

Effect of Dispersion State of Organoclay on Cellular Foam Structure and Mechanical Properties of Ethylene Vinyl Acetate Copolymer/Ethylene-1-Butene Copolymer/Organoclay Nanocomposite Foams

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ABSTRACT: In this study, our goal is 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/organoclay (Cloisite 15A, Cloisite 30B) nanocomposite foams were prepared. To investigate the effect of compatibilizer on the dispersion state of organoclay in cellular foam structure and mechanical properties of the EVA/EtBC/organoclay foams composites were prepared with and without maleic anhydride grafted EtBC (EtBC-g-MAH). The dispersion of organoclay in EVA/EtBC/organoclay foams was investigated by X-ray diffraction and transmission

electron microscopy. The EVA/EtBC nanocomposite foams with the compatibilizer, especially EVA/EtBC/Cloisite 15A/EtBC-g-MAH foams displayed more uniform dispersion of organoclay than EVA/EtBC nanocomposite foams without the compatibilizer. As a result, EVA/EtBC/Cloisite 15A/EtBC-g-MAH foams have the smallest average cell size and highest 100% tensile modulus followed by EVA/EtBC/Cloisite 30B/EtBC-g-MAH foams. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3879–3885, 2007

Key words: organoclay; density; compatibility; dispersions; composites

INTRODUCTION

Ethylene-vinyl acetate copolymer (EVA) foams are extensively used for various purposes, especially for the fabrication of midsole, a layer that lies between insole and outsole of running shoes.¹ Recently, ethylene-1-butene copolymer (EtBC) has been blended with EVA to increase the physical properties of EVA foams such as tensile strength, rebound resilience, and compression set.^{2,3} Among many physical properties, low density is highly desirable for the application of foams. The simple method to obtain foams with lower density is to use more blowing agents. However, the mechanical properties of foams also decrease with lower density. In this study, our purpose is to obtain lower density of EVA/EtBC foams without sacrificing mechanical properties through popular and friendly means.

In recent years organoclay based polymer nanocomposites have attracted considerable attention

from both a fundamental research, and an application point of view due to 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.^{4–20}

EVA/clay nanocomposites were successfully prepared by melt intercalation method and their mechanical properties were improved.^{21–26} By using EVA-g-MAH as a compatibilizer, the dispersion of clays was greatly improved in EVA/clay nanocomposites.²⁴ Therefore, our idea to obtain lower density of EVA/EtBC foams without sacrificing mechanical properties is to prepare EVA/EtBC/organoclay nanocomposite foams with higher amount of blowing agents. However, there has been very little information available regarding crosslinked polymer nanocomposite foams prepared using chemical blowing agents.

This study is very interesting because of not only the application aspect, obtaining lower density of EVA/EBC foams without sacrificing mechanical properties, but also the academic aspect, answering the basic question regarding the crosslinked polymer nanocomposite foams prepared using chemical blowing agents. The basic question is as follows: how does the organoclay dispersion in the nanocomposite

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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 ³) : 0.935
	Ethylene-1-butene copolymer(EtBC)	Mitsui Chemical Inc., Japan	ML1 + 4(100°C) : 40, density : 0.91 g/cm ³
	EtBC-g-MAH	Dupont, USA	Melt Index (g/10 min) : 3.7, density : 0.88 g/cm ³
Clay	Cloisite 15A, Cloisite 30B	Southern Clay, USA	Modifier concentration : 125 mequiv/100 g, modifier concentration : 90 mequiv/100 g
Blowing agent	JTR-M	Kumyang, Korea	Decomposition temperature : 142–148°C, Gas volume : 165 mL/g
Cross-linking agent	Dicumyl Peroxide	Akzo Nobel, Netherlands	
Cross-linking coagent	Zinc Oxide	Gil-Chun Chem., Korea	
	Stearic acid	LG Chem., Korea	

foams affect cellular foam structure and mechanical properties of EVA/EtBC/organoclay nanocomposite foams? Answering this question can give valuable information to those who plan to use nanocomposite foams in many applications since polymer foams are widely used in construction, transportation, sports, packaging, medical devices, and agriculture. The polymer nanocomposite foams are one of the latest technologies in polymer foam fields.

