

# Optimization of PE/Binder/PA Extrusion Blow-Molded Films. I. Heat Sealing Ability Improvement Using PE/EVA Blends

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**ABSTRACT:** The optimization of three-layer films (PE/binder/PA) manufactured by extrusion blow molding presents significant industrial challenges. The main issue consists in combining use properties (e.g., impermeability to water steam and oxygen, welding properties) with high mechanical, optical, and adhesion performances, while maintaining cost-effectiveness. This article shows that the introduction of EVA in the PE layer improves the heat sealing ability and optical properties without degradation of the mechanical and adhesion performances. In the most favorable case, this modification leads to a 40% reduction of

the heat sealing time, the other performances remaining either identical or higher. This leads to cost reduction of this manufacturing step while improving the flexibility of the process (wider process temperature window). The properties modifications observed can be explained by microstructure modifications (crystallinity, orientation, and molecular mobility). © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 974–985, 2006

**Key words:** blends; blown film; coextrusion; heat sealing; mechanical properties; optical properties; peeling; tearing

## INTRODUCTION

In spite of many efforts carried out by raw material producers, no existing polymer is able to combine all the properties required by some challenging industrial packaging applications. Material optimization proves to be very delicate when many performances are simultaneously required: high mechanical strength, impermeability to some specific gases or liquids, good optical (transparency, brightness, etc.) and aspect (sensory properties, effect of texture, etc.) qualities, and aptitude for a later processing (seal ability, printing ability, blocking, etc.) or recyclability.<sup>1</sup> However, being able to produce film packaging with such tailored properties is a major concern for plastics converters and a key issue for their competitiveness and their opening towards new markets. For many food-packaging applications, the encountered difficulties can partly be overcome using multilayer PE/PA structures combining the specific properties of each component. Taking into account the performances looked for to design the adequate structural stacking sequence (polymers and thicknesses selection), the remaining issue is then the cost-effectiveness.

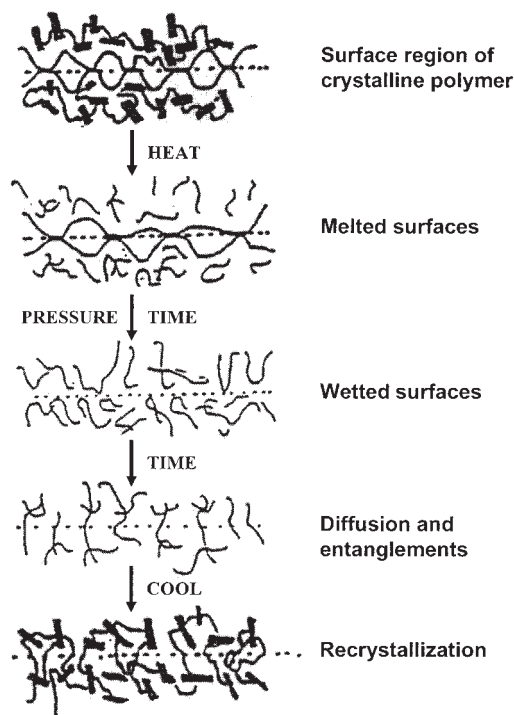
In practice, seal ability is a key performance for all packaging applications, where the assembly of two extruded films is required (e.g., manufacturing of bags).

The heat sealing process is one of the main techniques used for thermoplastic parts assembly.<sup>2</sup> The two elements to be joined are heated to soften them and to induce interpenetration and cohesion during the cooling phase. Reproducible and high quality assembly requires the adaptation of the sealing time, temperature, and, to a lesser extent, pressure.<sup>3–5</sup>

Stehling and Meka<sup>6</sup> described the molecular mechanisms involved in the heat sealing of single-layer films of semicrystalline polymers (Fig. 1). Both films are brought in contact and heated through the jaws. The crystalline regions melt, and the pressure increases the molecular contact and the wetting of the two surfaces. If the contact time is sufficient, the polymer chains of the two surfaces diffuse through the interface and create entanglements (100 Å). Finally, cooling and crystallization strengthen the assembly.

These authors also showed (Fig. 2) that the seal resistance of two polyolefin films passes by a maximum on a limited temperature interval.<sup>6</sup> For polyethylene, the temperature of seal initiation ( $T_{si}$ ) is characterized by a given ratio of amorphous phase, whereas the plateau initiation temperature ( $T_{pi}$ ) corresponds to the complete melting of the material.<sup>6,7</sup> In addition, at low temperatures (lower than the plateau

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**Figure 1** Mechanisms of semicrystalline film sealing by the heat sealing process.<sup>6</sup>

initiation temperature), failure is obtained by separation of the two films, which is characteristic of a poor cohesion due to an imperfect interdiffusion. Clean failure by tearing only appears beyond this critical temperature ( $T_{pi}$ ), corresponding to the complete fusion of the polymer surface, leading to a satisfying development of the interdiffusion mechanism.<sup>4</sup>

However, even if it is possible to obtain seal strengths that are satisfying and compatible with the industrial applications targeted using PE single layer films, their sealing range remains nevertheless narrow. As a consequence, a rigorous control of the sealing parameters is necessary, with limited setting possibilities for the sealing process.

An alternative can be found in the use of PE/EVA blends. In fact, the EVA obtained by copolymerization of vinyl ethylene and acetate has a unique combination of properties that allows its use for applications requiring a good seal ability, high resistance, and clearness over a large range of temperatures.<sup>8</sup> The EVA melting peak is wide. The seal ability range of PE/EVA blends is, therefore, wider than that of neat PE single layer films. The use of such blends, which modify the film morphology,<sup>9</sup> can potentially increase the productivity and the added value. However, the effect on other performances, such as optical<sup>10–13</sup> and mechanical<sup>14–18</sup> properties, has not been established yet.

The scientific literature has widely reported results concerning the optimization of the seal ability of single

layer films, mainly based on polyolefin, and the mechanisms involved in the sealing process. The case of complex multilayer structures is, however, rarely discussed in spite of the major industrial interest.

However, some technical publications report the use of PE/EVA blends for the production of multilayer packaging films, sheets for the automotive industry, adhesives, or peelable films.<sup>8,19–21</sup> Generally, the influences on properties other than the seal ability are not assessed, and the phenomena involved in the improvement of the seal ability are not analyzed.

This issue was, therefore, taken into account in the present study. First, the incidence of variable EVA contents in the PE layer (from 0 to 50 wt %) on the seal ability of a PE/binder/PA film will be quantified. In parallel, the influence of such a modification on other performances, such as the slip ability and the optical and mechanical properties, as well as on the productivity of the manufacturing process, will be analyzed. Finally, the properties changes will be connected to the modification of the structure and the morphology of the materials.

