

# Effect of Compatibilizer and Silane Coupling Agent on Physical Properties of Ethylene Vinyl Acetate Copolymer/Ethylene-1-Butene Copolymer/Clay Nanocomposite Foams

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**ABSTRACT:** In this study an attempt was made to obtain lower density of ethylene-vinyl acetate copolymer (EVA)/ethylene-1-butene copolymer (EtBC) foams without sacrificing mechanical properties. For this purpose EVA/EtBC/clay nanocomposite foams were prepared. To investigate the effect of compatibilizer and silane coupling agent on the physical properties of the EVA/EtBC/clay foams, maleic anhydride-grafted EtBC (EtBC-g-MAH) and the most commonly used silane coupling agent in rubbers, bis(3-triethoxysilylpropyl) tetrasulfide (Si-69) were used in the preparation

of EVA/EtBC/clay nanocomposite foams. The formation of EVA/EtBC/clay nanocomposite foams was supported by X-ray diffraction results. And, using a compatibilizer and silane coupling agent, lower density of EVA/EtBC/clay nanocomposite foams were obtained without sacrificing mechanical properties except compression set. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3259–3265, 2006

**Key words:** nanocomposites; clay; mechanical properties; compatibility; density

## INTRODUCTION

Because of the advantage of their low density, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction, the markets for foams have been growing rapidly worldwide. Polymer foams are widely used in construction, transportation, sports, packaging, medical devices, and agriculture.

Ethylene-vinyl acetate copolymer (EVA) foams are extensively used for various purposes. Especially, EVA foams are very popular in many athletic and casual shoes, for the fabrication of midsole, layer that lies between insole and outsole of running shoes.<sup>1</sup> Recently, to increase the physical properties of EVA foams such as tensile strength, rebound resilience, and compression set, ethylene-1-butene copolymer (EtBC) has been blended with EVA. In the application of foams, low density is highly desirable. Usually lower density can be obtained with more blowing agent. However, the mechanical properties of foams also decrease with lower density. In this study, our purpose

is to obtain low density EVA/EtBC foams without sacrificing the mechanical properties through popular and friendly means.

In recent years, clay-based polymer nanocomposites have attracted considerable attention from both fundamental research and applications point of view because of their remarkable improvement in materials properties. Owing to the nanometer dimension thickness and extremely high aspect ratio of silicate layers, these nanocomposites exhibit dramatic improvements in the mechanical, thermal, and barrier properties.<sup>2–5</sup>

EVA/clay nanocomposites were successfully prepared by melt intercalation method and their mechanical properties were improved.<sup>6–11</sup> Therefore, a possible method to obtain lower density of EVA/EtBC foams without sacrificing mechanical properties is to add clay to the EVA/EtBC foams. However, until now there has been very little information available regarding EVA/EtBC/clay nanocomposite foams. EtBC, being a hydrophobic polymer like polypropylene, polyethylene, etc., is expected to find difficulty in dispersing clay thus forming nanocomposites. Thus to overcome this problem maleic anhydride-grafted EtBC (EtBC-g-MAH) was used as a compatibilizer in this study to improve the compatibility between polymer and clay and consequently the improvement of mechanical properties. In addition to the incorporation of EtBC-g-MAH, one more

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**TABLE I**  
**Important Characteristics of the Materials used in this Study**

Class of materials	Materials	Supplier	Characteristics
Polymer	Ethylene vinyl acetate copolymer (EVA)	HYUNDAI, Korea	VA content (%), 18% Melt Index (g/10 min), 2.2 Density (g/cm <sup>3</sup> ), 0.935
	Ethylene-1-butene copolymer (EtBC)	Mitsui Chemical Inc., Japan	ML1+4 (100°C), 40; Density, 0.91 g/cm <sup>3</sup>
	EtBC-g-MAH	Dupont, USA	Melt Index (g/10 min), 3.7 Density, 0.88 g/cm <sup>3</sup>
Clay	Cloisite Na <sup>+</sup>	Southern Clay, USA	Modifier concentration, 0 mequiv/100 g
Blowing agent	JTR-M	Kumyang, Korea	Decomposition temperature, 142–148°C, gas volume, 165 mL/g
Crosslinking agent	Dicumyl Peroxide	Akzo Nobel, Netherlands	
Coupling agent	Si-69	Degussa, Germany	
Crosslinking coagent	Zinc Oxide	Gil-Chun Chem., Korea	
	Stearic acid	LG Chem., Korea	

efficient way of increasing compatibility, the surface treatment of filler by silane coupling agents<sup>12–14</sup> has been applied here.

