ADVANCES IN POLYOLEFIN FOAMING TECHNOLOGY

Colin Li Pi Shan[1], Brian Yu[1], Xian Jiang[2], Kyle Kummer[1]
[1]The Dow Chemical Company, Dow Packaging and Specialty Plastics
[2] E.I. du Pont de Nemours and Company, Inc.

Abstract

Polyolefin foams offer the industry a number of versatile options to create resilient and light weight solutions. Through proper resin selection and formulation, a variety of moldable and extruded foams can be tailored for use in protective and industrial insulation, comfort matting, and other consumer goods. Elastomeric polyolefin foams can be formulated with ethylene-vinyl acetate copolymers, poly(ethylene-alpha) olefin elastomers, and olefin block copolymers to deliver the desired hardness, resiliency, mechanical performance, and haptics. This presentation will discuss the structure-property-foaming relationships of EVA, POE, and OBC that impact the balance of foaming and curing and end-use properties.

Introduction

Polyolefin foams offer the industry a number of versatile options to create resilient and light weight solutions. There are several polymers with different molecular architectures to choose from. Ethylene-vinyl acetate (EVA) and ethylene-methyl acrylate (EMA) copolymers produced from the free radical process give rise to arborescent and comb architectures that have high melt strength and excellent foamability (1). Homogeneous ethylene-alpha olefin copolymers produced with single-site molecular catalysts can be lower in density and used to make softer foams. Olefin block copolymers produced by chain shuttling catalysis shift the paradigm with high melting points and lower density resulting in foams with high resiliency and low shrinkage (2). The merits of each polymer technology can be further enhanced via the blending of polymers into customized compounds to achieve the desired property balance. To achieve the desired balance of curing and foaming, the selection and interaction of the polymer architecture is critical. In chemically initiated foams whereby the gas evolution and crosslinking are typically controlled by temperature, the cell expansion is governed by the melt rheology and crosslinking rate (3). Depending on the end-use, sometimes large and heterogeneous distribution of cells sizes (50-100μm) are observed but ideally, small and homogeneous distribution of cell sizes are preferred. The selection of polymers can be used to define the feature set of the foams based on the balance of processability, mechanical performance, and haptics.

This report will discuss the structure-property-foaming relationships of EVA, POE, and OBC polymers that are typically used for making polyolefin elastomeric foams. The foaming response and foam properties from each of these polymers are compared.

Experimental

Materials used in this study:

The following are the properties of the polymers used in this study. The polymers are representative of those used for foaming of soft and flexible goods (refer to Table 1).

Ethylene-vinyl acetate copolymer (EVA): ≈ 18-25% VA, 2.5 MI (such as Elvax® 460 EVA)

Polyolefin Elastomer (POE): ethylene-octene copolymer, 0.87-0.9 g/cc, 1-5MI (such as ENGAGE™ 8200 POE)

Olefin Block Copolymer (OBC): ethylene-octene olefin block copolymer, 0.867 – 0.885 g/cc, 1-5MI (such as INFUSE™ 9507, INFUSE™ 9500, INFUSE™ 9530 OBC)

Table 1 – Polymer Types for Foaming

Property/Type	EVA	POE	OBC
Density (g/cc)	0.94	0.87-0.90	0.867 – 0.885
MI (190°C, g/min)	2.5	1-5	1-5
Melting Point (°C)	87	60-100	115-120
Crystallization Temp (°C)	70	50-90	100
Glass transition Temp DSC (°C)	-24	-52	-62
Comonomer Type	Vinyl acetate	Octene	Octene
Comonomer Distribution	Narrow	Narrow	Broad
Branching	High	Low	Low

Formulation of Foam Compounds:
Table 2 lists the ingredients that are compounded into the polymer prior to foaming.

Luperox DC40P: dicumyl peroxide with active peroxide content around 40 wt%.

