A New Ziegler-Natta Octene LLDPE for High Performance Blown Film Applications: Benefits of Coextruded Vs Blended LDPE/LLDPE Films

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ABSTRACT

In this work a new family of high-performance LLDPE resins, made by an advanced Ziegler-Natta catalyst, is presented. Moreover, the advantages of a three layer coextrusion Vs a monolayer LLDPE/LDPE blend of the same resins are investigated.

Experimental results show that the addition of a small amount of LDPE (up to 20%) into LLDPE in a coextruded structure can achieve the best optical performances (i.e. strong haze reduction) together with a significant hot tack force increase.

It has been observed that the synergistic effect in LDPE/LLDPE blends may relate to radical changes in viscoelasticity and relaxation times of these blends. Therefore, viscoelastic properties are studied.

Finally, the correlation between morphological structure, surface roughness and sealing behaviour is discussed.

INTRODUCTION

Linear low density polyethylene resins are manufactured by copolymerizing ethylene with selected alpha-olefin comonomers, such as 1-butene, 1-hexene and 1-octene.

Compared with LDPE, the presence of small amounts of alpha-olefin introduces short chain branches (SCB) which strongly improve the physical properties of the resins as much as longer is SCB extent and broader is SCB distribution (SCBD).

A significant amount of work in the area of characterizing the molecular structure of LLDPE has been carried out over the time(1-6). It’s generally recognized that both the existence of SCB ans SCBD are the key factors to improve fracture mechanical properties (i.e.impact, puncture and tear resistance) and heat sealing performances (hot tack and heat seal strength).

In these last years, several high performance LLDPE resins for film applications have been developed through advanced Z-N or single-site catalyst.

These new resins (e.g. “super-hexenes”, metallocene-catalysed PE) are reported to have superior properties over conventional polyethylenes, principally due to their narrow molecular weight distribution and more uniform comonomer distribution.

However, these property improvements are not made without sacrifice in processability. It’s well known that LLDPE polymers, at high shear rates, “shear thin” less than LDPE, so that LLDPE meets more difficulties during processing.

Blends of LDPE and LLDPE have been extensively used in industry mainly to overcome these inconveniences. The addition of LDPE modifies the extensional viscosity of LLDPE and improves the productivity of LLDPE in film blowing(7). In addition to that, LDPE is able to reduce the tendency of melt fracture to occur.

On the other hand, blending of high performance resins has a detrimental effect on mechanical film properties, although there are exceptions in certain compositions.

The aim of this paper is to present a new advanced Ziegler-Natta octene LLDPE for high performance film applications and, at the same time, to determine the best way to utilize it in blend with LDPE to achieve optimum processability and mechanical properties. Monolayer blended films made by this C8-LLDPE and LDPE were compared to three-layer coextruded films of A:B:A structure where A is C8-LLDPE/LDPE blend and B is pure C8-LLDPE.

The compatibility of C8-LLDPE/blend through a rheological study was also investigated.

EXPERIMENTAL

a) Materials and sample preparation

The high performance C8-LLDPE presented in this work is an octene based linear low density polyethylene produced by Polimeri Europa, Clearflex H&T LFH208, having MFI~0.7g/10’ and density~0.919g/cm³. It is copolimerized by solution process. From now on, we identify it as “HP-C8”.

The blending of LLDPE was obtained by adding a LDPE grade produced by Polimeri Europa, Riblene FL30, having MFI~2g/10’. This grade was a homopolymer made by high-pressure process.

The three-layer films were manufactured by using a Ghioldi/Bielloni blown film line equipped with a typical LDPE barrier screw. The die diameter is 200mm; the extruders have 40mm diameter and 24:1 L/D ratio. For all the runs the die gap was positioned at 2mm (80mil), the blow-up ratio was 2.5, the output rate 60kg/h, the film thickness
25μm and the melt temperature was 220°C in each layer. The three-layer coextruded films A:B:A were always produced with pure LLDPE as the middle layer (B). The inner and outer layers were made by blends of HP-C8 and LDPE in different proportions. The layer distribution was kept constant and equal to 25/50/25.