To investigate the effect of the compatibilizer and the silane coupling agents on the physical properties of the EVA/EtBC/clay foams, EtBC-g-MAH and the most commonly used silane coupling agent in rubbers, bis(3-triethoxysilylpropyl) tetrasulfide (Si-69), were used in the preparation of EVA/EtBC/clay nanocomposite foams.

## EXPERIMENTAL

### Materials and foam preparation

Names and important characteristics of the materials used in this study are summarized in Table I. Unmodified montmorillonites were purchased from Southern Clay Products (USA) under the trade name of Cloisite Na<sup>+</sup>. EVA/EtBC masterbatch is the blend of EVA and EtBC (70/30) provided by local compounding company. The recipes of the EVA/EtBC masterbatch are described in Table II.

EVA/EtBC masterbatch, clay, compatibilizer, and Si-69 were mixed in a Haake internal mixer at 110°C for 10 min. Then the obtained EVA/EtBC hybrids were mixed with chemical blowing agent and crosslinking agent in a two-roll mill. The recipes of the compounds are described in Table III. Cloisite Na<sup>+</sup> and DCP (crosslinking agent) content was fixed at 3 and 0.7 phr, respectively, based on the total amount of EVA/EtBC materbatch. The chemical blowing agent used was azodicarbonamide-based blowing gas release system (JTR-M). Azodicarbonamide is odorless and easily dispersed. It is activated by organic acids, bases, and metal compounds. The content of the blowing agent (3–5.5 phr) was adjusted for a wide range of foam density.

After mixing in a two-roll mill the mixture was put in a mold and the foams were obtained by compression-molding. The mixture was pressed at 14.7 MPa, in a hydraulic press at 155°C for 40 min, respectively. After removal of the pressure, expansion takes place immediately. Then the obtained foams were left at room temperature for at least 24 h before any sample preparation. All of the skin is removed from the foam before testing.

### Foam testing

X-ray diffraction (XRD) studies were conducted by a Rigaku D/max 2200H X-ray diffractometer (40 kV, 50 mA). The scanning rate was 0.5°/min. The basal spacing of the silicate layer,  $d$ , was calculated using the Bragg's equation,  $n\lambda = 2d \sin\theta$ . To investigate cellular structure, the cross sections of the EVA/EtBC-based foams were microtomed at low temperature and were examined with scanning electron microscope (JEOL JSM-35CF). Transmission electron microscopy (TEM) images were taken from cryogenically microtomed ultra thin sections using EF-TEM (EM 912 Omega, Carl Zeiss, Germany). ATR-FTIR was carried out in a JASCO 6200 FTIR spectrophotometer with resolution of 4 cm<sup>-1</sup>.

Density of the foam was measured by a buoyancy method using a gravimeter (Ueshima, MS-2150). In

**TABLE II**  
**Composition (in phr) of the EVA/EtBC Masterbatch**

Materials	Content (phr)
EVA	70
Ethylene-1-butene copolymer (EtBC)	30
Zinc oxide	3
Stearic acid	1

TABLE III  
Recipes (in phr) of the Foam Compounds

Materials	Code			
	EVA/EtBC	EVA/EtBC/ Cloisite Na <sup>+</sup>	EVA/EtBC/ Cloisite Na <sup>+</sup> /EtBC-g-MAH	EVA/EtBC/Cloisite Na <sup>+</sup> /EtBC-g-MAH/Si-69
EVA/EtBC masterbatch	100	100	100	100
EtBC-g-MAH			5	5
Cloisite Na <sup>+</sup>		3	3	3
JTR-M	3-5	4-4.5	4-5.5	4-5.5
DCP	0.7	0.7	0.7	0.7
Si-69				0.05

the measurement the samples used are  $1 \times 1 \text{ cm}^2$  of area and the thickness 1 cm and density was determined by averaging the density of five samples. The samples were automatically weighed first in air. Then they were automatically weighed in water. The density of the foam was determined using Archimedes' principle.

