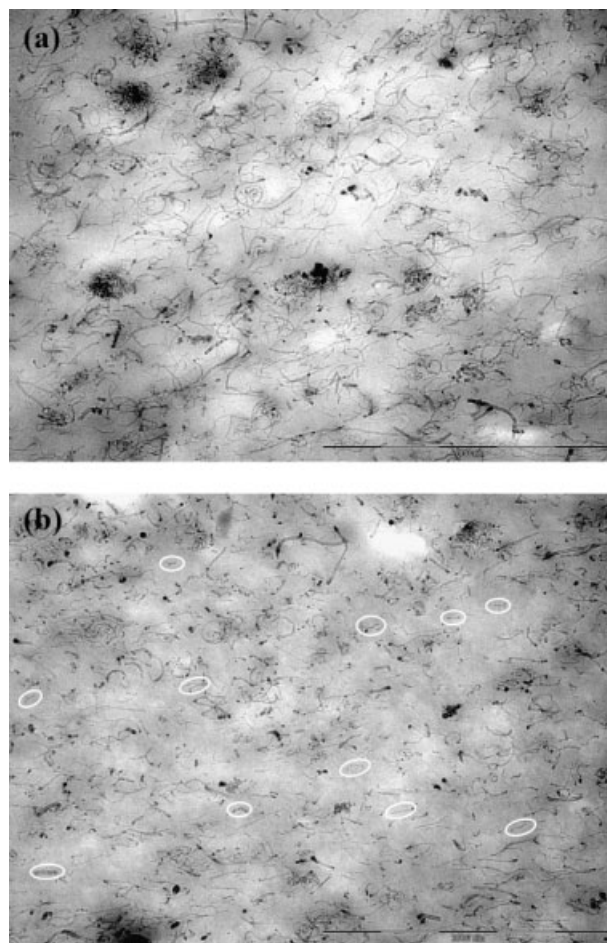


Figure 7 TEM photographs of EVA/MWCNT nanocomposite foam: (a) surface layer (thickness: 1 mm) which was removed from sample by skiving machine (b) remaining sample.

the lower surface resistivity of surface layer. Also, TEM photographs showed very uniform dispersion of CNT in the samples and surface resistivity was uniform over the sample surface.

CONCLUSIONS

A remarkable increase of the mechanical properties is observed for the EVA/MWCNT foams. In this study the addition of MWCNT in EVA nanocomposite foams leads to the improved elastic recovery of the EVA/MWCNT foams deduced from the compression set measurements, in addition to the reinforcing effect. As far as we know, this work is the first observation of improvement of elastic recovery of polymer nanocomposite foam by addition of MWCNT. This result may have significant implications toward the elastomer applications of polymer/MWCNT nanocomposites. At 5 phr of MWCNT, the surface resistivity of nanocomposite foams begins to decrease and their mechanical properties improve significantly. The increase of surface resistivity of nanocomposite

foams with 8 and 10 phr MWCNT was observed with increasing thickness of removed surface layers. The length of MWCNT in the surface layer which was removed from sample by skiving machine is much longer than the length of MWCNT in the sample. This might have contributed to the lower surface resistivity of the surface layer.

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