Luperox DC40P-SP2: Scorch protected dicumyl peroxide with active peroxide content around 40 wt%.
AC9000: Azodicabonamide type blowing agent
ZnO: Zinc oxide
ZnSt: Zinc stearate
Atomite: Calcium carbonate

Table 2 – Representative Foam Formulation

Foam Ingredients	EVA	POE	OBC
EVA	100		
POE		100	
OBC			100
Luperox 40DC SP2	0.9	0.9	0.99
Luperox 40DC	1.35	1.35	1.485
AC9000	X	Y	Z
ZnO*	0.1X	0.1Y	0.1Z
ZnSt*	0.1X	0.1Y	0.1Z
CaCO3	5	5	5

Recipe reported in parts per hundred rubber, phr
*The loading of ZnO and ZnSt is 10% of the blowing agent (AC9000) dosage (X,Y,Z)

Experimental Methods:

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry was measured on a TA Instruments Q1000 DSC equipped with an RCS cooling accessory and an auto sampler. The thermal behavior of the sample is investigated with the following temperature profile: the sample is rapidly heated to 190°C and held isothermal for 3 minutes in order to remove any previous thermal history. The sample is then cooled to -90°C at 10°C/min cooling rate and held at -90°C for 3 minutes. The sample is then heated to 150°C at 10°C/min heating rate. The cooling and second heating curves are recorded.

Dynamic mechanical spectrometer (DMS)

The viscoelastic melt properties were measured on a TA ARES G2 Rheometer conducted at 190 °C with 5% strain and a frequency sweep from 0.1 to 100 rad/s.

Rubber Process Analyzer (RPA)

The cure behavior was measured using an Alpha Technologies RPA-2000 at 180 °C for 10 minutes with 7% strain, and torque and pressure were recorded.

Foam Compounding Process

Polymer pellets were added to the 1.5 liter Banbury mixer. Then, ZnO, ZnSt and $CaCO_3$ were added after the polymer had melted (around 5 minutes). The blowing agent and peroxide were added last after the fillers were uniformly dispersed and mixed for another 3 to 5 minutes for a total mix time of 15 minutes.

Foam Preparation

Roll milled blankets were cut into squares and placed inside a pre-heated bun foam mold. Two compression molding processes were involved: preheating first to eliminate air pockets inside the sample and between the stacked layers prior to curing, and then curing/foaming. The preheating was conducted for 8 minutes at 110 °C (low melting polymer like Elvax® EVA or ENGAGE™ POE) or 120 °C (high melting polymer like INFUSE™ OBC) and pressed at 10 tons for 4 minutes to form a solid mass in the mold before foaming. The preheated mass was transferred to the foaming press and held for 8 minutes at 100 kg/cm^2 and 180 °C. Once the pressure was released, the bun foam was removed quickly from the tray and placed in a vent hood on several non-stick sheets and the top side length is measured as soon as possible. The foams are allowed to cool for 24 hours. The length is then measured again and the foam expansion ratio can be calculated (length of the cool foam/length of the mold).

Shore A Hardness

The hardness was an average of five readings (5 seconds latency) measured across the surface of the sample.

Oven Shrinkage

After skin layers (top and bottom) were removed from the bun foams, samples were cut using the vertical band saw, measured mass and thickness, placed in a pre-heated oven at 100 °C, and removed after 40 minutes. Samples dimensions were re-measured after 24 hours of cooling at room temperature.

Resiliency - Falling Ball Rebound

A 5/8" diameter steel ball was dropped from a height of 500 mm onto the bun foam skin and foam layers (before and after aging) to determine the %Rebound or Resilience. The %Rebound is calculated as rebound height (in mm)*100 /500.

Tear Strength

Foam layers were measured by ASTM D624 (Tear, Type C) mechanical property test at 20 inches/minute. The sample thickness was approximately 3 mm.

Compression Set

Compression Set (C-Set) was measured per ASTM D395 method B under conditions of 50% compression at 50 °C for 6 hours. Two buttons were tested per foam and the average reported.

Discussion

Polyolefin foams are commonly produced with EVA, POE, and more recently OBC polymers to produce soft and flexible foams over a Shore A range from 20 – 50. The expansion of the foams includes the kick-off of the chemical blowing agent, gas expansion, and curing of the polymer. The resulting foam density and cellular architecture are governed by the polymer's composition and branching architecture. The foaming rheology is a combined response to the polymer's sensitivity to peroxide (cure rate) and melt elasticity resulting in a balance of foaming and curing (3).