A Universal Testing Machine (Model 4466, Instron MA, USA) was used to obtain the tensile strength of the foams 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. 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.

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.

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

where  $T_o$  is the original sample thickness;  $T_f$ , the final sample thickness;  $T_s$ , the spacer thickness.

## RESULTS AND DISCUSSION

### Characterization of nanocomposite foams

Figure 1 shows the XRD patterns of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam and EVA/EtBC/Cloisite Na<sup>+</sup> foam. For EVA/EtBC/Cloisite Na<sup>+</sup> foam, peak appeared at 1.5 nm, and for EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam, peak appeared at 1.6 nm corresponding to (001) plane. The peak at 1.5 nm for EVA/EtBC/Cloisite Na<sup>+</sup> foam and the peak at 1.6 nm for EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam indicate the intercalation of polymer molecules into the interlayers of Cloisite Na<sup>+</sup> resulting in the expansion of the interlayer distance. There-

fore, EVA/EtBC/clay nanocomposite foams are successfully prepared.

The degree of expansion of the interlayer distance for EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH (1.3 nm → 1.6 nm) is higher than that for EVA/EtBC/Cloisite Na<sup>+</sup> (1.3 nm → 1.5 nm). The higher degree of expansion of the interlayer distance for EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam may be due to the intercalation of hydrophobic EtBC into the interlayers of Cloisite Na<sup>+</sup> because of the compatibilizer (EtBC-g-MAH). It is generally believed that hydrophobic polymers such as EtBC can not intercalate into the organoclay without a compatibilizer. For EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH/Si-69 foam, peak (figure is not shown in this article) is observed at 1.6 nm. There is no change in the peak position compared with EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam.

Figure 2 shows typical images of the cellular structure of the EVA/EtBC foams and EVA/EtBC/Cloisite Na<sup>+</sup> nanocomposite foams. EVA/EtBC/Cloisite Na<sup>+</sup> foams have smaller cell sizes than EVA/EtBC foams. Generally the residues of chemical blow-

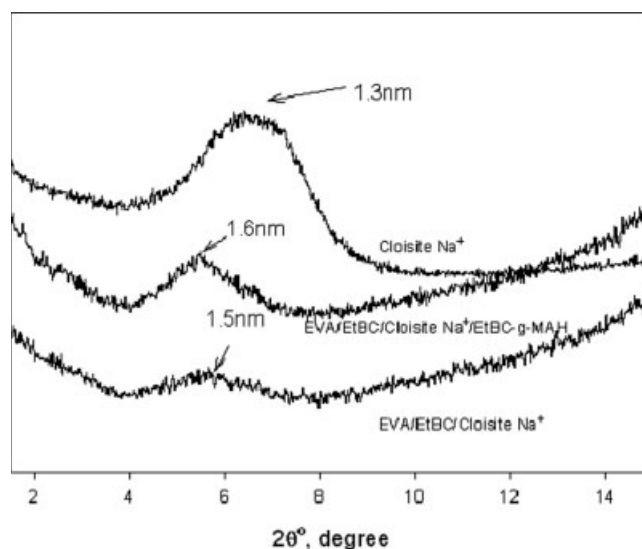
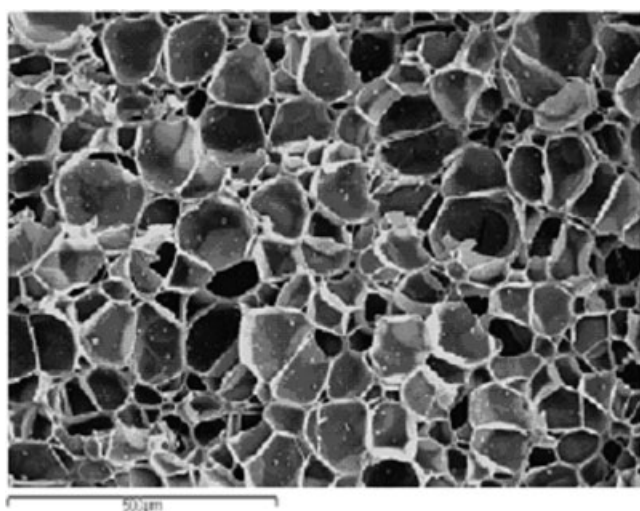
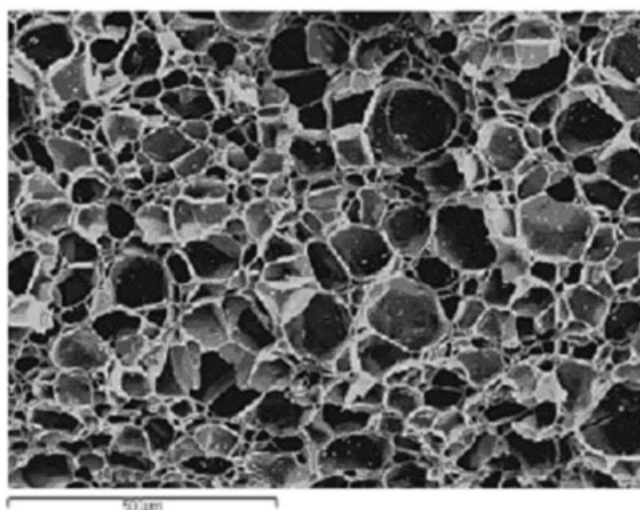