Mono-layer blown film extrusion was performed on a Macchi line. The die diameter is 280mm; the extruder, having 55mm diameter and 30:1 L/D ratio, is equipped with a grooved feed barrel. The output rate was held constant at 60kg/h and the die gap was positioned at 2mm (80mil). Blow-up ratio and film gauge were held fixed at 2.5 and 25μm (1 mil) respectively. The melt temperature was 220°C.

b) Structural analysis

The molecular weight (Mw) and molecular weight distribution (MWD) were determined by Gel Permeation Chromatography with a Waters GPC 150, equipped with four TSK gel 4M-H6 mixed columns. 1,2,4 trichlorobenzene was used as solvent at 135°C.

The content of SCB, classified by its molecular weight, and SCBD were determined combining GPC and FTIR analysis. A LC-Transform (mod 410 Lab. Connection) equipped with a sample collection germanium disc was used as interface between GPC separation and infrared analysis. The content of SCB was obtained by infrared spectroscopy using a methyl symmetric deformation band at 1378 cm⁻¹ with respect to the area of the reference band at 4305-4355 cm⁻¹ (8).

The differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer Pyris-1 DSC. The samples of about 10mg weight were sealed in aluminium pans; the thermograms were obtained at a heating rate of 5°C/min.

c) Rheological and mechanical tests

Rheological properties were measured using a plate-plate rotational rheometer (RDA II by Rheometric Scientific). All the samples were obtained from compression molded plaques directly from the investigated films. The strain level was kept within the linear viscoelastic region (10%); the angular frequency dependance of shear storage modulus G’ and loss modulus G” was measured at 190°C in the frequency range of 0.01 to 100 rad/s. η’ (real part of complex viscosity) and η” (imaginary part of complex viscosity) of the blends were also calculated and used for the Cole-Cole plot.

Tensile properties were measured using a Instron dinamometer. The ASTM D882 specimens were kept at 23°C and 50% humidity for 48 hrs before the test; the crosshead speed was fixed at 500mm/min. At least ten specimens of each sample were tested and the standard deviation value has been reported.

The total Haze was measured by means of a Haze Gard plus instrument (BYK-Gardner) following ASTM D1003 method.

Elmendorf Tear test were performed by means of a pendulum tear tester from ATS Faar (ATS100 Model) following ASTM D1922 procedure. The tests were performed in machine direction (MD) meaning that the notch made on the sample was aligned to the machine direction of the film extrusion.

Dart impact strength measurements were determined following ASTM D1709 (method A and B) procedure. The dart heads are made by aluminium and the diameter of the incremental weights were kept equal to the diameter of the dart head (38.1mm-method A; 50.8mm-method B).

For thermal shrinkage measurements, a piece of film specimen (100mm*100mm) was placed between two aluminium plaques. Silicone oil inside a thermostatic bath was used as fluid for heat transport. The film specimen, together with the plaques, was heated at a fixed temperature (usually ranking from 100°C to 150°C) for 10s. The percentage of free thermal shrinkage for each direction (MD, TD) was calculated as follows:

\[
\text{thermal shrinkage} \% = \frac{(L_0 - L_f)}{L_0} \times 100
\]

where \(L_0\)=100mm (initial length) and \(L_f\) is the length of the specimen after shrinking.

The hot tack (in machine direction, MD) of films was determined using a Davinor hot tack tester. Two films having 15mm as width were placed between the sealing bars and pressed (P=1.5 bar) at different temperatures for 0.5s. The hot tack strength was measured immediately after the sealed film was cooled for 0.6s.

RESULTS AND DISCUSSION

Advanced Ziegler-Natta catalysts are finding ever increasing application due to their ability to create attractive resins with superior strength over conventional polyethylenes.