The resultant foam density and properties depend on the expansion ratio of the bubbles or cells but its hardness, resiliency, and mechanical strength are influenced additionally by the nature of the polymer.

Figure 1 compares the crystallinity distribution of an EVA, POE, and OBC polymer as described in Table 1. Shown is an enthalpy corrected DSC which better represents the weighted proportion of the crystallizable polymer. The EVA and POE have similar crystallinity distributions while the OBC due to its hard/soft block nature has a high melting point from its hard segment (about 121°C) and a nearly amorphous soft segment. The corresponding order of crystallization of the polymers were: OBC (100°C) >> EVA (70°C) > POE (50°C). Although the foaming occurs in the melt state, the setup and shape retention is influenced by the crystallinity distribution. OBC polymers have been demonstrated to have lower shrinkage and excellent dimensional stability due to lamellar reinforcement of the hard segment present.

Figure 2a and 2b compares the melt oscillatory shear rheology and Van-Gurp Palmen behavior of an EVA, POE, and OBC. The differences in branching architecture are apparent from the shear thinning and phase angle response (4). The EVA polymer due to its aborescent-like structure produced from free-radical polymerization, exhibits high shear thinning and high elasticity. Compared to EVA, the POE and OBC produced from single-site catalysts are relatively linear and exhibit less shear thinning and low elasticity. This is evidenced in the Van-Gurp Palmen plot (VGP). It was observed that the POE and OBC have a similar and much higher phase angle response (90° at 1000 Pa) than the EVA polymer (70° at 1000 Pa). The steepness of the change in phase angle for the EVA also reflects on its high shear thinning character. Since the elasticity of the polymer provides resistance to bubble expansion and limits the size of bubbles before breaking, it would be expected that the EVA polymer would have a larger expansion ratio than the more linear POE polymer.

Figure 3a compares the expansion ratio at different blowing agent levels between EVA, POE, and OBC. Table 2 shows the corresponding recipes. For this particular set of foam compounds with similar peroxide loading (except for OBC which had 10% higher amount of peroxided added), the response of the expansion ratio to the blowing agent was observed to be the lowest with the POE and highest for the EVA and OBC. It is understood that the differences in the expansion ratio observed between the polymers is due to the combined effect of the rate of curing and viscosity.

Figure 3b compares the degree of curing at different blowing agent levels between EVA, POE and OBC; the degree of cure is reported by the MH-ML from the RPA measurement of the foamed compounds. It was observed that the POE had the highest degree of cure, EVA had an intermediate level, while the OBC had the lowest (despite having 10% additional peroxide in the formulation). It was also observed that each of the polymers had a different response to the blowing agent level; steep decrease in curing level with blowing agent for POE and EVA and a flat response for the OBC.

It is surmised that the observed differences, were a result of the balance of foaming and curing for each polymer formulation. The lower expansion ratio for the POE can be explained by the faster and higher degree of cure which limited its bubble growth. Relative to the POE, the OBC had a higher expansion ratio which is due to its lower degree of cure and lower resistance to bubble growth. The EVA polymer showed an intermediate degree of cure to the POE and OBC but resulted in a similar expansion ratio to the OBC. This is presumably due to the combined effect of its high degree of cure and higher melt elasticity than the POE/OBC. The results reinforce that the foaming formulation needs to be optimized for each polymer (type and structure) to achieve the desired expansion ratio.

Figure 4 summarizes the foam properties of EVA, POE, and OBC that have been formulated to have a similar expansion ratio. The data shown is for comparison purposes only as adjustments to peroxide concentration and blowing agent may be needed for the specific manufacturing process. The key foam properties are summarized by its hardness, tear strength, compression set, resiliency, and shrinkage after oven aging. The comparison parameters shown in the spider plot are relative to EVA for each of the foam properties.

Hardness: POE and OBC showed lower hardness and softer hand feel than EVA due to the lower Tg and density of POE and OBC.

Tear: POE and OBC showed lower tear strength than EVA. The foam tear properties depend on the crosslinking density but EVA has the additional hydrogen bonding between the VA functional groups that are not present in POE/OBC.

