Improvement of Tensile Properties and Elastic Recovery in Ethylene Vinyl Acetate Copolymer/Multiwalled Carbon Nanotube Nanocomposite Foams

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Received 1 November 2010; accepted 19 January 2011
DOI 10.1002/app.34185
Published online 12 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, ethylene vinyl acetate (EVA) copolymer/multiwalled carbon nanotube (MWCNT) nanocomposite foams were prepared to improve tensile properties without sacrificing elongation at break and compression set of EVA foams by using melt compounding method, the most compatible with current industrial applications. Without any modification of MWCNT and special treatment, a significant improvement of the mechanical properties including elastic recovery was observed for the EVA/MWCNT foams with only 1 phr MWCNT. Improvement of tensile strength and modulus without sacrificing elongation at break and elastic recovery of EVA/MWCNT foams with 1 phr MWCNT may have significant implications toward the elastomeric applications. Cell size and cell density of EVA and EVA/MWCNT foams were also investigated for various content of dicumyl peroxide. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3696–3701, 2011

Key words: nanocomposites; compounding; mechanical properties; carbon nanotube

INTRODUCTION

Because of the advantage of their light weight, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction, the markets for foams have been growing rapidly worldwide such as the automotive, packaging, construction, marine, sports, and leisure markets. Ethylene vinyl acetate (EVA) copolymer foams are extensively used for various purposes, especially for the fabrication of midsole, a layer that lies between insole and outsole of running shoes. High melt strength is required in the foaming to enhance the resistance of the cellular material to thermal collapse. The high melt strength can be achieved by crosslinking EVA with dicumyl peroxide (DCP).

Generally, addition of fillers into elastomers leads to the improvements in tensile strength and modulus coupled with a reduction in elastic recovery and elongation at break. However, there is a strong demand to improve tensile strength and modulus without sacrificing elastic recovery and elongation at break in industrial and commercial applications of foams.

Recently, carbon nanotube (CNT)-based polymer nanocomposites have attracted considerable attention from both fundamental research and application of view due to the unique combination of mechanical, electrical, and thermal properties of CNT. There are some reports about clay-based polymer nanocomposite foams,[1–10] but there are few studies about CNT-based polymer nanocomposite foams. The polymer nanocomposite foams are one of the latest technologies in polymer foam fields.

In this study, our purpose was to improve tensile strength and modulus without sacrificing elongation at break and compression set of EVA foams using multiwalled carbon nanotube (MWCNT). Since CNT has high strength and exceptional resilience, CNT can be deformed to large strain without permanent deformation.[11,12] Because melt compounding method is the most compatible with current industrial practices, melt compounding method is used to mix EVA copolymer and MWCNTs. And then EVA/MWCNT foams were obtained by compression molding.

EXPERIMENTAL

Materials and foam preparation

EVA having 22% vinyl acetate content was provided by Hanwha (Seoul, Korea). MWCNTs were synthesized by thermal CVD method. According to the provider (CNT CO., Incheon, Korea), typical tube diameters were in the range 10–50 nm with tube

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Contract grant sponsors: Dongseo University.

lengths of 1–25 μm. MWCNTs (purity: 95%) were used as received because MWCNTs without surface modification were competitive in cost for industrial applications. DCP provide by Akzo Nobel (Amsterdam, Netherlands) was used as a crosslinking agent. The chemical blowing agent used was azodicarbonamide-based blowing gas release system (JTR-M, Kum Yang, Busan, 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, Tokyo, Japan) at 110°C for 20 min (20 rpm). Since the addition of <1 phr (parts per hundred rubbers) MWCNT led to the insignificant improvement of tensile properties in our preliminary study, 1 phr MWCNT was mixed based on the amount of EVA. Then, the obtained EVA/MWCNT mixtures were mixed with chemical blowing agent (5 phr) and various content of 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 took place immediately. For comparison purpose, EVA foams without MWCNT were also prepared using various content of DCP by the same method.