Figure 1 XRD patterns of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam and EVA/EtBC/Cloisite Na<sup>+</sup> foam.





(a)

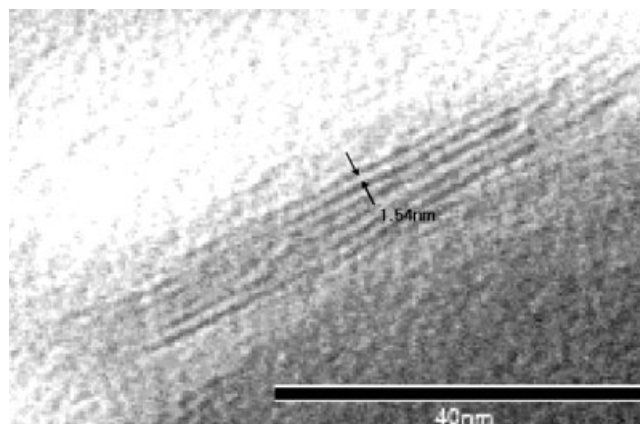


(b)

**Figure 2** Typical SEM images of the cellular structure: (a) EVA/EtBC foam, (b) EVA/EtBC/Cloisite Na<sup>+</sup> foam.

ing agent act as nucleating agents. Similarly, clay can provide nucleating sites in the heterogeneous nucleating process. As a result, more nucleation sites are available in EVA/EtBC/Cloisite Na<sup>+</sup> foams than in EVA/EtBC foams. EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foams and EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH/Si-69 foams showed similar cellular structure of EVA/EtBC/Cloisite Na<sup>+</sup> foams (figure is not shown in this article).

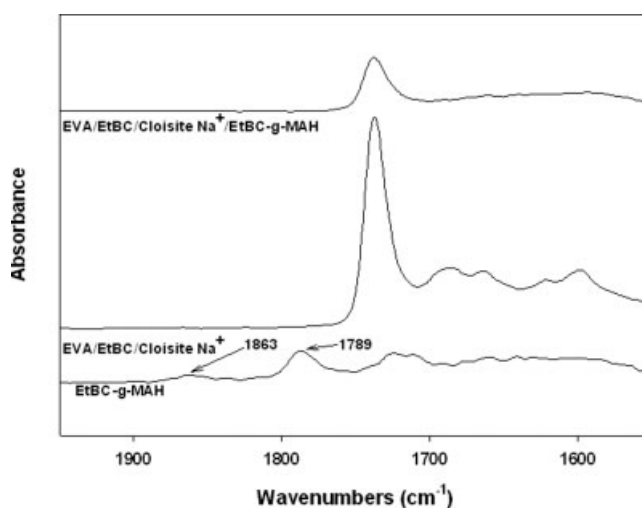
To confirm further the dispersion states of the Cloisite Na<sup>+</sup> in the EVA/EtBC/Cloisite Na<sup>+</sup> foams, TEM studies were carried out. Figure 3 presents the TEM photograph of an ultra-thin section of the EVA/EtBC/Cloisite Na<sup>+</sup> foams exhibiting intercalated morphologies. The dark lines are silicate layers. The original interlayer distance of Cloisite Na<sup>+</sup> is 1.3 nm.



