Low-Density Polyethylene

Thomas I. Butler

Introduction

Low-density polyethylene (LDPE), sometimes referred to as high-pressure, low-density polyethylene, conventional polyethylene, or branched polyethylene, has been commercially produced since its discovery in the 1930s. These polymers are produced in large volumes by either of two free radical polymerization processes, a stirred reactor (autoclave) or a tubular reactor. In the polymerization process, ethylene monomer combines at high pressures and temperatures to form long polymer chains with many branches.

Polyethylene is a thermoplastic material particularly well suited for fabrication into many products. The properties that make LDPE attractive as raw material for film applications are as follows:

1. Light weight.
2. Economical cost.
3. Flexibility (low modulus).
4. Toughness.
5. Chemical resistance.
6. Ease of sealability.

Polymer Characterization

The long polyethylene molecule will have several branches in the carbon backbone as seen in Figure 29-1. These branches consist of short-chain branches (SCB) and long-chain branches (LCB). LDPE polymers are characterized by their average molecular weight (measured as melt index), crystallinity (measured as density), and molecular weight distribution or MWD (measured by gel permeation chromatography or GPC). These three characteristics provide a polymer with its properties during processing and in the end-use applications.

Proper control of the polymerization process conditions produces polymers with the desired average molecular weight, density, and MWD. Film extrusion grades of polyethylene range in
melt index from 20 to 0.1 g/10 min. increasing the average molecular weight (a lower melt index) of the polymer produces stronger film tensile and impact properties and lower optical properties. However, higher molecular weight polymers will be more difficult to process in terms of extruder amps and pressure due to the higher viscosity and will result in a higher melt temperature. Increasing average molecular weight of a polymer will improve melt strength but reduce the ability to drawdown to a thin gauge. Table 1 details melt and solid state properties.

Figure 29-1 Polyethylene Polymers.

![Polyethylene Polymers Diagram](image)

Table 29-1 Melt Index Effects (at Constant Density and MWD).

<table>
<thead>
<tr>
<th>Decreasing Melt Index (Increasing Molecular Weight)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Properties</td>
<td>Solid State Properties</td>
</tr>
<tr>
<td>Melt Strength Improves</td>
<td>Optics Decrease</td>
</tr>
<tr>
<td>Processability Decreases</td>
<td>Tensile Strength Increases</td>
</tr>
<tr>
<td>Drawdown Decreases</td>
<td>Impact Strength Increases</td>
</tr>
<tr>
<td>Die Swell Increases</td>
<td>Heat-Seal Strength Increases</td>
</tr>
</tbody>
</table>
In the solid state, the LDPE molecules will form spherulites where the polymer chain folds into crystalline regions called lamella. In regions where the molecular chain is disrupted from folding, usually by the presence of SCB, amorphous regions are formed. Figure 29-2 illustrates the lamella and amorphous regions of the spherulite. The size distribution of the spherulites will influence the optical and mechanical properties of the film. Decreasing the density will decrease the melting point, stiffness, and minimum heat-seal temperature and increase the impact and tensile strength of the polymer. LDPE polymers have densities ranging from 0.910 to 0.925 g/cc with medium density polyethylenes normally classified as having densities from 0.926 to 0.940 g/cc and high- density polyethylenes having densities with >0.941 g/cc. Table 29-2 details density effects at constant MW and MWD.

Table 29-2  Density Effects (at Constant MW and MWD).

<table>
<thead>
<tr>
<th>As Density Decreases</th>
<th>Solid State Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Properties</td>
<td></td>
</tr>
<tr>
<td>Insignificant Effects</td>
<td>Stiffness Decreases</td>
</tr>
<tr>
<td></td>
<td>Impact Strength Increases</td>
</tr>
<tr>
<td></td>
<td>Permeability Increases</td>
</tr>
<tr>
<td></td>
<td>Heat Sealability Increases</td>
</tr>
<tr>
<td></td>
<td>Melting Point Decreases</td>
</tr>
<tr>
<td></td>
<td>Optics Increase</td>
</tr>
</tbody>
</table>

Figure 29-2 Detailed Structure of a Spherulite.
LCB has a negligible effect on the crystallinity (density), but it does provide significant improvement in the melt strength and melt elasticity properties of the polymer. The LCB increases entanglement of the polymer molecules which results in good bubble stability. Increasing LCB will increase low shear rate viscosity but decrease high shear rate viscosity.

LDPE polymers contain a mixture of molecules ranging from low molecular weight to high molecular weight chains. The MWD is a measure of the fractions of various molecular weights. Polymers can be designed to have broad, medium, narrow, symmetrical, or asymmetrical distributions. It is difficult to make generalizations about the effects of MWD curves, but many of the resultant properties of the polymer will depend upon the specific molecular weight fractions incorporated into the polymer design. Table 29-3 details MWD effects at constant MI and density.

Table 29-3 MWD Effects (at Constant MI and Density).