To investigate the effect of dispersion state of organoclay on cellular foam structure and mechanical properties, nanocomposites of EVA/EtBC/organoclay are prepared with Cloisite 15A, Cloisite 30B in presence and in absence of maleic anhydride grafted EtBC (EtBC-g-MAH). Foams were made out of it.

EXPERIMENTAL

Materials and foam preparation

Names and important characteristics of the materials used in this study are summarized in Table I. Organically modified montmorillonites (organoclays) were purchased from Southern Clay Products (USA) under the trade name of Cloisite 15A and Cloisite 30B. Organic modifier of Cloisite 15A is dimethyl dihydrogenated tallow quaternary ammonium and organic modifier of Cloisite 30B is methyl tallow bis-2-hydroxyethyl quaternary ammonium. EVA/EtBC masterbatch is the blend of EVA and EtBC (50/50) provided by local compounding company. The recipes of the EVA/EtBC masterbatch are described in Table II.

EVA/EtBC masterbatch, organoclay, and compatibilizer 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. Organoclay, compatibilizer, and DCP (crosslinking agent)

content were fixed at 3, 5, and 0.7 phr, respectively, based on the total amount of EVA/EtBC masterbatch. 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 (4–6.5 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 cryogenically microtomed and were examined with FE-Scanning Electron Microscope (JEOL JSM-35CF). Transmission electron microscopy (TEM)

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

Materials	Content (phr)
EVA	50
Ethylene-1-butene copolymer (EtBC)	50
Zinc Oxide	3
Stearic acid	1

TABLE III
Recipes (in phr) of the Foam Compounds

Materials	Code				
	EVA/EtBC	EVA/EtBC/ Cloisite 15A	EVA/EtBC/ Cloisite 30B	EVA/EtBC/ Cloisite 15A/EtBC-g-MAH	EVA/EtBC/ Cloisite 30B/EtBC-g-MAH
EVA/EtBC masterbatch	100	100	100	100	100
EtBC-g-MAH				5	5
Cloisite 15A		3		3	
Cloisite 30B			3		3
JTR-M	4–5.5	4.5–6	4.5–5.5	5–6	5–6.5
DCP	0.7	0.7	0.7	0.7	0.7

images were taken from cryogenically microtomed ultra thin sections using EF-TEM (EM 912 Omega).

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

RESULTS AND DISCUSSION

Characterization of nanocomposite foams

Figure 1 shows the XRD patterns of EVA/EtBC/organoclay nanocomposite foams. For Cloisite 15A,

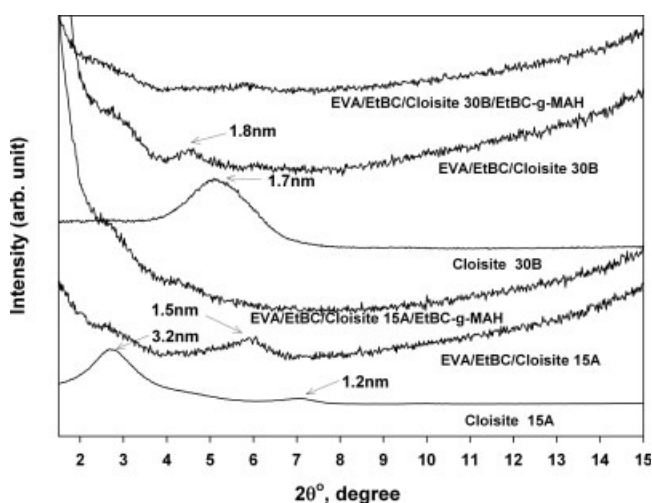


Figure 1 XRD patterns of EVA/EtBC/organoclay nanocomposite foams.

