Research and Manufacture of Stretch Films using LLDPE blends

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Abstract. New linear low-density polyethylene (LLDPE) blends were investigated to use as stretch and breathable films. In our investigation different types of LLDPE blends were prepared by extrusion. The characteristic melting and crystallization temperatures of these LLDPE blends were determined. Specimens were injection moulded and their tensile properties were measured. The LLDPE blends with the best thermal and mechanical results were chosen to prepare film by film blowing in laboratory conditions. Tearing properties of the films were also investigated. Our aim was to determine the most appropriate LLDPE blend for stretch film usable under industrial conditions.

1. Introduction

Polyethylene (PE) is one of the most important and widely used polymer in packaging industry, film and tube forming technology [1]. They are used for a variety of applications and in different film processes: blown film, cast film and biaxially oriented films (double bubble process) [2]. Stretch film was made from many types of LLDPE. One publication mentioned that coating of calcium carbonate with stearic acid is an essential process for breathable film applications [3]. It was revealed in this paper that not only the CaCO₃ type and quantity but the stretching process has an enormous effect on breathability performance. The quality of porosity, the amount of interconnecting pores were determined to play an important role in breathability. A Croatian research group investigated many types of fillers, like zeolite, nanoclay and precipitated CaCO₃ in LDPE composites film for packaging to make films with better gas barrier and mechanical properties [4]. In our research new LLDPE blends were made and used to prepare film under laboratory conditions. Our aim was to determine the most appropriate LLDPE blend for stretch film usable under industrial conditions.

2. Experimental

2.1. Materials

Three LLDPE materials were used for the preparations of the LLDPE blends: Braskem PE LL5400S produced by Nexeo Solutions, is an LLDPE developed for blown film extrusion with polyethylenes; Exceed™ 3518 Series produced by Exxon Mobil Chemical, is a metallocene ethylene-hexene copolymer and Dowlex™ 2107GC produced by Dow Chemical, is an LLDPE resin for high line speed processes. Nine LLDPE blends were made of the three LLDPE materials, the ratio of the materials is shown in Table 1.
Table 1. The ratio of the LLDPE blends.

|        | Exceed™ 3518 Series<sup>a</sup> | Dowlex™ 2107GC<sup>a</sup> | Braskem PE LL5400S<sup>a</sup> |
|--------|----------------------------------|-----------------------------|-------------------------------|
| 1.     | 6                                | 4                           | —                             |
| 2.     | 9                                | 1                           | —                             |
| 3.     | 1                                | 9                           | —                             |
| 4.     | —                                | 6                           | 4                             |
| 5.     | —                                | 9                           | 1                             |
| 6.     | —                                | 1                           | 9                             |
| 7.     | 6                                | —                           | 4                             |
| 8.     | 9                                | —                           | 1                             |
| 9.     | 1                                | —                           | 9                             |

<sup>a</sup>Abbreviations: A100 = Exceed™ 3518 Series, B100 = Dowlex™ 2107GC, C100 = Braskem PE LL5400S; LLDPE blends marked as follows: A60_B40 means the ratio is 6:4 = Exceed™ 3518 Series: Dowlex™ 2107GC etc.

The blends were made by a Collin Teach-line extrusion line with an E20T single-screw extruder: nozzle temperature was 250 °C, the zones of the extruder were 210 °C, 205 °C and 195 °C (from the capillary to the hopper), the speed of the extrusion was 120 l/min and the cooling system for the filament was a water bath. The granulates were made with an automatic grinder connected to the extruder after the water bath.

2.2. Methods

2.2.1. **DSC analysis method.** The characteristic melting and crystallization behavior of LLDPE blends were measured by Thermal Analysis TA Q200 (TA Instruments) heat-flux differential scanning calorimeter (DSC) according to ISO-11357-1 standard. Sample weights for the analysis were in the range of 3-5 mg. Sample holder was an aluminum pan and the reference was an empty pan. The instrument was calibrated by Indium. The measurements were performed in nitrogen atmosphere with 50 mL/min flow rate. The temperature program started from 30°C up to 220°C. A “heat-cool-reheat” method was used for the analysis [5]. The heating/cooling rate was 20°C/min.

2.2.2. **Tensile properties analysis method.** The test pieces for measurements of the tensile strength were made with a Demag IntElect 100-500 type injection molding machine according to ISO 294-1 standard. The tensile properties were measured by Instron 3366 universal testing machine. The data was recorded at a crosshead speed of 1-500 mm/min, the speed limit was changed at 1% of tensile. All specimens were conditioned at room temperature (25°C) for at least 24 h. Five-five samples were tested, and the average values were reported for each composition.