<table>
<thead>
<tr>
<th>As MWD Narrows</th>
<th>Solid State Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder Amps Increase</td>
<td>Impact Strength Increases</td>
</tr>
<tr>
<td>Extruder Pressure Increases</td>
<td>Stress Crack Decreases</td>
</tr>
<tr>
<td>Melt Strength Decreases</td>
<td>Tensile Increase</td>
</tr>
<tr>
<td>Extrudate Swell Decreases</td>
<td>Tear Strength Increases</td>
</tr>
</tbody>
</table>

LDPE polymers can have the same MI and density but have different MWD. Figure 29-3 illustrates GPC curves of LDPE polymers having a broad, medium, and narrow MWD. These three polymers would, therefore, process on extrusion equipment quite differently and have significantly different film properties.

Figure 29-3  Comparison of a Polyethylenes of the Same Molecular Weight with Different Molecular Weight Distributions.
Figure 29-4 shows the influence of MWD on the viscosity curves of the three LDPE polymers with the same melt index. The broad MWD polymers are more shear rate sensitive such that with increasing shear rates the viscosity will decrease more than the narrow MWD polymers. This example shows why melt index does not describe the processability of a polymer at extrusion rates.

**Figure 29-4. Comparison of Flow Curves of Different MWD with the Same MI.**
Figure 29-5 details two LDPE polymers with the same melt index but with different shapes of the GPC curve. By tailoring the polymer to the desired end-use market, the LDPE resin can provide a wide variety of film applications with the required performance properties. Choosing the correct resin for the needs of the application is critical to achieve desired performance and fabrication characteristics.

**Figure 29-5.** Comparison of Polyethylenes of the Same Molecular Weight with Different Molecular Weight Distributions.
Typical Applications and End Uses

LDPE film resins have found utility in a wide variety of applications. Film produced with LDPE, blends using LDPE, or coextrusions using LDPE provide considerable variability in properties such as flexibility, clarity, toughness, and processability. This allows products to be designed for applications ranging from very thin film 7.5 microns (0.3 mils) to very thick applications 760 microns (30 mils), and from high clarity to translucent films. Historically, films have been described as being 254 microns (10 mils) or less and sheeting as 10 mils or greater, but today those boundaries have become less defined.

The elastic nature of polyethylene will produce films with good toughness (impact resistance and tensile strength) properties. The relative low cost and low specific volume ($/cubic ft) of polyethylene has made it an attractive material of choice for many packaging applications when competing with metal, glass, and paper. The ability and ease of polyethylene to be heat-sealed to itself permits several types of sealing equipment to be used for end-use applications.

The largest market for LDPE film grade polymers is bags and liners to include the following: trash bags, shopping bags, produce bags, bread and bakery bags, grocery sacks, shipping bags, liners, garment bags, and many other general purpose consumer and industrial packaging applications. The film market is characterized by a wide range in performance specifications.

LDPE polymers are also used in bundling applications such as shrink film, pallet stretch, and pallet stretch-cling film applications designed to protect products or stabilize pallets during shipment and storage construction and agriculture film applications range from mulch film, greenhouse coverings, irrigation tubing, liners, and agriculture product storage and protection.

LDPE film is used in lamination applications where the good sealability can be combined with the properties of other substrates such as paper, metal (foil), or other plastics.

When an application requires specific performance properties, the selection of the proper grade of LDPE to match the fabrication requirements with the film properties needs is critical.

Typical Polymer Properties

The physical properties of an LDPE film grade polymer are dependent not only on the intrinsic polymer properties, but are directly influenced by the fabrication process conditions. The physical properties of LDPE will vary with melt index, density, and MWD. Table 29-4 details LDPE properties. Table 29-5 details typical LDPE film properties. The two film fabrication processes, blown and chill roll cast, will produce films with slightly different properties.

Table 29-4 LDPE Properties
A comparison of film properties from blown and cast film will demonstrate some of these differences. The first difference noted would be the melt temperature of the two extrusion systems. The cast film will have a 100-250°F (38°C-121°C) higher melt temperature than the blown film. In this comparison, the specific output (lb/hr/in of die length) was similar, but cast film rates would generally be significantly (1.5-2 times) faster than blown film rates. The quick quenching rate of the cast film chill roll allows higher rates compared to the air ring or internal bubble cooling (IBC) of the blown film process.

The quick quenching in the cast film process produces a lower film density. The cast film has a positive influence on optical properties in reducing haze and increasing gloss. In this case, dart
impact is improved with the cast film. This is probably due to the lower film density. Cast films will sometimes have lower impact if orientation in the cross direction is critical.

The advantage of blown film process is improved cross direction orientation obtained when the bubble is expanded from the die diameter. Control of the orientation in the cross direction can improve properties such as machine direction tear, impact strength, and balance properties such as shrink. Figure 29-6 shows some of the elements of the blown film bubble. It is important to note some critical operating variables that aid in correlating orientation effects when comparing different types of blown film lines. Table 29-6 details critical elements of blown film.