Foam testing

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. The tensile properties were measured according to ASTM D412. Also, the tear strength was measured using unnicked 90° angle test pieces at a crosshead speed of 500 mm/min in the Universal Testing Machine (ASTM D624). All measurements were performed for five replicates of specimens and averaged to get the final result. The rebound resilience was measured according to DIN 53512. The sample was placed in the sample holder and the pendulum was released from a horizontal position. The pendulum rebounded after impacting the sample and the angle of rebound was read. Since the scale is graduated into 100 equal divisions, the percent rebound resilience is read directly from the scale.

The densities of the foams were 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. The spacer thickness is the thickness to which the sample is compressed at the beginning of the test, which is 50% of the original sample thickness.

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

where T_o is the original sample thickness, T_f the final sample thickness, and T_s the 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.

Compression load-deflection measurements were performed using a Universal Testing Machine fitted with a compression jig. Test samples were compressed up to 50% of their original thickness at crosshead speed of 10 mm/min. The gel fraction was measured by extraction in boiling xylene for 72 h using a Soxhlet extractor, until the sample attained a constant weight. The gel fraction was calculated using the following equation.

$$\text{Gel fraction} = (W_2 - W_0)/(W_1 - W_0) \quad (2)$$

where W_0 is the weight of MWCNT in the sample, W_1 the initial weight of the sample, and W_2 the weight of the insoluble portion.

To investigate cellular structure, the cross-sections of the EVA and EVA/MWCNT foams were cryogenically microtomed and were examined with field emission gun-scanning electron microscope (SEM, FEI Quanta 200, USA). About 700 cells in each SEM image were analyzed to obtain the average cell size and cell density. The cell size was determined by measuring the maximum diameter of each cell. The cell density (N_f), the number of cells per unit volume, is determined from eq. (3)[13]:

$$N_f = (nM^2/A)^{3/2} \quad (3)$$

where n is the number of cells on the SEM micrograph, M the magnification factor, and A the area of the micrograph (cm^2).

RESULTS AND DISCUSSION

Figures 1 and 2 show the effect of DCP content on the tensile and tear strength of EVA and EVA/MWCNT foams, respectively. The tensile strength of EVA and EVA/MWCNT foams increases with increasing content of DCP. This increase is due to the increased crosslinking density. The tensile and tear strength of EVA/MWCNT foams are higher than those of EVA foams. Figure 3 shows 100%

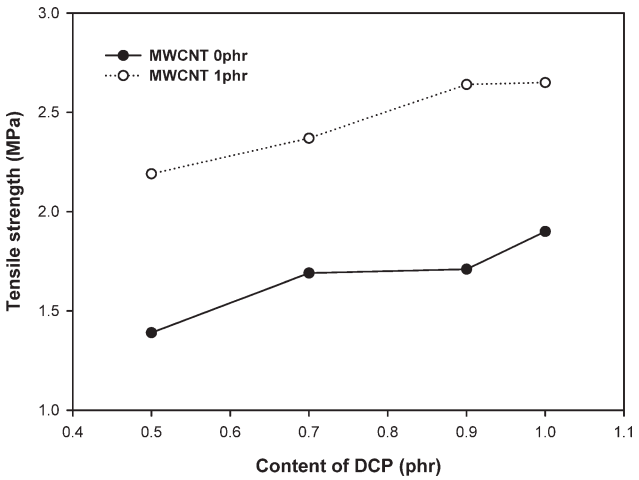

Figure 1 Effect of DCP content on the tensile strength of EVA and EVA/MWCNT foams.

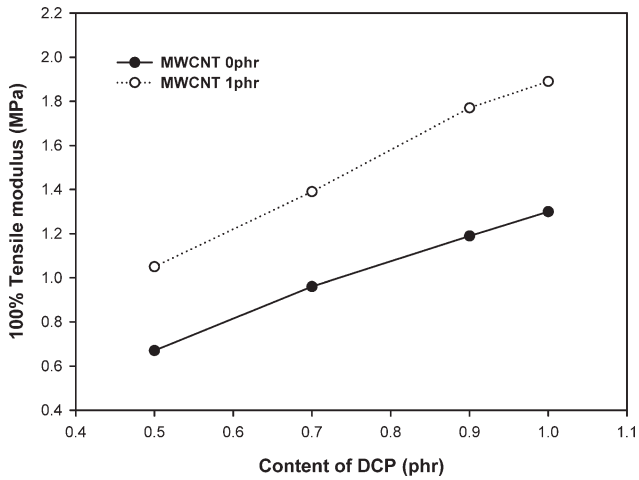

Figure 3 Hundred percent tensile modulus of EVA and EVA/MWCNT foams.