A comparison between HP-C8 and a standard C8-LLDPE, in terms of molecular weight distribution, short chain branching distribution, thermal characteristics, sealing behavior and impact resistance is given in Figure 1 through 4-b, respectively.
**Fig. 1** – Molecular weight distribution of HP-C8 in comparison to a conventional C8-LLDPE

**Fig. 2** – MW and SCB distribution of HP-C8 in comparison to a conventional C8-LLDPE

**Fig. 3** – DSC thermogram of HP-C8 in comparison to a conventional C8 LLDPE

**Fig. 4a** – Hot Tack behavior of HP-C8 in comparison to a conventional C8-LLDPE

**Fig. 4b** – Dart impact resistance of HP-C8 in comparison to a conventional C8-LLDPE
Despite an overlapped molecular weight distribution (fig.1), a more homogeneous comonomer distribution (fig.2) is clearly observed. As a consequence, the crystalline morphology is significantly affected and the melting peak of HP-C8 is demonstrated to be lower than that of a conventional C8-LLDPE (fig.3).

The heat sealing window of HP-C8 (fig.4a), dominated by the melting behavior of polyethylene films\(^{(9)}\), is shifted towards lower temperature. This superior performance means that HP-C8 is able to increase the packaging speed and to improve the package integrity, mainly in presence of contaminations (oils, fats, coffee, flour, etc.). On top of this, the dart resistance is strongly enhanced (fig.4b). Previous works\(^{(10-11)}\) put in evidence the effect of the SCB length and SCB distribution on the impact properties of LLDPE.

However, this new family of high performance LLDPE resins still lacks the extrusion processability of high pressure LDPE resins.

Blending of polyethylenes is widely used in film industry since it can easily take advantage of different materials optimising the overall performances of the final manufacture.

Coextrusion, better than monolayer blends, has gained a lot of attention in these last years. Some previous authors have investigated benefits od LLDPE/LDPE coextruded films vs blend-extruded ones\(^{(12-14)}\).

Our aim is to confirm the substantial improvement in physical properties of the coex-film in comparison to the blended extruded film of the same proportion, as already shown in literature. The HP-C8 was used together with a high-pressure LDPE having MFI=2g/10\(^{\circ}\) and density=0.924g/cm\(^3\) in many different proportions in order to obtain the optimal formulation. The compatibility between the two polymers has been investigated by rheological determinations.

The Cole-Cole plot representing the relationship between the real ($\eta'$) and imaginary viscosities ($\eta''$) of the blends at 190\(^{\circ}\)C is shown in fig. 5a.

\[\text{Fig.5a – Cole-Cole plot of HP-C8/LDPE blend with respect to the pure components}\]

This plot is often used to analyse the miscibility of polymer blends; a semicircular shape suggests good compatibility\(^{(15)}\). As seen in figure, the curves of each blend composition are close to semicircular shape. The dependance of complex viscosity on blend composition is reported in fig.5b.

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Complex viscosity shows a slight PDB (positive deviation blending) from linearity at low shear rates; at high shear rates the viscosity follows the rule of mixtures. We can conclude that compatibility in our blend fairly depends on shear rate; thus severe processing conditions (i.e. high shear rates) allow to achieve total compatibility for all the compositions investigated.

The impact strength and Elmendorf Tear resistance in MD for both coextruded and monolayer films are shown in figs 6-7.

Generally it is observed an antagonistic effect of LDPE on fracture properties of pure LLDPE and the decrease seems to be much more pronounced for dart impact in comparison to MD-tear strength. We believe that, taking into account the applied distribution layer 25/50/25, LDPE plays a fundamental role in determining the overall film properties. Its density (0.924 g/cm³) could be one of the key factors to explain why fracture mechanical properties are strongly depressed.
In contrast to the dramatic effect on dart impact strength, the effect on optical properties is sinergistically positive (fig.8).

Coextruded films have significantly lower haze than both pure components and monolayer films. The best results are achieved with the formulation 20LD/80HP-C8//HP-C8//20LD/80HP-C8. Over 20\%w/w of LDPE no difference is seen between coextruded and monolayer blended films.

Looking at tensile properties (i.e. 1\% secant modulus MD in fig.9a), a sinergistic effect is observed for coextruded films.
The monolayer blended films follow almost linearly the rule of mixture, while an increase (positive deviation) of rigidity is shown for three-layer films at all compositions investigated. Furthermore, the improved stiffness is supported by a decrease in stress and elongation at break in MD (fig.9b, 9c) which is much more evident for coextruded with respect to monolayer blended films.