peaks appear at 3.2 nm and 1.2 nm. The peak at 1.2 nm could be due to the unmodified clay present in the commercial product as an impurity. For EVA/EtBC/Cloisite 15A foam, the intensity of original peak of Cloisite 15A at 3.2 nm becomes much smaller and the peak shifts to a smaller angle. As a result only small bump is observed. The peak appeared at 1.5 nm is due to the intercalation of polymers into the unmodified clay. For EVA/EtBC/Cloisite 15A/EtBC-g-MAH foam, there is no apparent diffraction peak existing. This may indicate the coexistence of intercalated and exfoliated Cloisite 15A. Basically, the same trend is observed for EVA/EtBC/Cloisite 30B and EVA/EtBC/Cloisite 30B/EtBC-g-MAH foams even though the peak positions are different from Cloisite 15A. On the basis of the XRD results, it can be concluded that compatibilizer helps more intercalation and exfoliation of polymers into the Cloisite 15A and 30B.

To confirm further the dispersion state of the EVA/EtBC nanocomposite foams, TEM studies were carried out. Figure 2(a) presents the typical TEM photograph of an ultra-thin section of the EVA/EtBC/Cloisite 15A foams exhibiting intercalated morphologies. The dark lines are silicate layers. The original interlayer distance of Cloisite 15A is 3.2 nm. However, Cloisite 15A observed in Figure 2(a) has $\sim 4.2 \text{ nm}$ interlayer distance. The larger interlayer distance (4.2 nm) of Cloisite 15A than the original interlayer distance of Cloisite 15A is due to the intercalation of EVA into the Cloisite 15A. The exfoliated silicate layers are also indicated by circle. Figure 2(b) shows the TEM photograph of EVA/EtBC/Cloisite 15A/EtBC-g-MAH foam. Compared with TEM photograph of EVA/EtBC/Cloisite 15A foam, more exfoliated morphologies are observed in Figure 2(b).

Figure 3 shows the TEM photographs of EVA/EtBC/Cloisite 30B foam and EVA/EtBC/Cloisite 30B/EtBC-g-MAH foam. Besides the uniformly dispersed clay, there still remain some aggregated parts in EVA/EtBC/Cloisite 30B foam as shown in Figure 3(a). However, intercalated and exfoliated morphologies are observed in EVA/EtBC/Cloisite 30B/EtBC-g-MAH foams as shown in Figure 3(b). On the basis

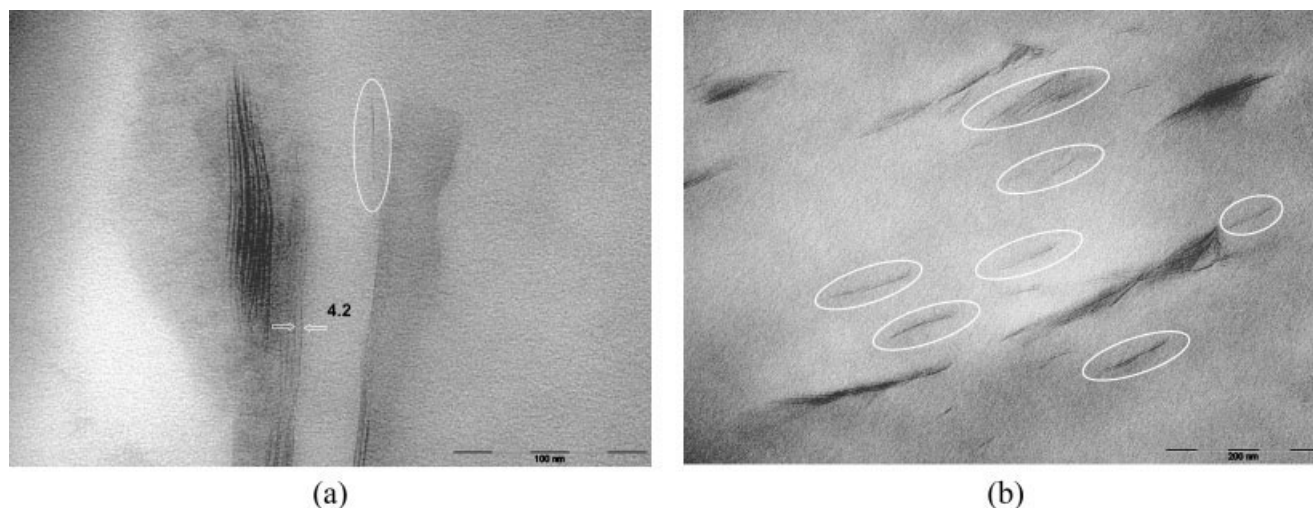


Figure 2 TEM photographs: (a) EVA/EtBC/Cloisite 15A foam, (b) EVA/EtBC/Cloisite 15A/EtBC-g-MAH foam.