## EXPERIMENTAL

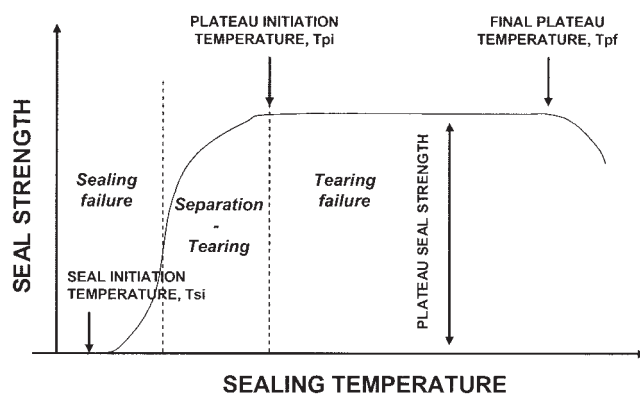
### Materials and manufactured structures

Table I shows the main characteristics of the polymers used in this study. PE/binder/PA (internal/central/external layer) film structures with variable EVA contents from 0 to 50% in weight in the PE layer have been manufactured (Table II).

In some particular cases, especially for the mechanical and/or physicochemical characterization, films are extruded without PEGMAH binder to allow the easy separation of the PE and PA layers.

### Manufacturing equipment and conditions

The 470 mm wide films (blow up ratio 1.5) are manufactured on a three-layer coextrusion line made up of



**Figure 2** Incidence of the sealing temperature on the seal strength of two polyolefin films.<sup>4,6</sup>

**TABLE I**  
Materials Characteristics

Material	Supplier	Reference	Melt flow index (g/10 min)	Density (g/cm <sup>3</sup> )	Melting temp. (°C)
LDPE	E	R FF20	0.65	0.92	112
PA 6/66	BASF	UD C35	8.01*	1.13	195
PEgMAH	DP N	B 4288	4.7	0.923	104
EVA 9% vinyl acetate	E	G FF35	0.75	0.931	102

\* Measured at 215°C, 2.16kg.

three extruders (see main characteristics in Table III), a take up equipment with speed of 11.5 m/min, and a radiant channels three-layer die (diameter 200 mm, gap 0.8 mm), set to 235°C. The extrusion temperatures of the various layers (internal, central, external) are maintained constant for all experiments (Table III).

#### Equipment and processing conditions for heat sealing

The films are sealed using heating jaws (215 × 12mm) onto a THIMONIER thermal sealing machine (type SI5-63 CA). Different experimental conditions have been tested with varying sealing times (from 0.2 to 0.7 s), pressures (from 2 to 5 bar), and temperatures (from 130 to 190°C).

#### Characterization equipment and conditions

##### Mechanical behavior in tension

The stress/strain relationships in tension are established in accordance to the ISO 527.3 standard on a ZWICK 1474 tensile machine equipped with a 1 kN force cell. The samples (150 mm × 15 mm) are cut out in coextruded films conditioned at 23°C (50% RH).

The crosshead speed is fixed at 2 mm/mn for the determination of the Young's modulus at 1% strain, and at 100 mm/mn for the measurement of the stress

and deformation at break. This equipment is also used for the peeling, tear, slip, and seal ability tests.

##### Seal strength

In the case of multilayer films, the measurement of the seal strength is generally carried out by peeling.<sup>6,22</sup> Seals are made perpendicular to the extrusion direction between the two inner PE layers of the multilayer films. Samples (15 × 150mm) are then cut out.

Figure 3 illustrates the principle of the test (a); the recorded load/displacement curve (b); and the three types of failure that can occur for a three-layer film, namely, separation between the two layers in contact (c), peeling by rupture of the lower cohesion layer (d), or tearing (e).

##### Tear strength

The tear strength corresponds to the force required for the propagation of a crack initiated in a given direction of the sample (either longitudinal or transverse direction). It is measured according to the NF T 54-108 standard in the extrusion direction and in the transverse direction. Samples dimensions are 130 mm × 50 mm. The initial crack length is 25 mm. The crosshead speed is constant and set to 100 mm/min.

**TABLE II**  
Composition of the PE/PEgMAH/PA Films

	EVA content in weight (%)	Internal layer		Central layer		External layer
		% in weight of LDPE in the support layer	% in weight of EVA in the support layer	% in weight of PEgMAH in the tie layer	% in weight of EVA in the tie layer	% in weight of PA in the external layer
Reference	0	100	0	100	0	100
EVA in internal layer	10	90	10	100	0	100
	20	80	20	100	0	100
	30	70	30	100	0	100
	40	60	40	100	0	100
	50	50	50	100	0	100

**TABLE III**  
Main Characteristics of the Co-Extrusion Line and Manufacturing Conditions

Layer	Extruder Reference	Screw		Processing conditions		
		Diameter D (mm)	Length (mm)	Thickness ( $\mu\text{m}$ )	Flow rate (kg/h)	Extrusion temperature ( $^{\circ}\text{C}$ )
Internal	D <sup>45</sup>	45	22 D	50	30	210
Central	RE <sup>35</sup>	35	31.4D	10	6	235
External	D <sup>40</sup>	40	32 D	30	22	240

### Peel strength

The adhesion of the various layers is characterized by peel tests at  $180^{\circ}$  with a crosshead speed of 100 mm/min. Samples ( $150\text{ mm} \times 15\text{ mm}$ ) are cut out in coextruded films, then sealed (Fig. 4-1). Then, the two films are manually separated to get a de-cohesion between the PA and the binder layers (Fig. 4-2). Finally, they are placed in the clamping device of the tensile machine (Fig. 4-3).

### Slip ability

Only the PE/PE slip ability (internal face/internal face) is measured. It is estimated from the measurement of the static ( $K_s$ ) and dynamic ( $K_d$ ) friction coefficients according to the NF T 54-112 standard. The tests are carried out over a 100mm distance in the extrusion direction after conditioning the film rolls at  $23^{\circ}\text{C}$  (50% RH) during 15 days.

### Optical properties

The optical properties of the films are characterized in terms of gloss, haze, and clearness. The gloss is mea-

sured in accordance to the ASTM D 2457 standard by a Gardner Micro Gloss 45 reflectometer with an incidence angle of  $45^{\circ}$ . Haze and clearness are measured following the ASTM D 1003 and ASTM D 1044 standards, using a Haze Gard Plus equipment.

