

# Study of the Thermoformability of Ethylene-Vinyl Alcohol Copolymer Based Barrier Blends of Interest in Food Packaging Applications

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**ABSTRACT:** The thermoforming capacity of a number of blends of an ethylene-vinyl alcohol copolymer (EVOH-32, with 32 mol % ethylene) with amorphous polyamide (aPA) and/or Nylon-containing ionomer with interest in multilayer food packaging structures have been studied. These blends were vacuum-thermoformed between 100 and 150°C onto male molds of different shapes and areal draw ratios. It was found that EVOH/aPA extruded blends did not improve the inherently poor formability of EVOH alone. In contrast, significant improvements in thermoformability were achieved by blending EVOH with a compatibilized-ionomer. Optimum forming capacity was achieved in a ternary blend by addition of a compatibilized-ionomer to EVOH/aPA blends in the range of 140–150°C. Analysis of

wall thickness data obtained in the thermoformed parts showed that wall thickness was significantly affected by the ionomer and amorphous polyamide content in the blend. The ternary blend showed a lower thickness reduction in the critical areas, as well as a higher uniformity in the part. A finite element analysis was used to evaluate the wall thickness distribution and the modeling results were compared with the thermoforming experiments. The simulations were performed for the vacuum-forming process employing a nonlinear elastic material model. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 3851–3855, 2004

**Key words:** barrier films; blends; ethylene-vinyl alcohol copolymer; thermoforming

## INTRODUCTION

Ethylene-vinyl alcohol random copolymers are a family of semicrystalline materials with excellent barrier properties to gases, solvents, and aromas and with outstanding chemical resistance. The superior gas-barrier properties of ethylene-vinyl alcohol copolymers (EVOH) used in multilayer food packaging structures can be compromised by its poor thermoformability, especially when deep draw and/or high forming speeds are required. This is a consequence of the high rigidity and fast crystallization kinetics of EVOH that impede uniform stretching of the material,<sup>1,2</sup> thus resulting in a narrow processing window around its melting point. Solid phase pressure forming (SPPF) is a compromise process, in which the part is formed at a temperature below the polymer melting point, resulting in an increase in both degree of orientation and mechanical properties. Polypropylene is habitually thermoformed at a temperature just below its crystalline melting point by SPPF.<sup>3</sup> However, solid phase pressure forming of EVOH in the region of 100–150°C is difficult to achieve<sup>2</sup>.

On the other hand, an important effort is dedicated to develop finite element analysis (FEA) programs to model a wide range of mold geometries and processing techniques, to predict and optimize the material distribution in a part of arbitrary geometry prior to any thermoforming process. Nevertheless, any simulation of the process must be validated with experimental data. In this respect, a nonlinear elastic material model has to be taken into account, since it is the simplest reasonable constitutive relationship available for modeling the thermoforming process. The objective of this study was to investigate the thermoformability of extruded sheets of blends of a high-barrier EVOH copolymer with an amorphous polyamide (aPA) and a compatibilized-ionomer<sup>4,5</sup> in the range 100–150°C, which is of wide interest in the thermoforming of food packaging multilayer systems.

## Limitations of EVOH in multilayer thermoforming

Thermoformed part walls are generally not uniform in thickness. Nonuniform wall thickness and thinning at the container base corners are mayor limitations of the thermoforming technology.<sup>6,7</sup> As the draw ratio is increased, localized thinning fissures and even cracking of the barrier layer can occur, especially at corners on the container, which may result in packaged product deterioration due to ingress of oxygen.

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TABLE I  
Optimum Thermoforming Windows for Some Polymers Used  
in Multilayer Food Packaging Structures

	Thermoforming Window (°C)				
	100	120	140	160	180
Polystyrene		←→			
Polypropylene			←→		
32 mol% EVOH	←→				←→
44 mol% EVOH			←→		←→

The presence of OH groups in the backbone chain of EVOH increases the intermolecular forces between polymer chains by hydrogen bonding and yields an outstanding barrier to permeants. However, their hydrophilic nature causes moisture sorption, which results in deterioration of the gas-barrier properties. Moreover, the oxygen permeability of EVOH copolymers may irreversibly be increased in the presence of steam during retorting processes,<sup>8</sup> a process habitually used for sterilization of packaged food.