Compression Set (@50C): OBC showed lower compression set than POE/EVA due to lamellar reinforcement of 120°C melting, hard segment blocks.

Resiliency: OBC showed 10% higher rebound than POE/EVA due to almost amorphous x-linked soft segments at room temperature.

Shrinkage: OBC showed minimal shrinkage while POE showed the most shrinkage relative to EVA. The differences in shrinkage are related to the crystallinity distribution and melting point of each polymer.

Figure 5 illustrates the differences in foam morphology at a similar expansion ratio. After oven aging, it was observed that the foam made with OBC had the largest and more open (honeycomb-like) cell structure. The foam made with POE had the most uniform and smallest cell structure while EVA had a heterogeneous and intermediate cell structure. The improved resiliency and lower shrinkage observed with OBC foams can be directly related to the foam structure.

Modified Foam Properties with Polymer Blends

The foam properties and cell structure can be further modified and tailored with polymer blends. In common industry practice, EVA is blended with POE and OBC to adjust the performance balance of soft, light weight, and resilient foams. For example, the addition of OBC to either EVA or POE can minimize the shrinkage of the foam and improve its resiliency.

It has been previously reported that the addition of EMA which has a higher melting point than EVA offers improvements in dimensional stability and resilience. EMA that is also produced in a free-radical polymerization process, has a similar rheology to EVA but has a broader composition distribution and higher melting point (1).

The addition of a polymeric ionomer such as Surlyn® ionomer resin which is an acid neutralized copolymer with either zinc or sodium ions can enhance the foam properties. Foams containing a few phr of ionomer can significantly reduce the cell sizes and result in improvements in tensile and tear properties (5).

Conclusions

This report discussed the structure-property-foaming relationships of EVA, POE, and OBC polymers that are typically used for making polyolefin elastomeric foams. Due to the combined effect of foaming and curing, the foaming response of the polymers is governed by its melt rheology and crosslinking rate. The rheology is influenced by molecular parameters such as its molecular weight distribution and branching topology and manifests itself as apparent viscosity and melt elasticity which in turn provides resistance to bubble growth. The curing rate and curing density is related to the type of composition, composition distribution, and molecular weight to form the cross-linked shell that encases the bubbles.

In this study, the POE had the highest cross-linked density (and rate) and resulted in the smallest bubbles and lowest expansion rate. EVA had an intermediate cross-linking density and resulted in medium sized bubbles. OBC had the lowest cross-linking density and resulted in the largest sized bubbles but a similar expansion ratio as EVA.

As the final foam properties depend on the targeted expansion ratio, for similar foam expansion ratios, EVA foams resulted in slightly higher hardness and higher tear strength than POE and OBC. POE foams due to its lower density resulted in softer foams. OBC foams due to its hard/soft block structure have excellent resiliency, lower shrinkage and higher dimensional stability due to lamellar reinforcement of the hard segment present.

Overall, the foam properties and cell structure can be further modified and tailored with polymer blends. In common industry practice, EVA is blended with POE and OBC to tailor the performance balance of soft, light weight, and resilient foams.

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Figure 1 – Polymer Crystallinity Distribution Comparison