### Roughness

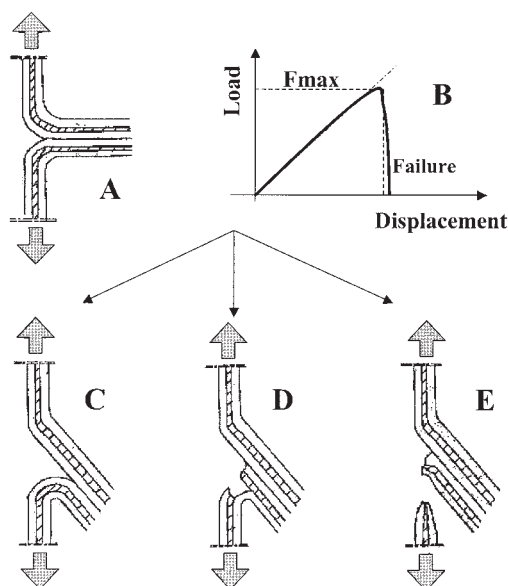
The surface roughness  $R_a$  is measured over a length of 2.5 mm with a Mitutoyo SurfTest 201 roughness controller.

### Thermal analysis

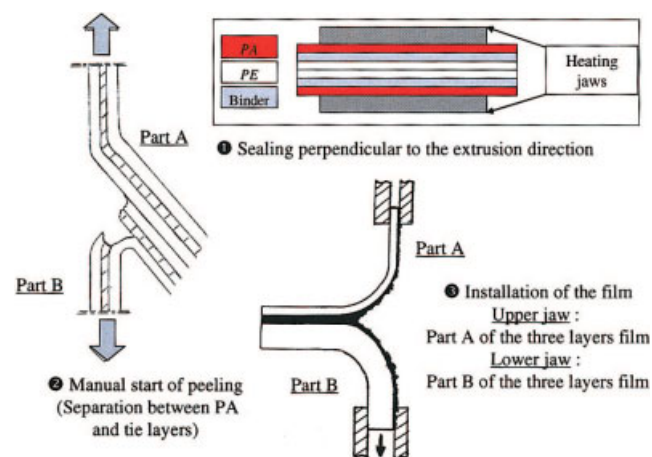
Differential scanning calorimetry is carried out on a Perkin-Elmer DSC 7 equipment between  $35^{\circ}\text{C}$  and  $220^{\circ}\text{C}$  at a temperature rise rate of  $20^{\circ}\text{C}/\text{min}$ . From the diagrams obtained, the crystallinity of the PE layer and the evolutions of the melting peaks of the film can be evaluated. A melting heat of  $287\text{ J/g}$  for a 100% crystalline polyethylene was used to calculate the crystallinity ratio.

### FTIR analysis

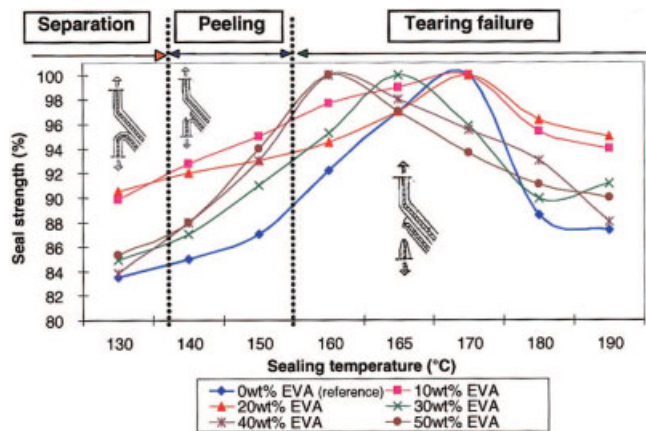
The infrared analysis is carried out by reflexion on the film's surface (PE layers), with or without sealing, on



**Figure 3** Measurement of the seal strength and failure types obtained.<sup>22</sup>



**Figure 4** Experimental device used for the measurement of the peel strength.<sup>10</sup> [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** Influence of the sealing temperature and EVA content in the PE layer on the seal strength. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

a Perkin–Elmer 1720X equipment. To measure the EVA content on the surface of a seal of the PE layer at various sealing temperatures, transmittances at  $1735\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$  were, respectively, taken as references for  $\text{C}=\text{O}$  groups of the EVA and  $\text{CH}_2$  groups of the PE chains.

## RESULTS

### Effect on seal ability

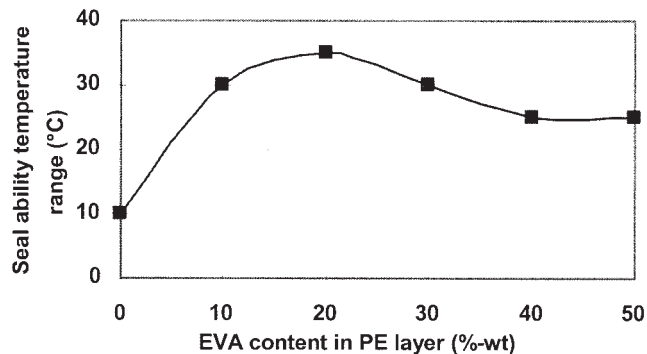
Figure 5 presents the evolution of the seal strength and the associated failure mode for films whose PE layer contains from 0 to 50% in weight of EVA, sealed with medium pressure and times (3 bar and 0.5 s) between 130 and  $190^\circ\text{C}$ . These results are presented in base 100 (value 100 corresponds, for each film, to the maximal seal strength observed between 130 and  $190^\circ\text{C}$ ).

Whatever the EVA content is, three sealing temperature zones leading to different failure modes can be distinguished:

Below  $140^\circ\text{C}$ , the failure occurs by separation, typical of a poor interdiffusion between the two PE layers during the sealing at low temperature, due to an insufficient mobility of the chains.

Between  $140$  and  $160^\circ\text{C}$ , the failure occurs by peeling. The quality of the sealing is better, but does not prevent a separation at the beginning of the sealed zone. This generates fracture initiation that propagates quickly in the internal and central layers. The lower cohesion zone, here the binder/PA interface, breaks first. As a consequence, this type of failure does not allow quantifying the seal strength but only shows that it is higher than the measured value.

Between  $160$  and  $190^\circ\text{C}$ , one can observe a failure by tearing (the three layers break at the same

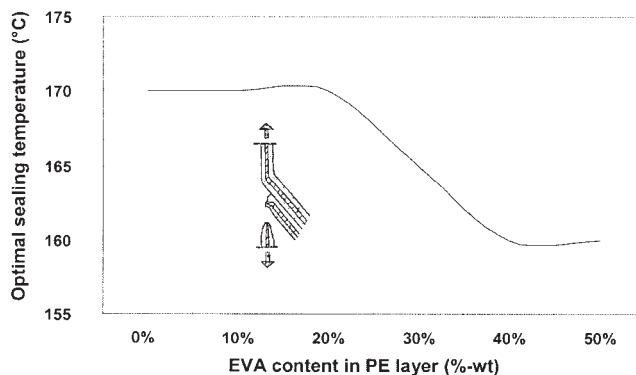


**Figure 7** Influence of the EVA incorporation in the PE layer on the seal ability temperature range.

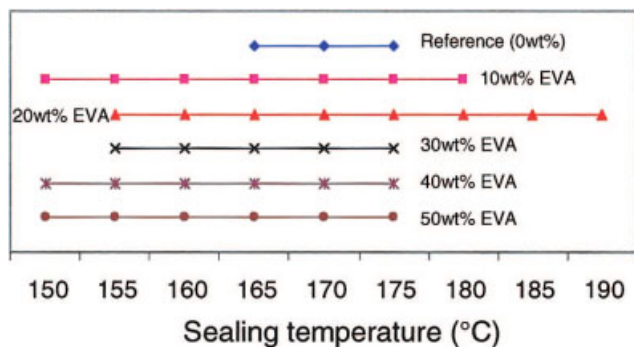
time after an important deformation without apparent crack initiation), showing again an improvement of sealing. However, here again, it is not possible to quantify the intrinsic seal strength but only to note that it is higher than the measured value.