of XRD and TEM results, it can be concluded that the EVA/EtBC nanocomposite foams with compatibilizer, especially EVA/EtBC/Cloisite 15A/EtBC-g-MAH foams displayed more uniform dispersion of organoclay than EVA/EtBC nanocomposite foams without compatibilizer. Compared with Cloisite 15A and 30B, Cloisite 15A shows more uniform dispersion than Cloisite 30B. Since the organic modifiers used in Cloisite 15A are more hydrophobic than those in Cloisite 30B, Cloisite 15A may be more effective clay for EtBC, hydrophobic polymer.

Figure 4 shows typical scanning electron microscopy (SEM) images of the cellular structure of the EVA/EtBC foams and EVA/EtBC nanocomposite foams. The EVA/EtBC foams and nanocomposite foams have a closed-cell structure. The cell size was determined by measuring the maximum diameter of each cell. About 250 cells in each SEM image were

analyzed to obtain the average cell sizes. Table IV summarizes the average cell sizes and standard deviation. Generally the residues of chemical blowing agent act as nucleating agents. Similarly, organoclay can provide nucleating sites in the heterogeneous nucleating process. More nucleation sites are available in EVA/EtBC nanocomposite foams than in EVA/EtBC foams. As a result, EVA/EtBC nanocomposite foams have smaller cell size than EVA/EtBC foams.

According to XRD and TEM result, the EVA/EtBC nanocomposite foams with compatibilizer, especially EVA/EtBC/Cloisite 15A/EtBC-g-MAH foams displayed more exfoliated organoclays than EVA/EtBC nanocomposite foams without compatibilizer. Exfoliated organoclays provide much larger surface area for cell nucleation than intercalated organoclays. As a result, EVA/EtBC/Cloisite 15A/EtBC-g-MAH