We can conclude that the lower haze of coextruded HP-C8/LDPE blend, together with the antagonistic effect on fracture properties can be related to relevant changes in the crystalline morphology of the films. In fact, the presence of LDPE, which contains many molecules with LCB, induces a transformation from a spherulitic-like superstructure (typical of a pure LLDPE having a very short melt relaxation time) to a row-nucleated structure that generally brings to smoother surface and hence lower haze values\(^{16-17}\). A linear dependance of total haze from Elmdendorf Tear reistance in MD\(^{18}\) fully confirm that the row-nucleated crystals orientation strongly determines the resistance to fracture propagation in a tear test\(^{19}\).

In figg.10a-b thermal shrinkage measurements are reported.

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**Fig.9b** – Stress at break of coextruded HP-C8/LDPE films vs monolayer blended HP-C8/LDPE films

**Fig.9c** – Elongation at break of coextruded HP-C8/LDPE films vs monolayer blended HP-C8/LDPE films

**Fig.10a** – MD Thermal Shrinkage of 10/90 LDPE/HP-C8: coextruded blend vs monolayer blend of the same composition
The coextruded blend 10% LDPE/90% HP-C8, in comparison to the monolayer blend having exactly the same composition, shows a higher shrinkage in MD and an expansion in TD. Since the thermal shrinkage is usually taken as a measure of amorphous chain extension, it’s reasonable to assume that the different kind of processing (coextrusion rather than monolayer blending) could change the balance between crystal and amorphous phase orientation, increasing the latter one.

Finally, as a further support of changes in crystallinity of the film induced by blending LDPE resin, hot tack curve of coextruded pure LLDPE vs coextruded blends LDPE/HP-C8 is presented in fig.11.

Fig. 10b: TD Thermal Shrinkage of 10/90 LDPE/HP-C8: coextruded blend vs monolayer blend of the same composition

Fig. 11 – Hot tack behavior of pure coex HP-C8 film vs blended HP-C8/LDPE coex-film: the blue curve refers to 10% w/w of LDPE in the total structure, while the green curve refers to an overall 50% w/w of LDPE
Only by adding a small amount (up to 20%) of LDPE into LLDPE a huge hot tack force increase can be observed. As clearly demonstrated by Shih et al.(19), when the films are bonded together if the sealing temperature is close to its crystallization temperature, the molten polyethylene is recrystallized. This induces some additional crystallinity beyond the residual crystallinity, thus leading to a much higher storage modulus. In other words, the resistance to external force becomes stronger and this is the reason why the blend LL/LD shows higher hot tack than pure LLDPE.

CONCLUSIONS

The performances of a new advanced octene based LLDPE, Clearflex H&T LFH208, were shown in comparison to a conventional C8-LLDPE. The outstanding sealing behavior, together with the excellent fracture properties, were explained through a more uniform comonomer distribution which induces relevant changes in the crystalline morphology of the resin. Moreover, the advantages of a three-layer coextruded vs a monolayer LD/HP-C8 blend were investigated. Coextrusion of LDPE/HP-C8 blend offers over coextrusion of pure HP-C8 a strong improvement in optical properties and a relevant hot tack strength. However, a significant reduction in fracture properties (impact and Elmendorf tear in MD) upon LDPE addition was observed. On the other hand, the expected enhancement in processability, keeping a good compatibility in the melt state between the two resins, was achieved. As a matter of fact, a proper design structure having LDPE in the skin layers is able to reduce the tendency for melt fracture to occur, so that the same formulation can be processed using a smaller die-gap with a further improvement of the film mechanical properties. Therefore, the choice of a well designed film structure is really important to produce cost savings and to achieve the best overall performances.