Moreover, whatever the composition of the PE layer is, the resistance of the assembly passes by a maximum for a sealing temperature between  $160$  and  $170^\circ\text{C}$ , the failure occurring then always by tearing. This optimal sealing temperature remains constant (about  $170^\circ\text{C}$ ) between 0 and 20 wt % of EVA content, then decreases quickly of approximately  $160^\circ\text{C}$  between 20 and 40 wt %, before stabilizing again beyond 40 wt % (Fig. 6). From an industrial point of view, the use of a PE/EVA blend in the internal layer is thus interesting since it limits energy spent during the sealing process.

Finally, for a given film, the incorporation of EVA strongly affects the extent of the seal ability temperature range, defined as the range required to obtain a seal strength at least equal to 94% of the maximum resistance (Fig. 7). Without EVA, the range of seal



**Figure 6** Influence of the EVA incorporation in the PE layer on the sealing temperature, leading to the maximum assembly resistance.



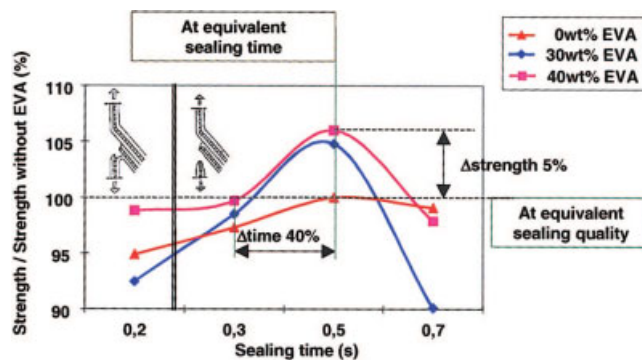
**Figure 8** Influence of the EVA incorporation in the PE layer on the seal ability temperature range. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ability temperature is very narrow (around 10°C). Obtaining a seal with sufficient quality requires a rigorous control of the processing conditions. With 0 to 20 wt % of EVA, this range strongly increases (up to 35°C), and stabilizes around 25°C for higher EVA contents. This evolution is particularly interesting from an industrial point of view since it allows a greater flexibility in the control of the sealing process.

Thus, in practice, a maximum reduction of the sealing temperature requires the incorporation of 40 wt % of EVA and is accompanied by a significant increase (in a ratio of 3 compared to pure PE) in the seal ability temperature range. On the other hand, the widest seal ability temperature range is obtained for an EVA content of 20 wt %, but that does not allow reducing the optimal sealing temperature. In all cases, an incorporation from 20 to 40 wt % of EVA in the PE layer increases the seal ability of extruded films (Fig. 8).

One industrial objective is to optimize the seal strength, but also to limit the costs related to this postextrusion operation. The optimal sealing temperature having been found, it remains to optimize the sealing pressure and time. To do that, the seal strength of various films containing 0, 30, and 40% of EVA was measured for sealing carried out at 170°C, and various values of pressure and time framing the medium conditions selected initially. The results are presented in Figures 9 and 10 in base 100 (value 100 corresponding to the resistance of the film without EVA).

For a given sealing temperature (170°C) and pressure (3 bar), the seal strength passes by a maximum for a sealing time of 0.5 s, the value initially selected for experiments (Fig. 9). For a sealing time lower than 0.3 s, the fracture is obtained by peeling. Taking into account the interdiffusion kinetics between the two layers of polyethylene, the contact time between the two films is too low and/or the heat transfer from the jaws towards the films is incomplete. Beyond a sealing time of 0.3 s, one observes failure by tearing, characteristic of a seal strength higher than the measured



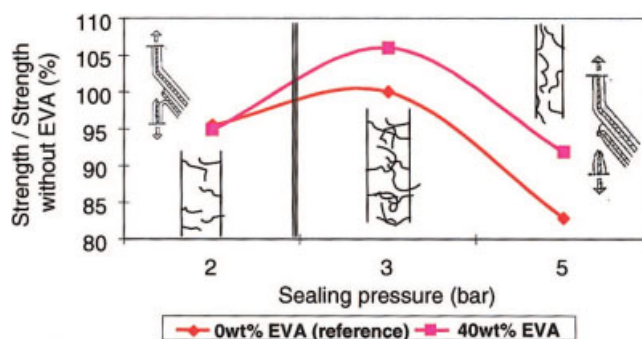
**Figure 9** Influence of the sealing time (170°C, 3 bar) on the seal strength for various EVA contents in the PE layer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

value. From an industrial point of view, for equivalent sealing quality, the addition of EVA reduces significantly the sealing time (40%); for equivalent sealing time, the seal strength is appreciably increased (5%).

For a given sealing temperature (170°C) and time (0.5 s), the seal strength passes by a maximum for a sealing pressure of 3 bar, the value initially chosen for the experiments (Fig. 10). At low pressure, the contact between the two sealed layers is not sufficient to allow an optimal interdiffusion. Conversely, a high pressure induces an important shearing at the seal edge, which can generate a failure initiation and a partial tearing during the mechanical test.

### Effect on slip ability

The values of the static and dynamic friction coefficients (PE face/PE face) of the studied films are listed in Table IV. Their evolution according to the EVA content is presented in Figure 11, in relative values compared to the initial value obtained for a layer of neat PE.