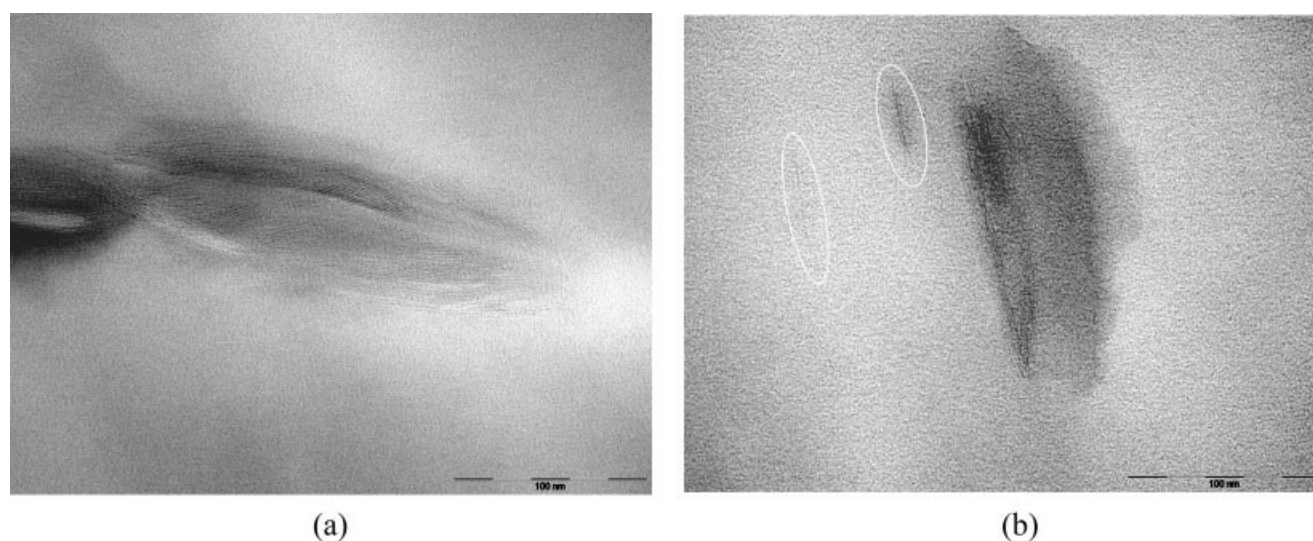


Figure 3 TEM photographs: (a) EVA/EtBC/Cloisite 30B foam, (b) EVA/EtBC/Cloisite 30B/EtBC-g-MAH foam.