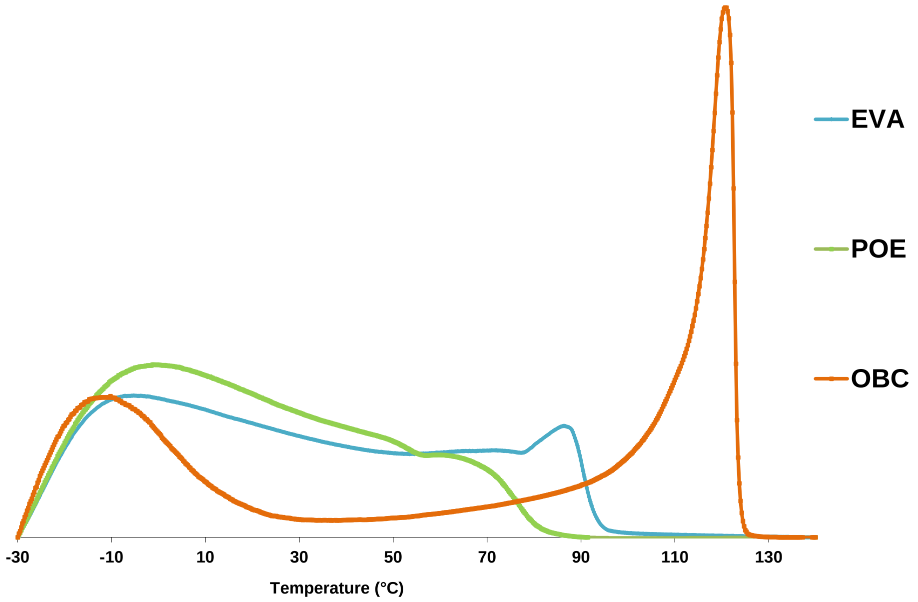

Figure 2 – (a) Polymer Oscillatory Shear Viscosity and (b) Van-Gurp-Palmen Comparison