**Figure 10** Influence of the sealing pressure (170°C, 0.5s) on the seal strength for various EVA contents in the PE layer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE IV**  
**Incidence of the EVA Incorporation in the PE Layer on the Slip Ability, the Optical Properties, the Tear and Peel Strengths, and the Mechanical Performances in Tension of PE/PEgMAH/PA Films**

EVA content in the PE internal layer (wt %)	Friction coefficients		Optical properties			Tear strength (N)	
	Static	Dynamic	Haze	Clearness	Gloss	Long. dir.	Trans. dir.
0	0.92 ± 7.69%	0.72 ± 0.56%	14.2 ± 5.1%	84.6 ± 0.9%	62.1 ± 2.6%	19.79 ± 5.9%	25.57 ± 5.9%
10	0.96 ± 4.21%	0.76 ± 6.57%	13.1 ± 2.4%	87.8 ± 0.26%	65.3 ± 2.1%	20.56 ± 3.9%	25.40 ± 4.2%
20	1.12 ± 7.21%	0.87 ± 3.81%	10.4 ± 7.2%	91.1 ± 1.81%	68.6 ± 2.0%		
30	1.57 ± 1.93%	0.94 ± 1.70%	10.5 ± 2.7%	92.1 ± 0.30%	66.5 ± 3.9%	20.17 ± 3.5%	24.93 ± 2.2%
40	1.12 ± 5.41%	1.02 ± 8.06%	9.5 ± 3.8%	93.2 ± 0.23%	72.0 ± 1.1%		
50	1.53 ± 11.1%	1.13 ± 11.1%	11 ± 5.8%	91.9 ± 0.61%	69.1 ± 0.9%	20.14 ± 5.3%	25.11 ± 3.4%

EVA content in the PE internal layer (wt %)	Peeling force (N)	Young's modulus (MPa)		Tensile strength (MPa)		Tensile strain at break (%)	
		Long. dir.	Trans. dir.	Long. dir.	Trans. dir.	Long. dir.	Trans. dir.
0	1.87 ± 4.51%	239 ± 6.1%	270 ± 3.7%	35 ± 6.9%	25 ± 6.4%	330 ± 6.1%	320 ± 3.4%
10	1.83 ± 3.80%	247 ± 4.4%	254 ± 10.5%	35 ± 5.1%	30 ± 5.3%	329 ± 5.5%	359 ± 3.6%
20	1.83 ± 2.62%	256 ± 6.2%	267 ± 12.4%	29 ± 16.2%	32 ± 4.4%	297 ± 11.1%	357 ± 4.9%
30	1.85 ± 2.54%	250 ± 2.3%	260 ± 6.3%	31 ± 8.4%	36 ± 5.6%	316 ± 5.7%	385 ± 3.1%
40	1.87 ± 2.85%	244 ± 1.6%	244 ± 6.8%	30 ± 12%	31 ± 8.7%	349 ± 7.2%	355 ± 3.1%
50	1.86 ± 3.30%	244 ± 10.6%	271 ± 6.3%	39 ± 14.9%	26 ± 6.2%	383 ± 11.2%	334 ± 7.5%

One can very clearly observe a significant linear increase in the dynamic friction coefficient with the EVA content, which can reach 60% of the initial value (without EVA). Because of the measurement technique used, the results obtained for the static friction coefficient are very dispersed. However, whatever the composition of the internal layer is, both dynamic and static friction coefficients follow an identical trend.

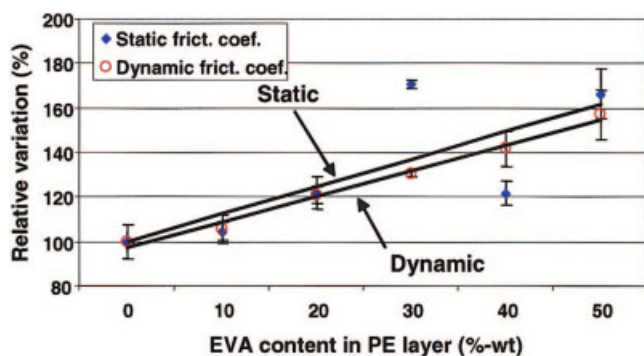
From an industrial point of view, this result can be penalizing, since the slip ability of the film internal surfaces decreases, making more difficult the possible opening operations during conditioning. To overcome this effect, the additional incorporation of slipping or antiblocking agents may be considered. In that case it would, however, be recommended to analyze their

incidence on the other properties of the film (in particular, optical properties and seal ability).

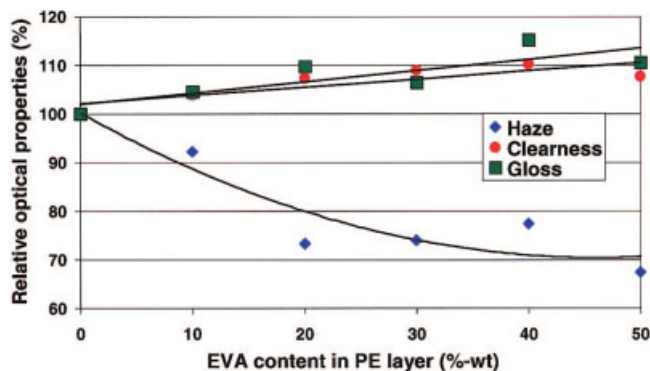
### Effect on optical properties

The haze, clearness, and gloss performances of films with EVA contents of 0 to 50 wt % are presented in Table IV. Figure 12 shows the evolution of these optical characteristics according to EVA content, in base 100 (value 100 corresponding to an internal layer of neat PE).

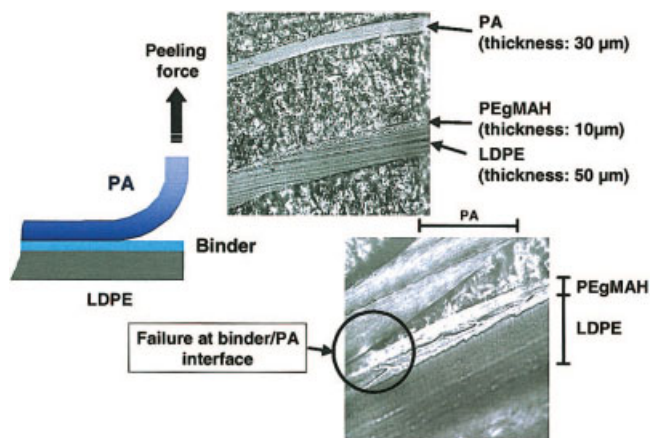
It clearly appears that the incorporation of EVA improves all the considered optical properties. The haze strongly decreases (up to 30%), and the gloss and



**Figure 11** Influence of the EVA incorporation in the PE layer on the friction coefficients (internal face/internal face). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 12** Relative evolution of the optical characteristics according to the EVA content incorporated in the PE layer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 13** Failure type after EVA incorporation in the PE layer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

clearness increase to a lower extent (up to 10%). Therefore, the incorporation of EVA has obvious industrial advantages. The films are glossier, have a less “milky” aspect, and are likely to let be distinguished, without distortion, finer details of the package content.

#### Effect on tear strength

The tear strength of films with various EVA contents is presented in Table IV. Taking into account data scattering, the noted variations are not significant. Thus, the tear properties of the three-layer film are not affected that much by the incorporation of EVA.