3. Results and Discussion

During extrusion, materials are influenced by thermal and mechanical effect. That is why polymers were melted and cooled at controlled circumstances (from 220°C to ambient temperature with 20°C/min cooling rate) to measure the behavior characteristic to the raw materials. The melting DSC curves of Exceed™ 3518 Series (A) and Dowlex™ 2107GC (B) blends are shown in a heat flow (W/g) - temperature (°C) diagram (Figure 1.). The characteristic temperatures (starting ($T_{em}$), peak(s) ($T_{pm1}$ and $T_{pm2}$), end temperature ($T_{efm}$)) and enthalpy change ($\Delta H_m$) values were determined and summarized in Table 2. Most of the melting curves of the LLDPE blends have two peaks ($T_{pm1}$ and $T_{pm2}$) which are typical for LLDPE copolymers. The melting of the materials is a complex process. There is a wide, shoulder like peak around 110 °C, and a sharp, well defined peak around 120 °C. For example A10_B90 has 109.4°C ($T_{pm1}$) and 123.6°C ($T_{pm2}$) for melting peak temperatures (Figure 1.), it is related to the different crystalline sizes and chain regularities.
Figure 1. Melting DSC curves of Exceed™ 3518 Series (A) and Dowlex™ 2107GC (B) blends.

Table 2. Characteristic temperatures of the melting of the materials.

| Sample     | T_{em}  | T_{pm1} | T_{pm2} | T_{efm} | ΔH_{m} |
|------------|---------|---------|---------|---------|--------|
| A100       | 92.4    | -       | 117.4   | 124.7   | 108    |
| B100       | 81.6    | 106.7   | 124.3   | 129.1   | 99     |
| A90_B10    | 92.8    | 109     | 118.3   | 125.2   | 110    |
| A10_B90    | 67.1    | 109.4   | 123.6   | 128.3   | 112    |
| A60_B40    | 86.0    | 108.7   | 118.7   | 125.6   | 119    |
| B90_C10    | 91.6    | 108.8   | 123.5   | 128.3   | 105    |
| B10_C90    | 68.2    | -       | 126.6   | 131.8   | 100    |
| B60_C40    | 62.7    | 209     | 124.0   | 128.3   | 110    |
| A90_C10    | 90.7    | 109.0   | 118.7   | 125.1   | 118    |
| A10_C90    | 74.3    | -       | 125.3   | 129.6   | 100    |
| A60_C40    | 86.3    | 110     | 124.0   | 129.9   | 107    |

*manually marked temperature value

The starting (T_{em}), peak (T_{pm}), end temperature (T_{efm}), and enthalpy change (ΔH_{m}) values were also determined during the crystallization sections and the data are shown in Table 3. The characteristic crystallization peak temperatures of Exceed™ 3518 Series (A) and Dowlex™ 2107GC (B) blends are shown in a heat flow (W/g) - temperature (°C) diagram (Figure 2.).

The A10_B90 blend has the highest and the pure Exceed™ 3518 Series (A) has the lowest starting crystallization temperature. All of the characteristic melting and crystallization temperatures are shown in Table 2 and Table 3.
Figure 2. Crystallization DSC curves of Exceed™ 3518 Series (A) and Dowlex™ 2107GC (B) blends.

Table 3. Characteristic temperatures of the crystallization section.

| Sample      | $T_{ec}$ [°C] | $T_{pc}$ [°C] | $\Delta H_c$ [J/g] |
|-------------|---------------|---------------|-------------------|
| A100        | 101.5         | 97.4          | 114               |
| B100        | 104.0         | 99.8          | 107               |
| C100        | 108.5         | 106.0         | 107               |
| A90_B10     | 102.5         | 99.1          | 119               |
| A10_B90     | 105.8         | 102.4         | 115               |
| A60_B40     | 103.8         | 100.7         | 124               |
| B90_C10     | 106.5         | 103.5         | 114               |
| B10_C90     | 109.1         | 105.7         | 104               |
| B60_C40     | 107.5         | 104.8         | 114               |
| A90_C10     | 103.7         | 100.9         | 120               |
| A10_C90     | 108.8         | 105.9         | 111               |
| A60_C40     | 105.3         | 102.5         | 107               |

The elongation at contraction were 21%-65% (shown in Table 4, Figure 3). Two blends, A10_B90 and A10_C90 had ~20% and the others had around 60%. From the measurement of the tensile strength the most important value was the length of the orientation section because it is related to the flexibility of the film. The orientation length was almost the same of the different LLDPE blends, the best was 298% of A10-B90. The LLDPE blends had 404%-636% elongation at break, with 10.45-18.11 MPa tensile strength. The A90-B10 blend had the biggest value of elongation at break (636%).
Table 4. Mean values of the measured parameters with deviation.