The forming process can be relatively difficult to achieve when a combination of polymers within a multilayer structure is employed. Several applications in packaging include flexible and rigid containers in which EVOH can be coextruded or coinjected as the internal layer of a multilayer construction in combination with other polymers such as polystyrene and polypropylene. The optimum thermoforming windows of these structural layer polymers (in the range between 110 and 150°C) does not overlap that of EVOH (32 mol % ethylene), as can be seen in Table I. To improve the processability, an EVOH copolymer with an ethylene content above 38 mol % is habitually

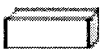


used by manufacturers, although the gas and low molar mass organic vapor barrier properties become lower than those of commonly used EVOH copolymers with lower ethylene content (32 mol % ethylene).

## EXPERIMENTAL

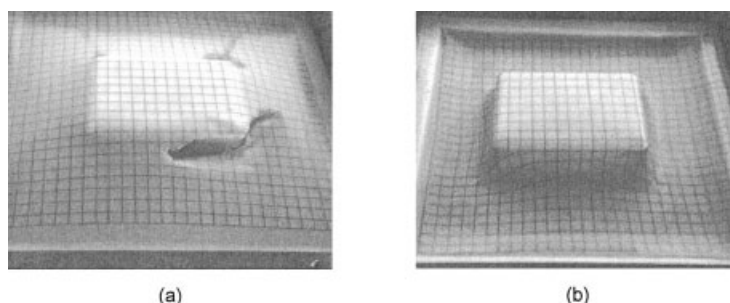
Extruded sheets were obtained from melt-mixed blends of EVOH-32 with aPA (Selar PA UX-2034) and/or Nylon-containing ionomer (Surlyn AM-7938). The EVOH copolymer used in this study is a commercial product of the Nippon-Gohsei Corp. (Japan).<sup>8</sup> The binary and ternary blends prepared were EVOH, EVOH/aPA (80/20), EVOH/ionomer (80/20), and EVOH/aPA/ionomer (80/10/10).

Vacuum thermoforming of 100- $\mu$ m-thick sheets onto male molds of different shapes and areal draw ratios was performed on a HEK Maxiformer machine. The sheets were heated to temperatures between 100 and 150°C prior to thermoforming. The mold temperature was held constant in all experiments at 35°C. A grid pattern (1.5  $\times$  1.5 cm) was imprinted on each

TABLE II  
Formability Results Obtained with Extruded Sheets for Both Different Temperatures and Draw Ratios

Geometry	Mold	Areal draw ratio (Ra)	Temperature (°C)	Sample			
				EVOH	EVOH/aPA (80/20)	EVOH/ion (80/20)	EVOH/aPA/ion (80/10/10)
	A	2.37	100	X	✓	✓	X
			120	X	X	✓	✓
			140	X	X	✓	✓
			150	X	X	✓	✓
			100	X	X	✓	X
	B	3.55	100	X	X	✓	X
			120	X	X	✓	~
			140	X	X	✓	✓
			150	X	~	✓	✓
			100	X	X	✓	X
	C	4.44	120	X	X	✓	~
			140	X	X	✓	✓
			150	X	~	✓	✓

✓, Good thermoformability; ~, discontinuities (defects in the sheet); X, failure.



**Figure 1** Thermoformed parts onto male mold (type A) at 140°C for (a) the EVOH sheet and (b) the ternary blend sheet.

plastic sheet to follow the deformation that occurred during the thermoforming experiment.