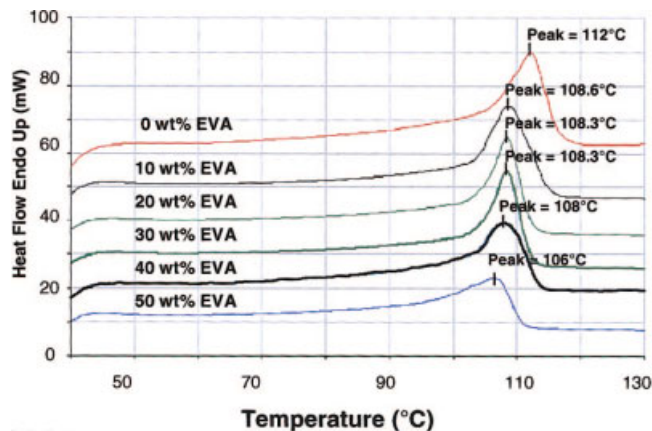
Moreover, the ratio of transverse/longitudinal direction tear strengths lies between 1.22 and 1.24, that is, the tear strength in the transverse direction is higher than the resistance in the machine direction (or longitudinal direction), from 22 to 24%.

#### Effect on mechanical behavior in tension

Table IV shows the mechanical characteristics of films according to the EVA content. Taking into account data scattering, the differences between the various materials are not significant. We can consider that the mechanical properties in tension (module, stress, and strain at break) of the three-layer film are not affected by the incorporation of EVA.

#### Effect on adhesion properties

Whatever the EVA content is, the adhesion tests lead to a failure of the binder/PA interface (Fig. 13). Therefore, the PE/binder adhesion is higher than that of the binder/PA. The peel force ( $1.85N \pm 3.7\%$ ), characteristic of PEgMAH/PA adhesion, is not affected by the EVA (Table IV).



**Figure 14** Influence of the EVA incorporation on DSC thermograms of the PE layer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

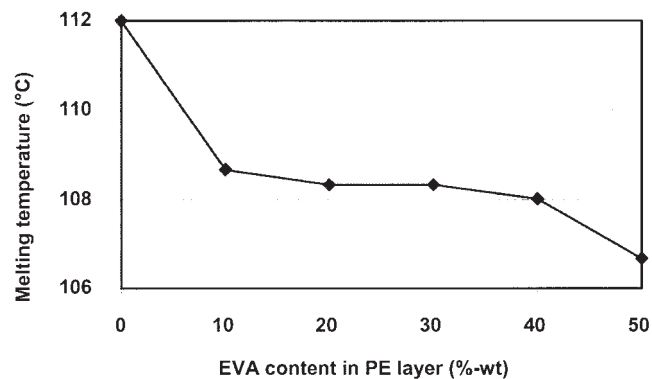
#### Experimental results summary

Whatever the composition of the PE layer of the studied film multilayer is, the global peel strength remains constant, since the initial mechanism of degradation (failure at the binder/PA interface) is not modified. In a similar way, the global mechanical properties in tension of the three-layer structure remain roughly constant. In fact, only the following performances are affected to a significant extent by incorporation of EVA:

**The seal ability:** the optimal sealing temperature is appreciably reduced, whereas the range of sealing temperature is notably increased.

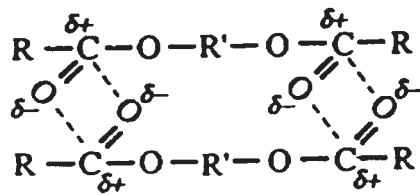
**The slip ability** (internal face/internal face) is slightly degraded, and may require the incorporation of other additives, such as slipping and/or antiblocking agents.

**Optical properties:** the three criteria of haze, clearness, and gloss are improved.



**Figure 15** Influence of the incorporation of EVA in the PE layer on the melting point.





**Figure 16** Van de Waals interactions between CO groups of EVA.

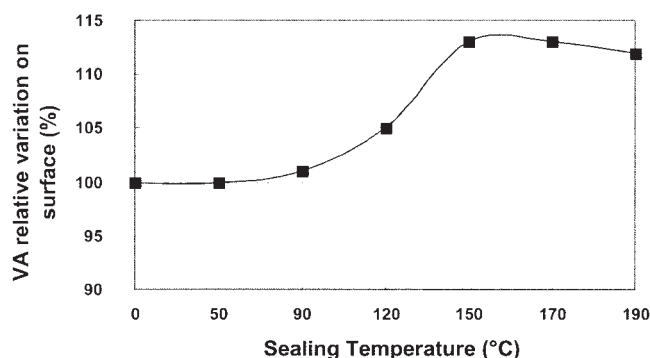
All these properties are generally strongly related to the microstructure and the morphology of the manufactured films. This is why the following section will focus on determining the structural parameters modified by the incorporation of EVA. In addition, even if such a PE/EVA blending has a negligible influence on the global mechanical properties of the film, its effect on the mechanical characteristics of the only internal layer will be nevertheless quantified for use in later optimization of mechanical dimensioning.

## DISCUSSION

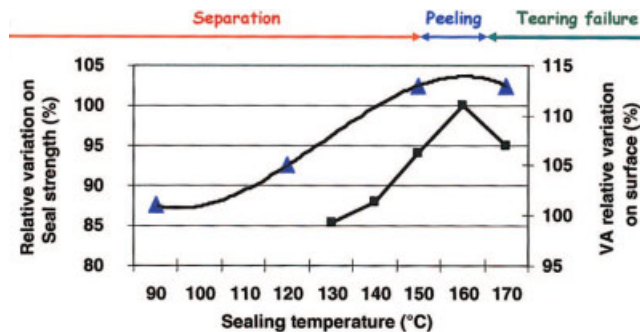
### Morphological modifications

DSC analyses of the internal layers show that the incorporation of EVA induces significant modifications of the physicochemical properties, as well as of the microstructure and the morphology of the PE layer, which can explain the evolutions of the measured properties (Fig. 14).

The incorporation of EVA induces a reduction in the melting point of the internal layer (Fig. 15). Thus, at equivalent temperature, the chains mobility is higher, allowing a more complete interdiffusion. In parallel, the temperature required to obtain a sufficient mobility is lower in a blend containing EVA. Moreover, the EVA chains have a lower viscosity than that of PE. Thus, they are more mobile, which reinforces the effect of the reduction in the melting point of the inter-



**Figure 17** Evolution of the vinyl acetate content on the seal surface from an IR analysis of film containing 50 wt % EVA in the PE layer (100% corresponds to the not sealed film).