| Sample    | Modulus E [MPa] | Elongation at contraction $\varepsilon_Y$ [%] | Tensile stress at contraction $\sigma_Y$ [MPa] | Orientation section length $\varepsilon_6$ [%] | Elongation at break (cross-head) $\varepsilon_B$ [%] | Tensile strength $\sigma_B$ [MPa] |
|-----------|-----------------|---------------------------------------------|---------------------------------------------|-----------------------------------------------|-----------------------------------------------|----------------------------------|
| A10_B90   | 172±2           | 61.09±1.71                                  | 9.52±0.08                                   | 298±6                                         | 538.20±0.13                                   | 14.63±1.83                      |
| A10_C90   | 198±2           | 21.28±0.75                                  | 9.89±0.07                                   | 285±12                                        | 413.45±0.24                                   | 11.94±1.75                      |
| A60_B40   | 174±2           | 63.92±0.45                                  | 9.83±0.11                                   | 270±14                                        | 565.34±0.33                                   | 16.76±1.72                      |
| A60_C40   | 191±4           | 58.43±0.59                                  | 9.97±0.14                                   | 285±10                                        | 512.39±1.72                                   | 14.37±3.99                      |
| A90_B10   | 179±3           | 64.91±0.70                                  | 10.17±0.09                                  | 265±31                                        | 635.94±3.14                                   | 18.11±2.54                      |
| A90_C10   | 192±2           | 62.09±1.26                                  | 10.31±0.03                                  | 270±12                                        | 524.37±0.43                                   | 16.48±1.67                      |
| B10_C90   | 192±3           | 22.45±0.37                                  | 9.73±0.15                                   | 270±19                                        | 403.61±1.74                                   | 10.45±3.08                      |
| B60_C40   | 180±2           | 53.76±0.94                                  | 9.51±0.07                                   | 275±11                                        | 427.75±1.29                                   | 11.42±1.85                      |
| B90_C10   | 175±1.57        | 58.25±0.70                                  | 9.43±0.08                                   | 285±6                                         | 442.89±0.19                                   | 11.86±1.57                      |

Figure 3. Elongation at contraction, orientation section, elongation at break.

According to the thermal and mechanical results A60_C40, A10_C90 and A10_B90 were chosen for manufacturing films. The parameters of blown film extrusion under laboratory conditions are shown in Figure 4. The equipment was Collin teach-line E 20 T extruder and Collin teach-line BL 50 T film blowing unit; $T_{z1}$, $T_{z2}$: temperature for zones of film blowing unit, $T_{e1}$, $T_{e2}$, $T_{e3}$: temperature for extruder zones, $T_{h}$: temperature of the extruder of the hopper, $p_e$: pressure of the extruder).
Figure 4. The parameters of blown film extrusion under laboratory conditions.

Table 5. The parameters of blown film extrusion under laboratory conditions.

| Temperature (°C) | p_e (bar) |
|------------------|-----------|
| $T_z1$           | 170       |
| $T_z2$           | 170       |
| $T_{e1}$         | 165       |
| $T_{e2}$         | 160       |
| $T_{e3}$         | 155       |
| $T_h$            | 24        |
|                  | A60_C40   |
|                  | 101-112   |
|                  | A10_C90   |
|                  | 152-184   |
|                  | A10_B90   |
|                  | 156-162   |

Screw speed (1/min) 570

The tearing strength was measured by Instron 3366 equipment. Data were recorded at a crosshead speed of 500 mm/min at 24°C. The size of the specimens were 10 cm x 5 cm with a 2-5 mm long notch. Six-six notched specimens were tested and the average values were reported for each composition (Table 6.).

Table 6. Results of the tearing strength measurement of the notched specimens (MD=machine direction, TD=transverse direction).

| Specimen       | A10_B90 | A10_C90 | A60_C40 |
|----------------|---------|---------|---------|
| Notch direction | MD      | TD      | MD      | TD      | MD      | TD      |
|                | F [N]   | F [N]   | F [N]   | F [N]   | F [N]   | F [N]   |
| Mean value     | 5.99    | 6.05    | 6.07    | 7.12    | 7.73    | 8.94    |
| Deviation      | 0.47    | 0.99    | 0.94    | 0.60    | 0.35    | 0.75    |

Figure 5. The tearing strength of the notched specimens (MD=machine direction, TD=transverse direction).
The toughest film was the A60_C40, because the force of the MD tear was 7.73 N and of the TD tear was 8.94 N, so this blend is the most suitable for stretch films (Figure 5.).

4. Conclusion
In our investigation different types of LLDPE blends were prepared by extrusion. The characteristic melting and crystallization temperatures of these LLDPE blends were determined. Most of the melting curves of the LLDPE blends have two peaks, which are typical for LLDPE copolymers. The first melting peak has a shoulder shape, while the second melting peak is a sharp, well defined peak. It is related to the different crystallite sizes and chain regularities. The A10_B90 blend has the highest and the pure Exceed™ 3518 Series (A) has the lowest starting crystallization temperature. Specimens were injection moulded and their tensile properties were measured. The LLDPE blends had 404%-636% elongation at break, with 10.45-18.11 MPa tensile strength. The A90-B10 blend had the biggest value of elongation at break (636%). According to the thermal and mechanical results A60_C40, A10_C90 and A10_B90 were chosen for manufacturing films in laboratory conditions. Tearing properties of the films were investigated. The toughest film was the A60_C40, so this blend is the most suitable for making stretch films.

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