## RESULTS AND DISCUSSION

### Evaluation of formability

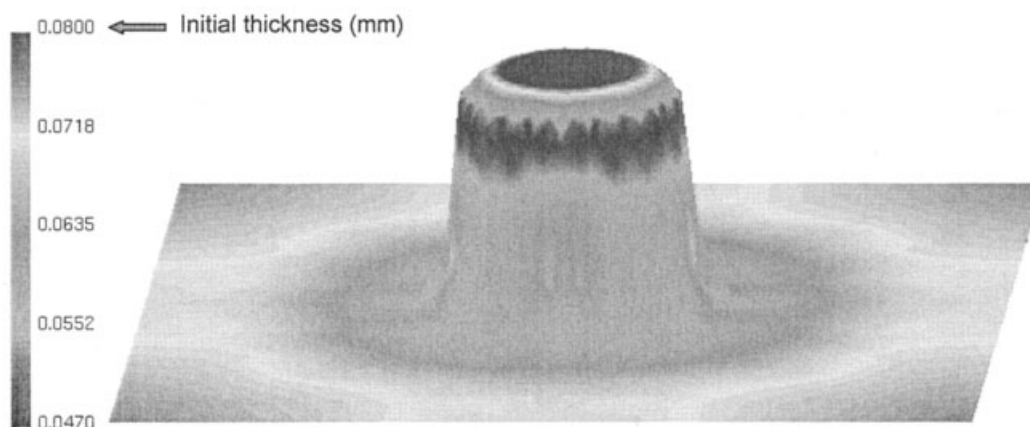
Typical results of the thermoforming tests carried out on the blends are given in Table II. Breaks and fibrillation of the thermoformed products were observed in the sheet of EVOH alone for all the shapes and temperatures studied [see Fig. 1(a)]. It was found that thermoforming could not be completed when the EVOH/aPA blend and temperatures in the range of 100–140°C were used. Thus, the addition of low contents of aPA did not improve the thermoforming characteristics of EVOH, since the PA reduces the stretching capacity of the blend compared to EVOH alone when the forming temperature was below or near the glass transition temperature of the aPA ( $T_g$  at 120°C).<sup>4</sup> Formability increased slightly at the temperature of 150°C, due to the higher chain mobility of the aPA, however, the sheet still exhibited some discontinuities (microvoids). In contrast, addition of a compatibilized-ionomer<sup>9</sup> (containing Nylon) provided an increase in the flexibility of the binary blend attributed to its low melting point (at 95°C)<sup>4</sup> and allowed a far wider thermoforming window than EVOH alone in terms of

temperature and draw ratios, as can be seen in Figure 1(b). Optimum forming capacity was achieved for the ternary blend in the range of 140–150°C, at which the aPA exhibits higher stretching capacity. Further tests are now being carried out to confirm these findings under a number of different testing conditions.

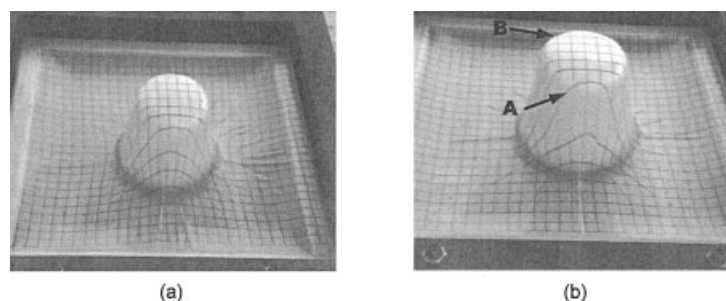
### Thermoforming modeling

In the case of a very thin sheet, most finite element analyses for the thermoforming process assume membrane approximation because of its fast calculating time and ease of coding. The finite element mesh used for the simulation was highly refined in certain regions with triangular elements of smaller size and was developed after a series of trial analyses; the refinement is focused on the region of the sheet that deforms into the edges and corners of the mold.

Tensile tests were conducted at the same temperatures employed in the thermoforming tests using an universal testing machine (Galdabini) equipped with an environmental chamber and a 1 kN load cell. The strain rate was set at 500 mm/min, since this is close to the speed of typical thermoforming operations. Nominal-stress versus deformation ratio curves obtained in tensile tests for extruded sheets were least squares



**Figure 2** Typical simulation results of vacuum forming onto male mold. The arrow indicates the initial thickness of the sheet.



**Figure 3** Thermoformed parts onto male mold (type B) at 140°C for (a) the ternary EVOH/aPA/ionomer blend and (b) the binary EVOH/ionomer blend.

fitted using a nonlinear constitutive model.<sup>10,11</sup> The finite element package (C-Mold) was used for modeling the thermoforming process of the extruded sheets and the wall thickness distribution predicted was compared with real thermoforming experiments. Figure 2 shows the typical shape and the thickness distribution simulated for an EVOH/aPA/ionomer blend at the temperature of 140°C. Because the thermoforming process takes place on a male mold, greater wall thickness at the bottom than at the rim is typical.<sup>7</sup> Figure 2 shows that the wall thickness decreases significantly along the part edges. Despite some small discrepancies, the simulation predicted the expected thickness distribution reasonably well.