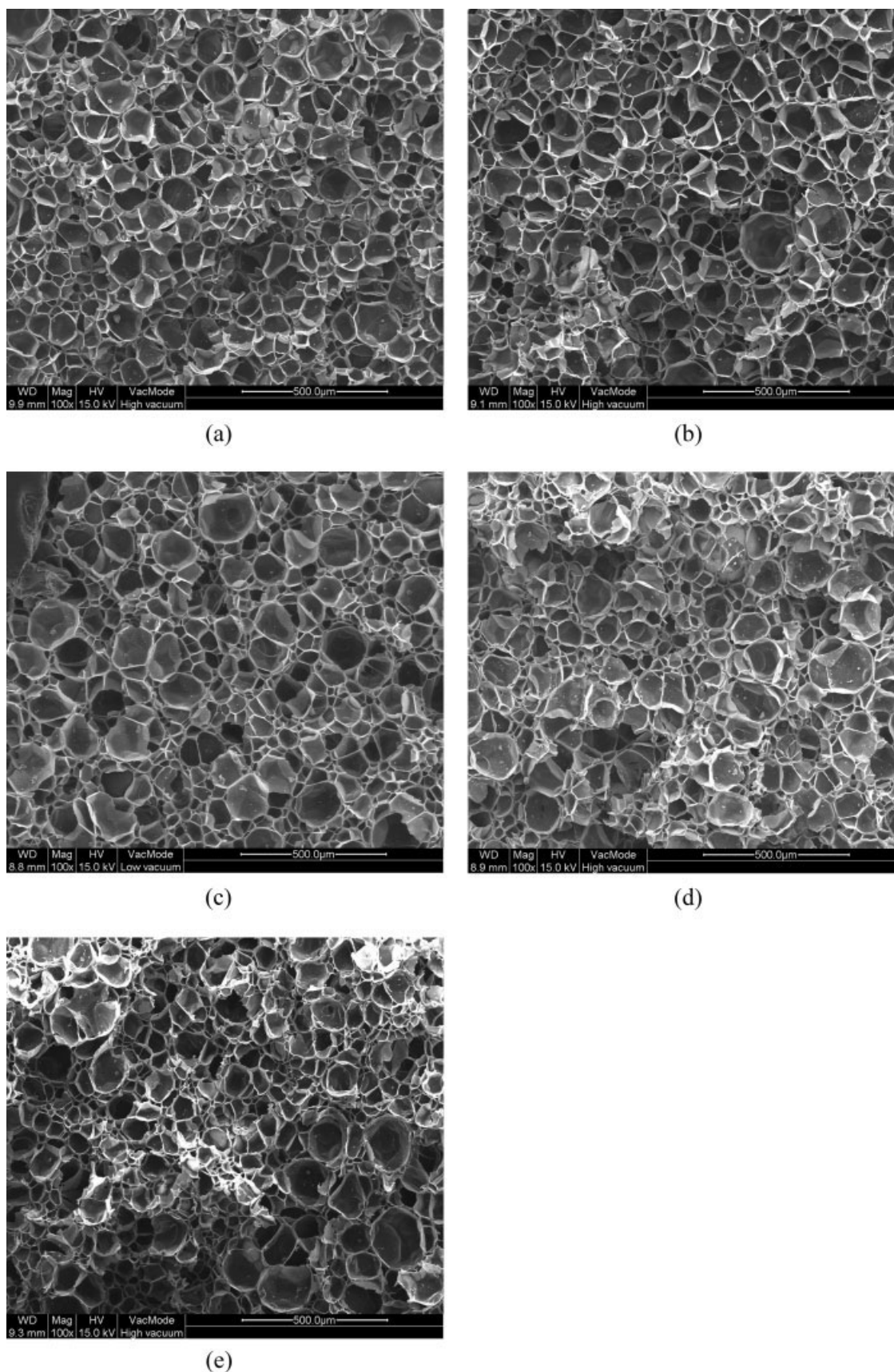


Figure 4 SEM images of foams with same density (0.16): (a) EVA/EtBC foam, (b) EVA/EtBC/Cloisite 15A foam, (c) EVA/EtBC/Cloisite 15A/EtBC-g-MAH foam, (d) EVA/EtBC/Cloisite 30B foam, (e) EVA/EtBC/Cloisite 30B/EtBC-g-MAH foam.

TABLE IV
Average Cell Sizes and Standard Deviations
of the Foams

Samples	Cell size (μm)
EVA/EtBC	76 ± 30
EVA/EtBC/Cloisite 15A	75 ± 32
EVA/EtBC/Cloisite 30B	75 ± 42
EVA/EtBC/Cloisite 15A/EtBC-g-MAH	59 ± 38
EVA/EtBC/Cloisite 30B/EtBC-g-MAH	67 ± 34

foams have the smallest average cell size and EVA/EtBC/Cloisite 30B/EtBC-g-MAH foams have the second smallest average cell size.

Mechanical properties

It is very interesting to study the effect of organoclays on the mechanical properties of nanocomposite foams. Figure 5–7 show the tensile strength, 100% tensile modulus, and elongation at break of foams as a function of density, respectively. With increasing density, the tensile strength and 100% tensile modulus of foams increase. The tensile strength of EVA/EtBC/organoclay nanocomposite foams is higher than that of EVA/EtBC foams.

Generally in composites, their modulus is related to the dispersion of fillers and well-dispersed fillers give higher enhancement of modulus to the composites. As a result, 100% tensile modulus of EVA/EtBC/Cloisite 15A/EtBC-g-MAH foams is the highest and that of EVA/EtBC/Cloisite 30B/EtBC-g-MAH foams is the second highest. On the basis of XRD and TEM results, nanocomposites foams with compatibilizer displayed better dispersion than nanocomposites foams without compatibilizer.

The elongation at break of EVA/EtBC/Cloisite 30B foams is the highest and that of EVA/EtBC/Cloisite 15A is the second highest. Because of poly-

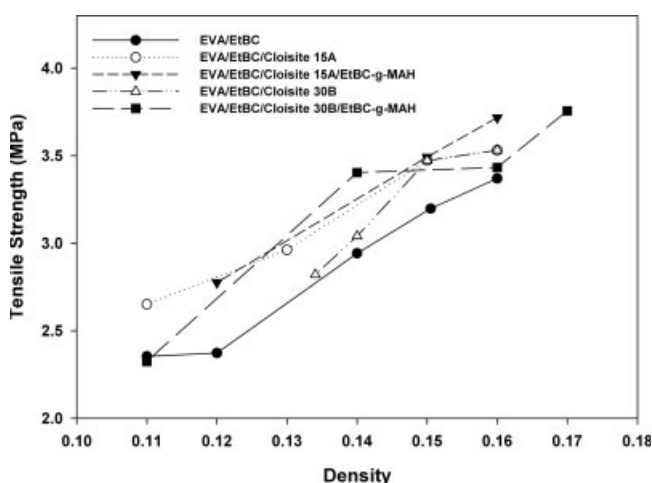


Figure 5 Tensile strength of foams with density.