tensile modulus of EVA and EVA/MWCNT foams. Hundred percent tensile modulus of EVA/MWCNT foams is higher than that of EVA foams. About 50% improvement in tensile strength, tear strength, and 100% tensile modulus is observed with addition of 1 phr of MWCNT into EVA matrix. The densities of EVA and EVA/MWCNT foams prepared in this study are about 1.2–1.3.

Generally, in polymer composites, tensile strength and modulus increase with addition of fillers, but their elongation at break decreases.[14,15] The lower elongation at break leads to poor energy absorption characteristics. Therefore, there is a demand to improve tensile strength and modulus without sacrificing elongation at break. The elongation at break of EVA/MWCNT foams is higher than that of EVA foams as shown in Figure 4. Therefore, EVA/MWCNT foams with 1 phr MWCNT can achieve the improvement of both tensile strength and elongation at break.

The addition of strong MWCNTs into the matrix leads to increased tensile strength and modulus. Since both tensile strength and elongation at break increase with addition of 1 phr MWCNT, the toughness of EVA/MWCNT foams improves. This toughness improvement could be due to the higher flexibility and deformability of the MWCNTs in the matrix. CNTs have been reported to be able to elastically deform under relatively large stress, leading to highly energy absorbing process.[16–18]

Figures 5 and 6 show the effect of DCP content on the compression set and rebound resilience of EVA and EVA/MWCNT foams. Compression set is the reduction in thickness after a material is aged in compression. The lower the compression set value is, the better the elastic recovery of the foam. With increasing content of DCP, the compression set of the EVA and EVA/MWCNT foams decreases. This decrease is due to the increased crosslinking density.

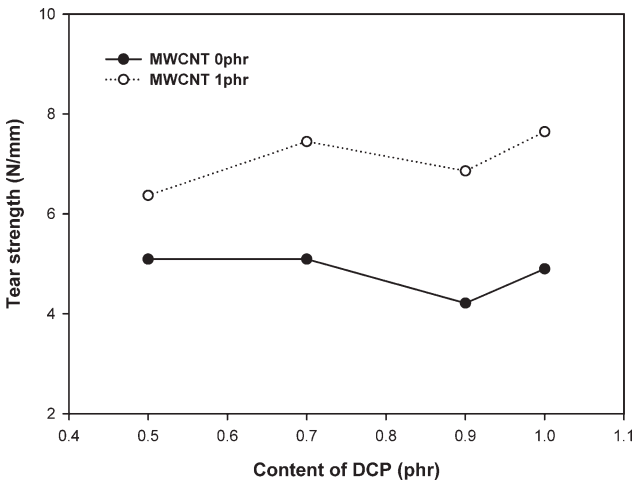

Figure 2 Effect of DCP content on the tear strength of EVA and EVA/MWCNT foams.

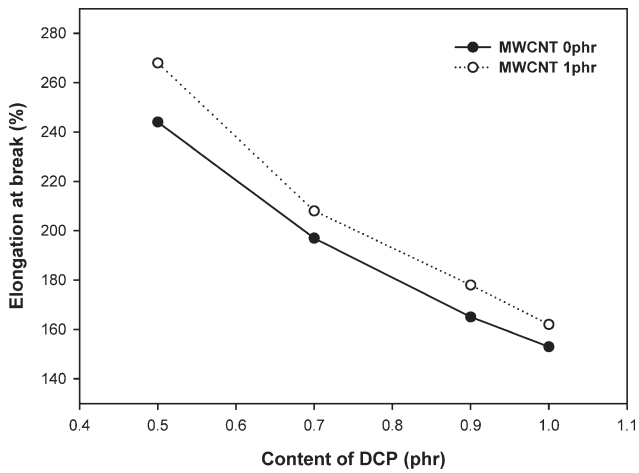

Figure 4 Elongation at break of EVA and EVA/MWCNT foams.