References

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A new Ziegler-Natta octene LLDPE for high performance blown film applications: benefits of coextruded vs blended LLDPE/LDPE films

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Summary

- Clearflex H&T LFH 208

- Polymer properties vs conventional C8-LLDPE

- Blending of H&T LFH 208 with LDPE
  - A rheological study to assess compatibility in the melt state
  - Why choose coextrusion over monolayer film blend?

This is......

H&T LFH 208

- Melting peak 119°C
- MFI ~ 0.7 g/10'
- MWD ~ 3.5
- Density ~ 0.919 g/cm³
- Mainly suitable for lamination purposes
High Performance octene copolymer (HP-C8) offers over std-C8:

1. MW and comonomer distribution
   - a more uniform small chain branch (SCB) distribution...
   - meaning that each molecular weight fraction (e.g. log (Mw) shown in x-axis) has around the same level of comonomer incorporation

2. DSC Melting temperature
   - a melting peak significantly lower....
   - that will be reflected in superior sealing performances

3. Hot Tack behavior
   - HP-C8 shows the lowest seal initiation temperature...
   - Hence, this resin is able to increase the speed in advanced packaging machinery

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*Note: monolayer film 100% LLDPE obtained on lab scale extruder/die/roll 25 micron; output 60kg/hr; T=230°C*
High Performance octene copolymer (HP-C8) offers over std-C8:

- HP-C8 exhibits the highest impact resistance...

Note: monolayer film 100% LLDPE obtained on lab scale extruder; thickness 25 microns; output 60kg/h, T=220°C

Blending of HP-C8 with LDPE:

- Films were produced on a three-layer Ghioddi/Bielloni blown film line
- The extruders have 40 mm diameter and 24:1 L/D ratio; the layers distribution was always 25/50/25
- The die gap was positioned at 2mm (80mil), the blow up ratio was 2.5, the output 60kg/h, the total thickness 25µm and the melt temperature was 220°C in each layer
- LDPE has MFI~2g/10' density 0.924g/cm³

Can the two resins stay together in the melt state?

The Cole-Cole plot exhibits a semicircular shape...

thus suggesting a good compatibility

(1) L.A. Utracki: Two phase polymer systems (1991)
Can the two resins stay together in the melt state?

The complex viscosity shows a slight PDB at low shear rate, while at high shear rate it follows the rule of mixture. Severe processing conditions (e.g., high shear rates) help to achieve total compatibility.

Blending of HP-C8 with LDPE:

The total haze is strongly improved... and coextrusion works better than monolayer blending.

Blending of HP-C8 with LDPE:

LDPE addition to HP-C8 has a detrimental effect on both impact strength.
Blending of HP-C8 with LDPE:

and Elmendorf MD-Tear resistance...

meaning that LDPE plays a key role in increasing the relaxation times of the blend and, hence, in changing the crystalline morphology of the film.

The coextruded film has higher rigidity than monolayer film and a synergetic effect (e.g., positive deviation from the rule of mixture) is observed.

The improved stiffness is supported by a decrease of stress and elongation at break.

.....more pronounced in three-layer film than in monolayer one.
Blending of HP-C8 with LDPE:

Coextrusion gives a higher thermal shrinkage in MD.

and an expansion in the opposite direction..., meaning that, by keeping constant the ratio LD/LL in the structure, processing is a key point in determining the chain extension in the amorphous phase.

The addition of small amount of LDPE can increase the hot tack of pure LLDPE film meaning that hot tack is mainly controlled by morphology (e.g. blend has an higher portion of residual crystallinity) and flow properties (e.g. blend has lower viscosity, indicating better wetting.)
Conclusions: Why would you choose HP-C8?

It offers over conventional C8

- a more uniform SCB distribution leading to:
  - Lower SIT (seal initiation temperature) at the same density
  - Higher strength at equal SIT
  - Better sealing in presence of contaminations
  - Higher impact resistance
  - Higher puncture strength
  - Lower n-hexane extractables, e.g. better organolepticals

Conclusions: blending of HP-C8 with LDPE

Monolayer film VS Three layer film

Conclusions: Benefits of coextrusion vs monolayer blend

- Better opticals
- Higher stiffness
- Higher thermal shrinkage
- Higher hot tack strength