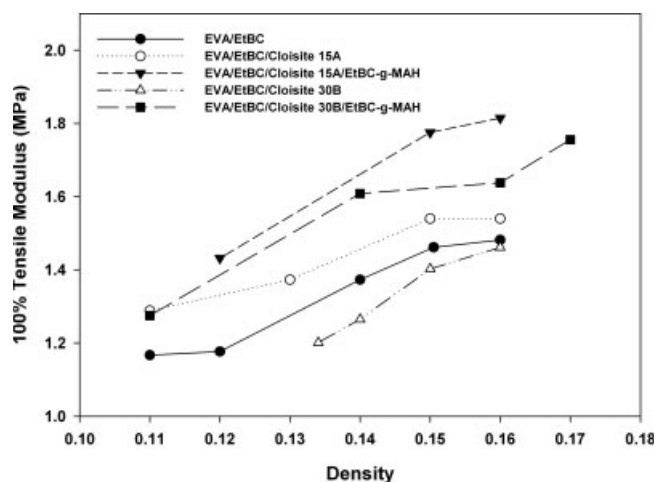


Figure 6 Hundred percent tensile modulus of foams with density.

mer chain slipping along the organoclay surface, elongation of EVA/EtBC/Cloisite 30B foams and EVA/EtBC/Cloisite 15A foams is higher than EVA/EtBC foams. When compatibilizer was used, the enhanced interactions between organoclays and polymers may lead to the smaller chain polymer slipping. As a result, the elongation of EVA/EtBC nanocomposite foams with compatibilizer is smaller than that of EVA/EtBC nanocomposite foams without compatibilizer.

CONCLUSIONS

On the basis of XRD and TEM results, it can be concluded that the EVA/EtBC nanocomposite foams with the compatibilizer, especially EVA/EtBC/Cloisite 15A/EtBC-g-MAH foams displayed more uniform dispersion of organoclay than EVA/EtBC nanocomposite foams without the compatibilizer.

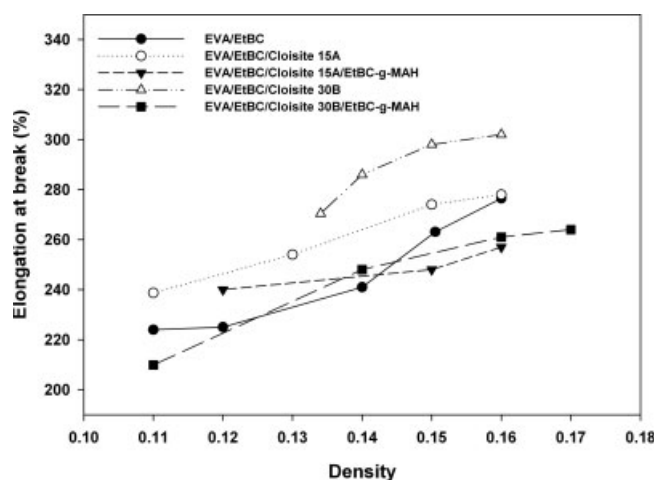


Figure 7 Change of elongation at break of foams with density.

Compared with Cloisite 15A and 30B, Cloisite 15A shows more uniform dispersion than Cloisite 30B. Since the organic modifiers used in Cloisite 15A are more hydrophobic than those in Cloisite 30B, Cloisite 15A may be more effective clay for EtBC, hydrophobic polymer.

Since organoclay can provide nucleation sites, EVA/EtBC/organoclay nanocomposite foams have smaller cell size than EVA/EtBC foams. Also since exfoliated organoclay provides much larger surface area for cell nucleation than intercalated organoclay, EVA/EtBC/Cloisite 15A/EtBC-g-MAH foams have the smallest average cell size and EVA/EtBC/Cloisite 30B/EtBC-g-MAH foams have the second smallest average cell size.

Also correlations between the dispersion state of organoclay and mechanical properties of foams existed. Hundred percent tensile modulus of EVA/EtBC/organoclay foams with the compatibilizer, which displayed better dispersion of organoclay than EVA/EtBC/organoclay foams without the compatibilizer is higher than that of EVA/EtBC/organoclay foams without the compatibilizer. However, the elongation at break of EVA/EtBC/organoclay foams without the compatibilizer is higher than that of EVA/EtBC/organoclay foams with the compatibilizer.

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