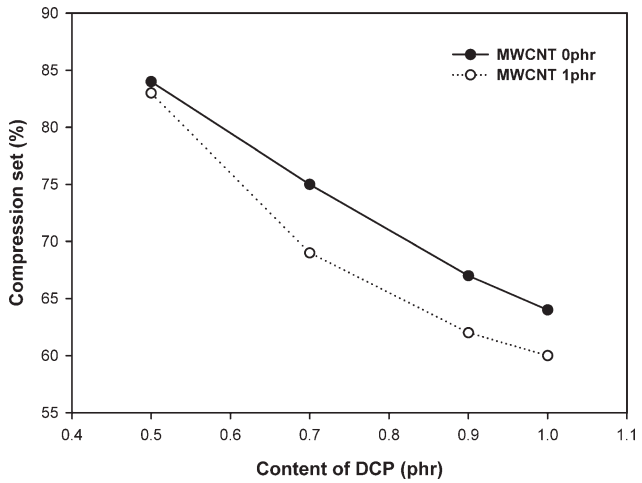

Figure 5 Effect of DCP content on the compression set of EVA and EVA/MWCNT foams.

The compression set of EVA/MWCNT foams is lower than EVA foams. Generally, improvements in tensile strength and modulus are coupled with a reduction in elastic recovery in polymer composites.

However, the addition of MWCNT into EVA foams leads to the improved elastic recovery of the EVA/MWCNT foams deduced from the compression set measurement in this study. This result is also confirmed by higher rebound resilience of EVA/MWCNT foams than EVA foams. The percent rebound resilience measured is inversely proportional to the hysteretic loss. The higher rebound resilience value is, the better the elastic recovery of the foam. Since elastic recovery is a very important property in elastomer applications, improvement of tensile strength and modulus without sacrificing elastic recovery of EVA/MWCNT foams may have significant implications toward the elastomeric applications.

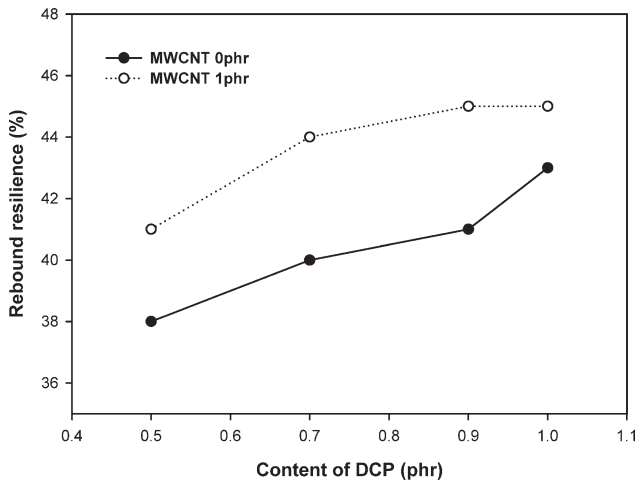

Figure 6 Effect of DCP content on the rebound resilience of EVA and EVA/MWCNT foams.

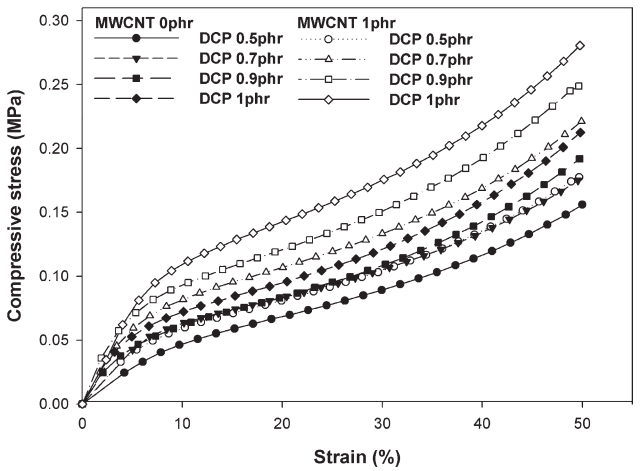

Figure 7 Effect of DCP content on the compressive stress–strain curves of EVA and EVA/MWCNT foams.