**Figure 18** Evolutions of the vinyl acetate content on the surface and the seal strength according to the sealing temperature for a film containing 50 wt % EVA in the PE layer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

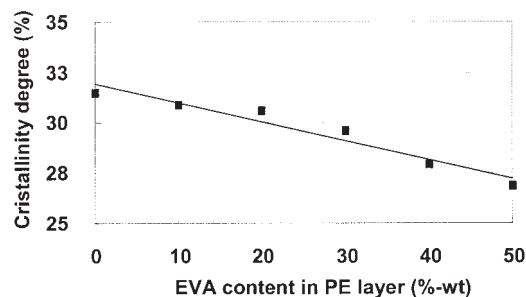
nal layer. As a consequence, the minimum sealing temperature is reduced.

In addition, even if it is not measured directly because of the failure type observed, it is possible to suppose that the EVA improves the seal strength due to stronger intermolecular forces being exerted on the diffused segments. In addition to the interpenetrations of the PE chains, the incorporation of EVA is accompanied by the creation of Van der Waals interactions between the CO groups of EVA (Fig. 16).

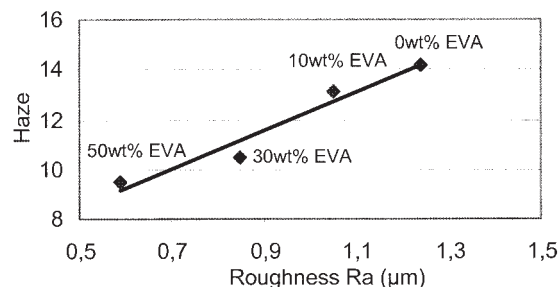
Moreover, infrared analysis by reflexion of the PE layer film surface at various sealing temperatures shows an increase in the vinyl acetate content going up to 13% for temperature above 150°C (Fig. 17). This illustrates the high dominating mobility of the EVA and reinforces the seal strength by the increase in acetates groups on the surface (Fig. 18).

Finally, the addition of EVA also causes a significant reduction in the crystallinity degree (Fig. 19) and the melting peak, widening towards the low temperatures, characteristic of a finer crystalline microstructure (Fig. 14).

This effect was previously observed by Brogly et al. Microscopy analyses clearly highlighted that the crystalline zones size decreases, whereas their number increases with the increase in vinyl acetate content.<sup>9</sup>



**Figure 19** Incidence of the EVA incorporation in the PE layer on the crystallinity degree.



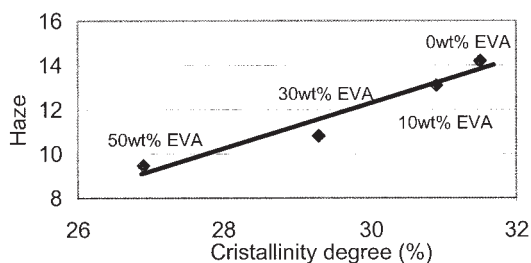
**Figure 20** Haze/Roughness relationship for various EVA contents in the PE layer.

### Optical properties modifications

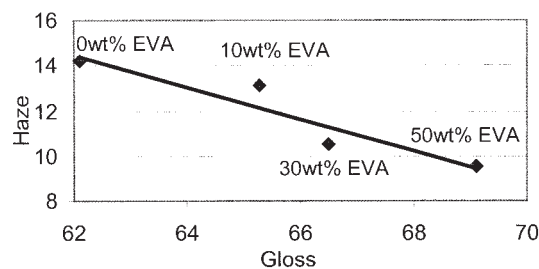
In addition, the relationship between roughness, haze, gloss, and slip ability is clearly established. This relationship is explained in the literature by a crystalline structure modification of the PE layer.

The dispersion of the light is affected by either the bulk or the surface morphology of the film.<sup>10,12</sup> The size and the organization of the crystalline structures control an important part of the optical properties.<sup>21</sup> If some crystalline structures exist on the visible light wavelength scale, important reflexions and dispersions occur, creating haze. Moreover, Sukhadia and al. showed that the majority of the haze contribution in the blow molding process was due to the film surface roughness (approximately 2/3).<sup>11</sup> Thus, the haze variations are caused by the light dispersion due to the surface irregularities.<sup>12</sup> The latter are generated either by the extrusion roughness, an effect of the molten flow on the die surface, or by the crystallization roughness, occurring by formation of crystalline aggregates on or very close to the film surface. This last mechanism is dominant here because of the constant extrusion conditions.

As Sukhadia et al.<sup>13</sup> noted, we can notice that the haze decreases with the reduction in the crystallinity degree, but also because the surface roughness decreases. The size of the crystalline zones decreases because of the improvement of the molecular mobility. The result is a low surface roughness and thus a reduced haze (Figs. 20 and 21).



**Figure 21** Haze/Crystallinity degree relationship for various EVA contents in the PE layer.



**Figure 22** Haze/Gloss relationship for various EVA contents in the PE layer.

Moreover, within the experimental range tested, the gloss is linearly connected to the haze (Fig. 22) and so is also dependent on the surface roughness and the film crystallinity.

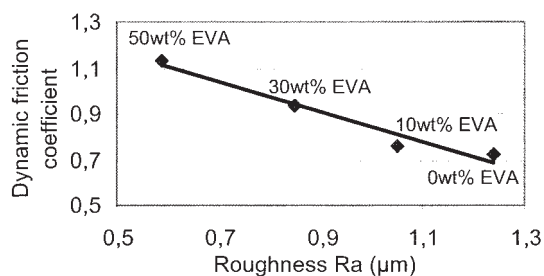
Finally, the EVA incorporation increases the friction coefficient, characteristic of the reduction in surface roughness, but also explains the increase in the sticky aspect of the film (Fig. 23). The vinyl acetate addition in a polyethylene increases the polarity of the molecule, thus creating attraction forces between the two surfaces due to interactions between EVA C=O groups.

### Mechanical properties modifications

Complementary mechanical tests were carried out on extruded films without binder to analyze the possible incidence of the EVA incorporation on the mechanical properties of the PE layer alone, knowing that it is insufficient to affect the mechanical properties of the whole multilayer film because of the high performances of PA (Table V).

Whatever the composition of the PE layer is, the mechanical behavior in tension is appreciably more ductile in the transverse direction (blowing direction) than in the longitudinal one (extrusion direction). The elongation at break is 25% lower in the longitudinal direction, while strength is 40% higher (Fig. 24).