**Figure 3** TEM photograph of an ultra-thin section of EVA/EtBC/Cloisite Na<sup>+</sup> foam.

However, Cloisite Na<sup>+</sup> observed in Figure 3 has  $\sim 1.5$  nm interlayer distance. The larger interlayer distance (1.5 nm) of Cloisite Na<sup>+</sup> than the original interlayer distance of Cloisite Na<sup>+</sup> observed in TEM photograph is due to the intercalation of EVA into the Cloisite Na<sup>+</sup>. The TEM results agree well with XRD results.

Figure 4 shows ATR-FTIR spectra of EtBC-g-MAH film, EVA/EtBC/Cloisite Na<sup>+</sup> foam, and EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam. EtBC-g-MAH film was prepared by compression molding at 155°C for 40 min, which was the same condition used for the foam preparation. Characteristic absorption bands of EtBC-g-MAH appear at 1789 and 1863 cm<sup>-1</sup> due to symmetric and asymmetric vibrations of saturated succinic anhydride groups, respectively. The absorption bands at 1789 and 1865 cm<sup>-1</sup> disappear for



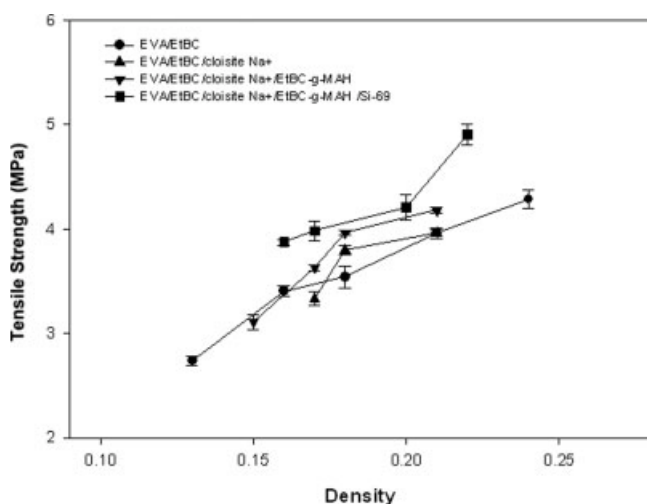
**Figure 4** ATR-FTIR spectra of EtBC-g-MAH film, EVA/EtBC/Cloisite Na<sup>+</sup> foam, and EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam.

EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam. This result indicates the possible chemical reaction between maleic anhydride groups and OH groups of the clay. Since the amount of Si-69 used in this study was so small (0.05 phr), it was difficult to find significant difference in the ATR-FTIR spectra of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH/Si-69 foams (figure is not shown in this article), compared with ATR-FTIR spectra of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foams.

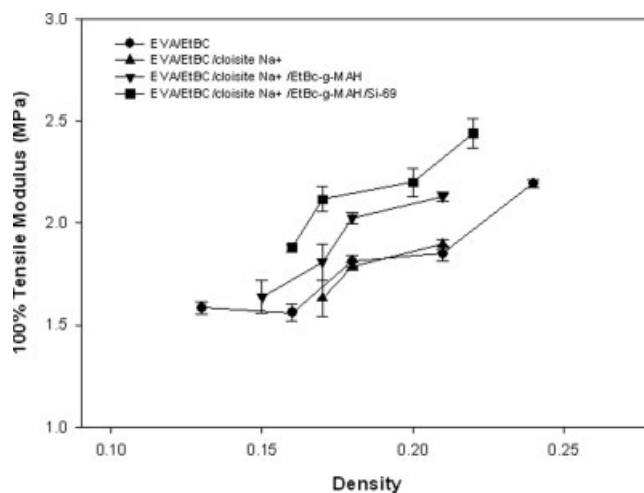
### Mechanical properties

It is very interesting to study the effect of a compatibilizer on the mechanical properties of nanocomposite foams. In the polymer/clay nanocomposites, compatibilizers are usually used to help the intercalation of hydrophobic polymers such as PP into the interlayer of clays.<sup>15-17</sup> However, there are few reports about the effect of compatibilizers on the mechanical properties of polymer/clay nanocomposite foams.