#### Evaluation of thickness distributions

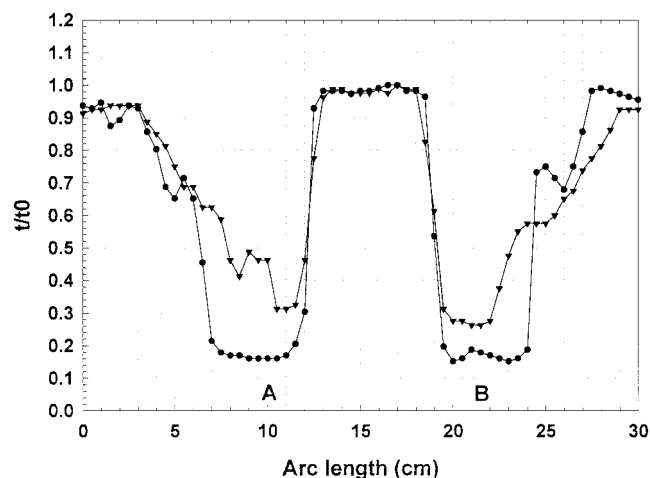
After the thermoforming process the wall thickness was measured along the top cross-section of the formed parts using a micrometer. Analysis of the wall thickness data obtained for the different thermoformed samples used in this study showed that the composition of the blends significantly affected the wall thickness distribution. However, sheet temperature did not have a significant effect on the wall thickness, such as that reported by some authors.<sup>12</sup> Figure 3 shows the thickness distribution for ternary EVOH/aPA/ionomer and binary EVOH/ionomer blends obtained at 140°C using a male mold with geometry B (see Table II). By analysis of the grid patterns stamped on the sheets prior to thermoforming, it was observed that the ternary blend was clearly thicker at locations where deformation was maximum, areas that correspond to the mold locations (A and B) indicated in Figure 3(b). This improvement in the thickness distribution of the EVOH/aPA/ionomer blend can be attributed to synergy between the contributed flexibility of the ionomer and the rigidity provided by the aPA. As a result of having slightly higher thickness in the critical regions of the part, optimum barrier properties to gases can be guaranteed, as well as a higher uniformity across the part.

Wall thickness distribution has a key influence on the properties of the formed part (mechanical and barrier). An excessive reduction in the barrier layer can limit the use of the thermoforming technology. Nevertheless, for more accurate and uniform wall thickness distribution, a female mold and techniques such as plug-assist forming, billow snap-back, and others can be employed.<sup>7,13–15</sup>

Figure 4 compares the thickness distribution along the top cross-section for binary EVOH/ionomer and ternary EVOH/aPA/ionomer blends. Although the differences in the thickness distribution along the cross-section are small, a reduction of thickness in the edges of 70% was approximately determined in the ternary blend, whereas this was of 82% in the binary blend. Thus, the results confirm a better wall thickness distribution for the ternary blend.

#### CONCLUSION

This study was aimed to improve the poor formability of EVOH copolymer (32 mol % ethylene) in the tem-



**Figure 4** Comparison of wall thickness distributions along the top cross-section for (▼) the ternary EVOH/aPA/ionomer blend and (●) the binary EVOH/ionomer blend.

perature range 100–150°C by blending this polymer with an aPA and a compatibilized-ionomer. It was found that EVOH/aPA extruded blends did not improve the poor formability of EVOH alone. In contrast, significant improvements in thermoformability were achieved by blending EVOH with a compatibilized-ionomer. Optimum forming capacity was achieved in ternary blends by addition of a compatibilized-ionomer to EVOH/aPA blends. Such blends exhibited a much wider forming window than EVOH alone in terms of draw ratio and temperature. Wall thickness distribution obtained from a number of different thermoformed parts was significantly affected by the ionomer and aPA content. The ternary blend showed a lower reduction of thickness in the critical regions, as well as a higher uniformity in the part. Finally, a finite element analysis was employed to model the drape-forming process of these blends. From this analysis, a wall thickness distribution was predicted, which was in good agreement with the experimental results.

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