These results are logical insofar as the blow up ratio is low. Then, the stresses generated during the manufacturing are primarily due to take up, which pref-



**Figure 23** Friction coefficient/roughness relationship for various EVA contents in the PE layer.

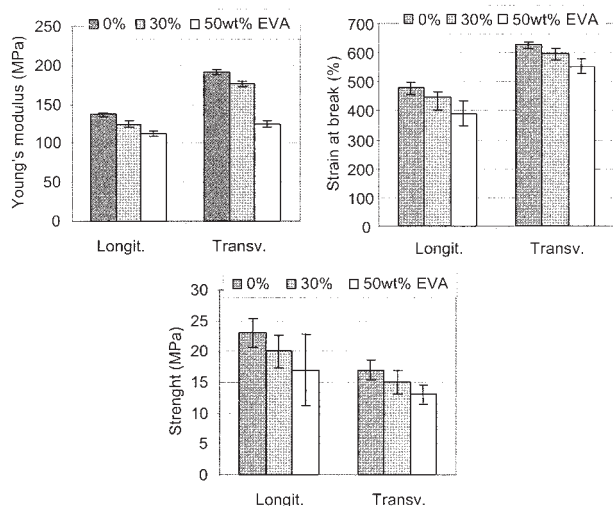
**TABLE V**  
Tensile Properties of the PA Layer

	Young's modulus (MPa)	Strength (MPa)	Strain at break (%)
Long. direct.	236 ± 8.6%	62 ± 10%	304 ± 4.6%
Trans. direct.	264 ± 9.9%	78 ± 10%	405 ± 6.1%

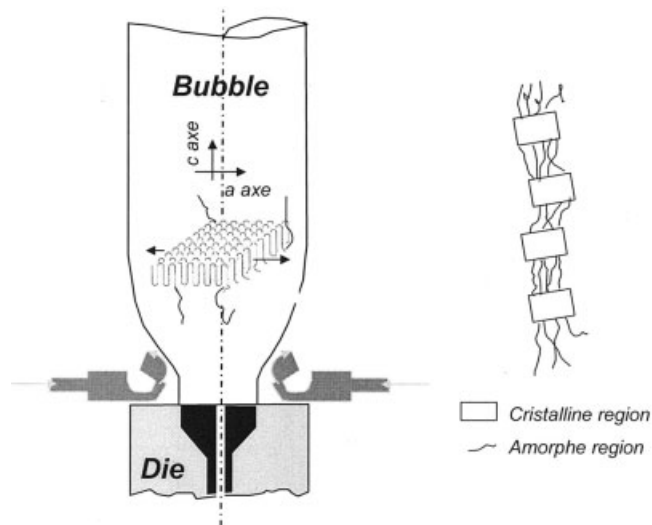
erentially orients the crystalline lamellae (an axis of the crystal) in the direction perpendicular to the maximum processing stress, that is, in the blowing direction (circumferential direction of the bubble, Fig. 25).

However, for the PA layer (Table V), whose lamellae are also oriented in the blowing direction, the strength at break is higher in the transverse direction, contrary to what is observed for the PE layer. This can be explained by the fact that the energy of the hydrogen bonds between the PA chains is 10 times more important than the Van der Waals attraction forces between the PE chains<sup>23</sup> (Fig. 26).

These relationships between processing and orientation also explain the variations observed for tear strength. Indeed, Lindenmeyer and Lustig<sup>14</sup> supposed that the tear strength is proportional to the chains number whose axis is in a perpendicular plane to the loading direction. The energy required to propagate a notch perpendicular to the chains (rupture of covalent bonds) is higher than that required if the notch is in the chains direction.<sup>15,16</sup> Kim et al.<sup>17,18</sup> do not relate the tear strength to the chains orientation but to that of the lamella clusters. The lamella normal orientation parallel to the machine direction explains the higher values of tear strength in the transverse direction (Fig. 25). This molecular orientation state explains that the



**Figure 24** Young's modulus at 1%, tensile strength, and strain at break in longitudinal and transverse directions for the PE layer at various EVA contents.

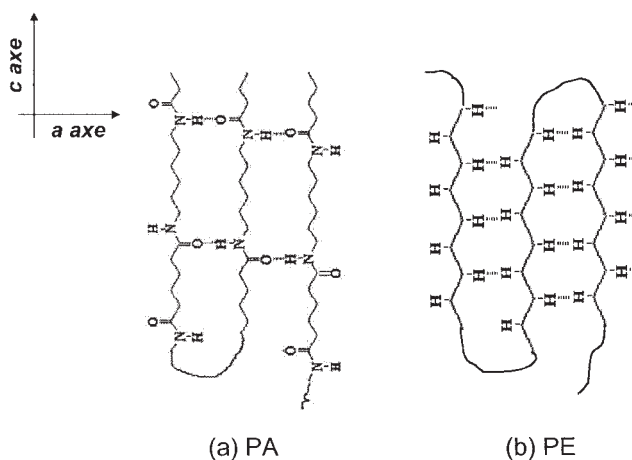


**Figure 25** Preferential orientation of the crystalline lamellae for a blow up ratio of 1.5.

tear strength is always higher in the transverse direction whatever the EVA content is.

Finally, the EVA incorporation induces a global reduction in all the tensile properties of the PE layer because of the weaker performances of the EVA compared to those of PE. A reduction in the modulus (15% in the longitudinal direction and 30% in the transverse direction), in strength (25% in the two directions), and in elongation at break (17% in the longitudinal direction and 10% in the transverse direction) is noted when the EVA content is increased from 0 to 50% in weight (Fig. 24).

Nevertheless, the EVA incorporation does not modify the mechanical properties of the three-layer film. Thus, this modification will not penalize the PE/binder/PA film in terms of mechanical behavior for future applications.



**Figure 26** Bonds between PA chains (A) and PE chains (b).

## CONCLUSIONS

The study of the seal ability of industrial three-layer PE/PEgMAH/PA films highlighted different failure modes typical of multilayer structures. At low temperatures, the film fails by separation, and at high temperatures by tearing. For intermediate temperatures, the failure occurs by peeling at the weakest interface (PA/binder).

The potential interest of incorporating EVA in the PE layer of a PE/PEgMAH/PA film was also confirmed. This modification positively influences the seal ability. The widening of the seal ability range was attributed to a decrease in the melting temperature of the internal layer, to a reduction in the crystallinity level, and to a finer crystalline structure, enhancing the interdiffusion phenomena at the interface of the sealed surfaces. The increase in the seal strength was also connected to the better interdiffusion of the PE chains, but also to the strong intermolecular forces appearing between the CO groups of EVA in the sealed layers (this mechanism is reinforced by the migration of the EVA to the surface of the internal layers during the sealing process).

Furthermore, this study shows that the use of PE/EVA blends notably improves the optical properties of the films, without impairing the mechanical and adhesion performance. Only the slip ability (PE layer/PE layer) is slightly deteriorated. However, this characteristic could be maintained at its initial value with the addition of additives, such as slipping and/or anti-blocking agents. All the evolutions of these performances can be connected to the aforementioned changes in the microstructure and the morphology.

Thus, at identical or even higher performances, this composition modification of the three-layer film by addition of EVA in the PE layer appreciably reduces (about 40%) the sealing cycle time, and, therefore, the costs related to this phase, while authorizing a greater flexibility in the adjustment of the extrusion blow molding process (wider sealing temperature range). This fully justifies the use of such PE/EVA blends in industrial packaging applications.

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