Figures 5 and 6 show the tensile strength and 100% tensile modulus of each foam as a function of density, respectively. With increasing density, the tensile strength and 100% tensile modulus of foams increase. Compared with similar density of foams, the tensile strength and 100% tensile modulus of EVA/EtBC foams are similar to those of EVA/EtBC/Cloisite Na<sup>+</sup> foams. Even though the formation of nanocomposite for EVA/EtBC/Cloisite Na<sup>+</sup> foams is supported by the XRD results (Fig. 1), there is no improvement in the tensile strength and 100% tensile modulus of EVA/EtBC/Cloisite Na<sup>+</sup> nanocomposite foams compared with those of EVA/EtBC foams. Since EVA has a polar group, EVA is expected to intercalate into the interlayer of Cloisite Na<sup>+</sup>. How-



**Figure 5** Tensile strength of each foam as a function of the density.



**Figure 6** Hundred percent tensile modulus of each foam as a function of the density.

ever, since EtBC is a hydrophobic polymer and immiscible with EVA, EtBC is hard to intercalate into the interlayer of Cloisite Na<sup>+</sup>. This immiscibility of EtBC leads to no improvement in tensile strength and 100% modulus for EVA/EtBC/Cloisite Na<sup>+</sup> nanocomposite foams.

The tensile strength and 100% tensile modulus of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH nanocomposite foams are higher than those of EVA/EtBC/Cloisite Na<sup>+</sup> nanocomposite foams. EtBC-g-MAH was used as a compatibilizer between Cloisite Na<sup>+</sup> and EtBC. And XRD results (Fig. 1) show the higher degree of expansion of the interlayer distance for EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam than EVA/EtBC/Cloisite Na<sup>+</sup> foam. The intercalation of hydrophobic EtBC into the interlayers of Cloisite Na<sup>+</sup> due to the compatibilizer (EtBC-g-MAH) may be the reason for the improvement of tensile strength and 100% tensile modulus.

To improve their mechanical properties, filler surface treatments are usually used in the polymer composites. The most widely used surface treatment is to use silane coupling agents and the most commonly used silane coupling agents in rubbers, bis (3-triethoxysilylpropyl) tetrasulfide (Si-69) were used in this study. The tensile strength and 100% tensile modulus of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH/Si-69 nanocomposite foams are higher than those of EVA/EtBC/Cloisite Na<sup>+</sup> nanocomposite foams. This result indicates that even in the clay nanocomposite foams, coupling agents can improve the mechanical properties of nanocomposite foams through reactions of the surface hydroxyl groups of clay and silanol groups of coupling agent (Si-69).<sup>18</sup>

Figure 7 shows the tear strength of each foam as a function of density. EVA/EtBC/Cloisite Na<sup>+</sup> foams show the lowest tear strength and tear strength of EVA/EtBC foams are similar to that of EVA/EtBC/

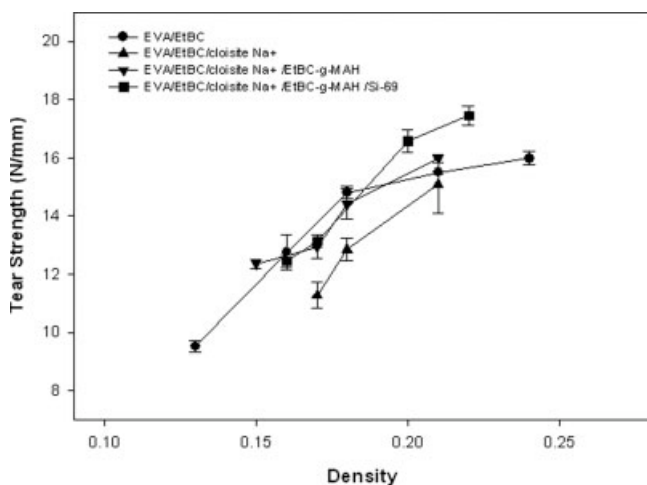
Cloisite Na<sup>+</sup>/EtBC-g-MAH foams. Since tear strength is sensitive to the interaction between the filler and matrix, the lowest tear strength of EVA/EtBC/Cloisite Na<sup>+</sup> foam indicates poor interaction between clay and polymer matrix. The tear strength of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH/Si-69 foam is the highest in the higher density region.