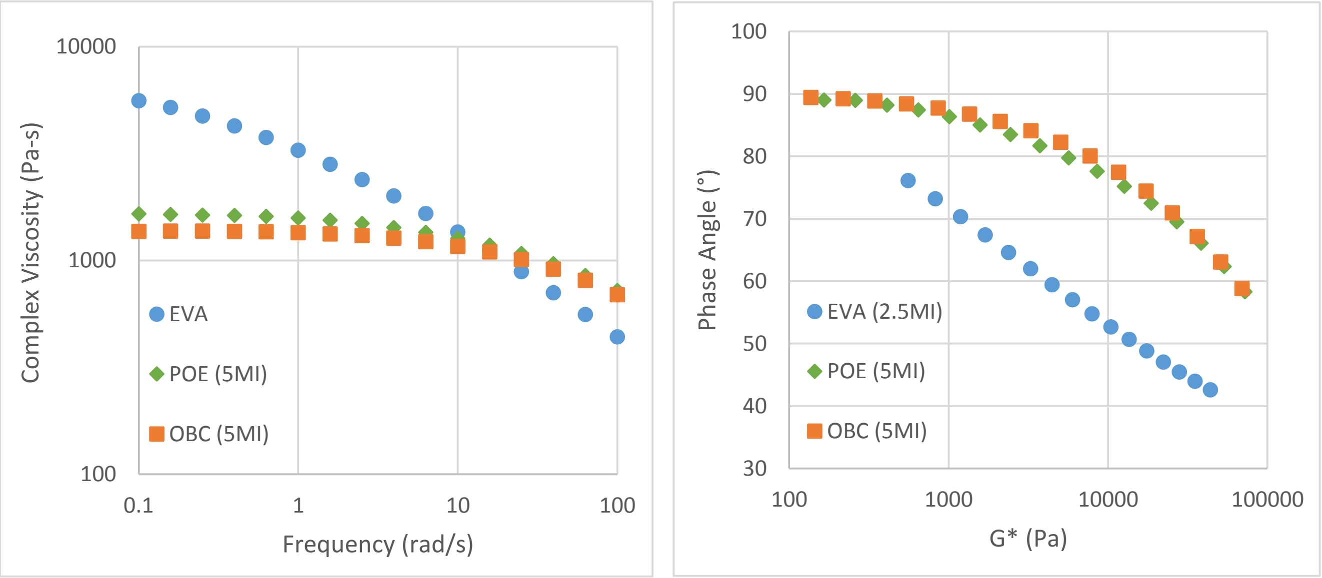

Figure 3 – (a) Foam Compound Expansion and (b) Degree of Curing

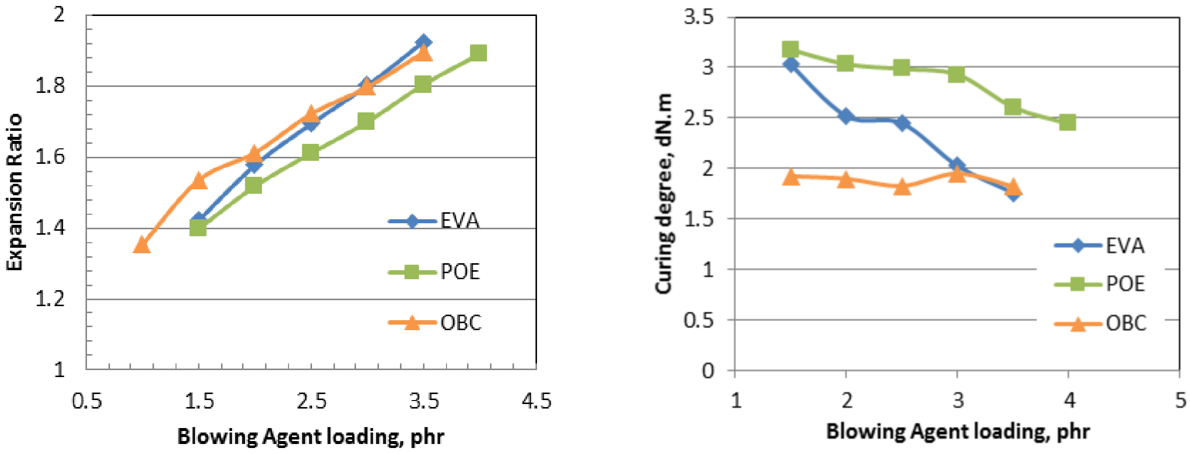

Figure 4 – Comparison of Foam Properties made with Different Polymers

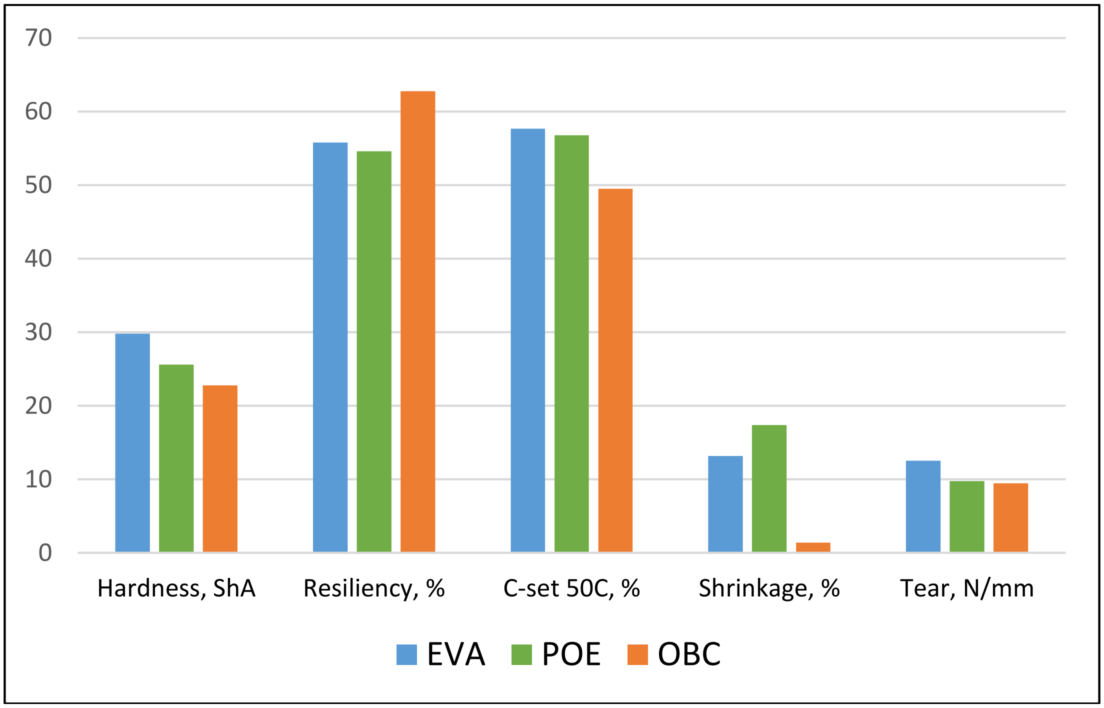

Figure 5 – Comparison of Foam Morphology of OBC, POE, and EVA