Figure 7 shows the effect of DCP content on the compressive stress–strain curves of EVA and EVA/MWCNT foams. Since foams are generally under the compressive stress during use, compressive stress is a very important property for the application. At 50% strain, compressive strength of EVA/MWCNT foams is higher than that of EVA foams with the same content of DCP. Interestingly, the difference in compressive strength between EVA/MWCNT and EVA foams increases with increasing content of DCP. Table I shows the volume expansion ratio of EVA and EVA/MWCNT foams. Expansion ratio was calculated as the ratio of the unfoamed sample density to the foamed sample density. The expansion ratio of EVA/MWCNT foams is smaller than that of EVA foams with the same content of DCP. The smaller expansion ratio of EVA/MWCNT foams is due to the higher melt viscosity of the materials during foam processing. The difference in the expansion ratio between EVA/MWCNT and EVA foams increases with increasing content of DCP. Since mechanical properties are inversely proportional to the expansion ratio, the increased difference in the expansion ratio may lead to the increased difference in the compressive strength between EVA/MWCNT and EVA foams.

According to this study, significant improvement of mechanical properties was obtained for EVA/

TABLE I
Volume Expansion Ratio

	Volume expansion ratio			
Materials	DCP 0.5 phr	DCP 0.7 phr	DCP 0.9 phr	DCP 1 phr
EVA foam	8.03	7.63	7.33	7.27
EVA/MWCNT foam	7.83	7.32	6.95	6.87

TABLE II
Gel Fraction

Materials	Gel fraction (%) DCP 0.5 phr	DCP 0.7 phr	DCP 0.9 phr	DCP 1 phr
EVA foam	73	80	84	85
EVA/MWCNT foam	70	78	82	82

MWCNT foams with only 1 phr MWCNT. Since this improvement could be due to not only strong MWCNTs but also the increased gel fraction of the foams with addition of the 1 phr MWCNT, gel fraction of EVA and EVA/MWCNT foams was investigated for the various content of DCP (Table II). With increasing DCP content, the gel fraction increases. However, there is no significant difference in gel fraction between EVA and EVA/MWCNT foams with same DCP content. Therefore, the improvement of mechanical properties is not due to the increased gel fraction of EVA/MWCNT foams.

Since the mechanical properties are strongly affected by cell size, cell size of EVA and EVA/MWCNT foams was investigated for various content of DCP. Figure 8 shows typical SEM images of the cellular structure of the EVA and EVA/MWCNT foams. The EVA and EVA/MWCNT foams have a closed-cell structure. Figure 9 shows the average cell size and cell density of the foams. With increasing content of DCP, the average cell size decreases and the average cell density increases. The decrease of average cell size is due to the higher melt viscosity of the materials during foam processing. The melt viscosity increases with increasing crosslinking density. The increase in the melt viscosity may restrain growth of cells and their coalescence, leading to the decrease of average cell size.

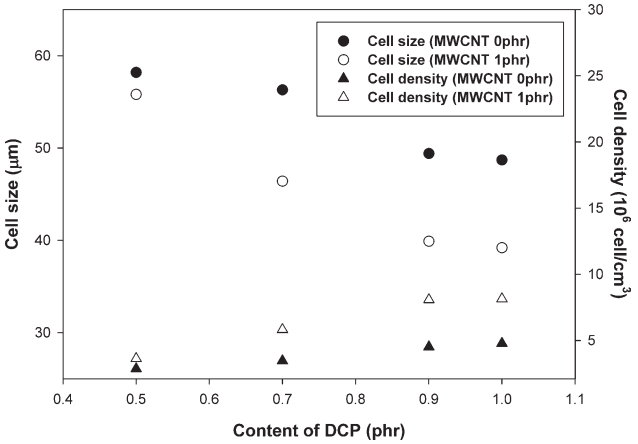

Figure 9 Average cell size and cell density of the EVA and EVA/MWCNT foams.