Figure 8 shows the compression set of each foam as a function of density. The lower the compression set is, the better the elastic recovery of the foam. EVA/EtBC foams display the lowest compression set and the compression set increases with addition of clay. This is a very important result because there are few reports regarding the effect of polymer/clay nanocomposites on the compression set. Compression set is a very important property for the application of foams. Therefore, to introduce the polymer/clay nanocomposite to the foam application, this worse elastic recovery of the foam should be solved.

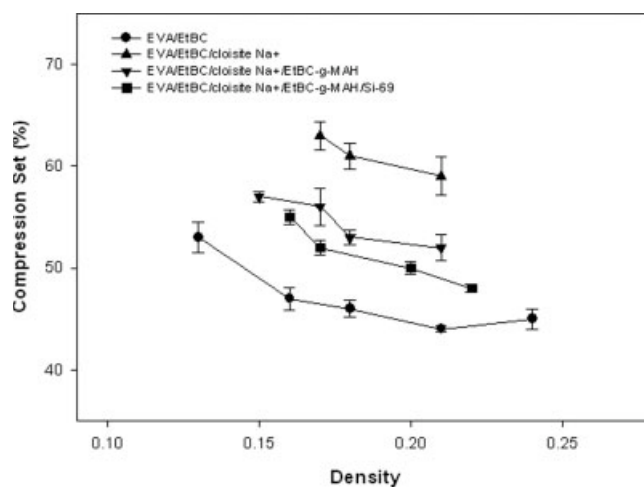
## CONCLUSIONS

According to the XRD results, EVA/EtBC/clay nanocomposite foams are successfully prepared. However, compared with similar density of EVA/EtBC foams, there is no improvement in the mechanical properties of EVA/EtBC/Cloisite Na<sup>+</sup> nanocomposite foams. Since EVA has a polar group, EVA is expected to intercalate into the interlayer of Cloisite Na<sup>+</sup>. However, since EtBC is a hydrophobic polymer and immiscible with EVA, EtBC is hard to intercalate into the interlayer of Cloisite Na<sup>+</sup>. This immiscibility of EtBC may lead to no improvement in the mechanical properties of EVA/EtBC/Cloisite Na<sup>+</sup> nanocomposite foams.

When EtBC-g-MAH was used as a compatibilizer, the degree of expansion of the interlayer distance



**Figure 7** Tear strength of each foam as a function of the density.



**Figure 8** Compression set of each foam as a function of the density.

for EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH (1.3 nm → 1.6 nm) is higher than that for EVA/EtBC/Cloisite Na<sup>+</sup> (1.3 nm → 1.5 nm). The higher degree of expansion of the interlayer distance for EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH foam may be due to the intercalation of hydrophobic EtBC into the interlayers of Cloisite Na<sup>+</sup>. As a result, the mechanical properties of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH were better than those of EVA/EtBC foams except compression set property. Based on further improvement in the mechanical properties of EVA/EtBC/Cloisite Na<sup>+</sup>/EtBC-g-MAH/Si-69, it can be concluded that even in the clay nanocomposites, coupling agents can improve the mechanical properties of nanocomposites through reactions of the surface hydroxyl groups of clay and silanol groups of coupling agent (Si-69).

EVA/EtBC foams display the lowest compression set and the compression set increases with addition of clay. Compression set is a very important property for the application of foams. Therefore to introduce the polymer/clay nanocomposite to the foam application, this worse elastic recovery of the foam should be solved.

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