Generally, the residues of chemical blowing agent act as nucleating agents. Similarly, MWCNT can provide nucleating sites in the heterogeneous nucleating process.[13] In the heterogeneous nucleating process, cell nucleation took place in the boundary between the matrix polymer and the dispersed filler particles. More nucleation sites are available in EVA/MWCNT foams than in EVA foams. As a result, EVA/MWCNT foams have smaller cell size and higher cell density than EVA foams. Also, another possible reason for smaller cell size in EVA/MWCNT foams is the increase in melt viscosity by addition of MWCNTs.

Total cell volume is proportional to the expansion ratio. The expansion ratio of EVA/MWCNT foams is smaller than that of EVA foams with the same content of DCP (Table I). Therefore, smaller cells result in smaller total cell volume in this study. Since mechanical properties are inversely proportional to the expansion ratio, the significant improvement of mechanical properties of EVA/MWCNT foams

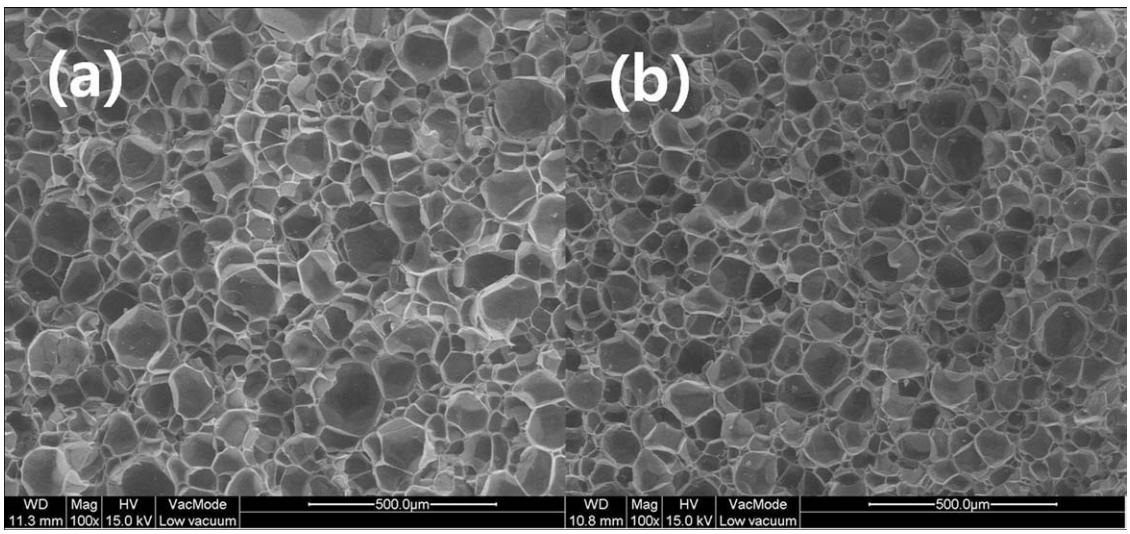

Figure 8 SEM images of cross-sections of (a) EVA foams (DCP: 1 phr) and (b) EVA/MWCNT foams (DCP: 1 phr).

could be due to not only strong MWCNT but also smaller total cell volume of EVA/MWCNT foams.

CONCLUSIONS

A significant improvement of the mechanical properties was observed for the EVA/MWCNT foams with only 1 phr MWCNT. Both tensile strength and elongation at break increase with addition of 1 phr MWCNT. Therefore, the toughness of EVA/MWCNT foams improves. This toughness improvement could be due to the higher flexibility and deformability of the MWCNTs in the matrix. Also, improvement of tensile strength and modulus without sacrificing elastic recovery of EVA/MWCNT foams with 1 phr MWCNT may have significant implications toward the elastomeric applications. It is noteworthy that this improvement of mechanical properties was obtained without any modification of MWCNT and special treatment. EVA/MWCNT foams have smaller cell size and higher cell density than EVA foams.

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