Figure 29-6   Elements of Blown Film

![Figure 29-6 Elements of Blown Film](image)

\[
\begin{align*}
\text{BUR} & = \frac{\left(\frac{2}{\pi} \cdot LF\right)}{D_d} \\
& = \frac{D_b}{D_d} \\
\text{DDR} & = \frac{h_o}{(h_f \times \text{BUR})} \\
\text{TUR} & = \frac{V_f}{V_o} \\
\text{FLH} & = \text{distance above die}
\end{align*}
\]

\[
\begin{align*}
D_d & = \text{Die diameter} \\
D_b & = \text{Bubble diameter} \\
h_o & = \text{Die gap} \\
h_f & = \text{Film Thickness} \\
V_o & = \text{Velocity at die exit} \\
V_f & = \text{Velocity at haul-off} \\
LF & = \text{Layflat}
\end{align*}
\]

Table 29-6   Critical Elements of Blown Film.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blow-Up Ratio (BUR)</td>
<td>Bubble Diameter / Die Diameter</td>
</tr>
<tr>
<td></td>
<td>= Layflat Width X 0.6366 / Die Diameter</td>
</tr>
<tr>
<td>Drawdown Ratio (DDR)</td>
<td>Die Gap / (Film Gauge X Bur)</td>
</tr>
</tbody>
</table>
Take-up Ratio (TUR) = Velocity @Nips / Velocity @Die

Specific Output = Lb/Hr / (Die Diameter X 3.14)

Frost Line Height = Inches From Top of Die to Point Where the Bubble Freezes

Machine direction orientation will increase as DDR increases. Cross direction orientation increases as BUR increases. Specific output (lb/hr/in of die circumference) relates to polymer flow rates, and machine direction orientation will increase with higher specific output.

The cast film process has the capability to produce film with less gauge variation. The width of the film produced on the cast film process is determined by the width of the slot die. The film width is further reduced by neck-in (the relaxation of the molten polymer as it exits the die), and the need for edge trim to remove the beads resulting from neck-in. Figure 29-7 details some elements of cast film extrusion. Critical operating variables of cast film are defined in Table 29-7.

Figure 29-7  Neck-In on Cast Film Extrusion.

Table 29-7  Critical Elements of Cast Film.

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neck-In</td>
<td>Die Width-Film Width</td>
</tr>
<tr>
<td>Air Gap</td>
<td>Distance From Die Lips To Contact Point On Chill Roll</td>
</tr>
<tr>
<td>Drawdown Ratio</td>
<td>Die Gap/Film Gauge</td>
</tr>
<tr>
<td>Chill Roll Temp</td>
<td></td>
</tr>
<tr>
<td>Melt Temp</td>
<td></td>
</tr>
<tr>
<td>Specific Output</td>
<td>Lb/hr/in of Die Length</td>
</tr>
</tbody>
</table>
There are several differences to be noted between blown film and cast film fabrication equipment. These are listed in Table 29-8.

**Table 29-8 Process Differences Between Blown and Cast Film.**

<table>
<thead>
<tr>
<th></th>
<th>Blown</th>
<th>Cast</th>
</tr>
</thead>
<tbody>
<tr>
<td>Die Shape</td>
<td>Annular</td>
<td>Flat</td>
</tr>
<tr>
<td>Quenching Method</td>
<td>Chilled Air</td>
<td>Chill Rolls</td>
</tr>
<tr>
<td>Cooling Temp, °F</td>
<td>50-90</td>
<td>80-120</td>
</tr>
<tr>
<td>Melt Temp, °F</td>
<td>300-480</td>
<td>450-600</td>
</tr>
<tr>
<td>Specific Output, lb / hr/ ln</td>
<td>7-25</td>
<td>20-40</td>
</tr>
<tr>
<td>Line Speed, fpm</td>
<td>30-500</td>
<td>300-1500</td>
</tr>
<tr>
<td>Gauge Uniformity, +/- %</td>
<td>5-25</td>
<td>1.5 - 2</td>
</tr>
<tr>
<td>Limitations</td>
<td>Cooling</td>
<td>Lower Pressure</td>
</tr>
<tr>
<td></td>
<td>Melt Stability</td>
<td>Fixed Layflat</td>
</tr>
<tr>
<td></td>
<td>Lower Optics</td>
<td>Little CD Orientation</td>
</tr>
</tbody>
</table>

**General Processing Guidelines**

The LDPE film polymers are relatively easy to process on either blown or cast film extrusion equipment. The selection of extrusion equipment for LDPE should be based on the requirements of the end-use application. The requirements for general-purpose packaging application might require equipment designed to produce film at the highest rates and the lowest temperatures, while lamination grade film requires high quality and consistent film properties. LDPE can be effectively processed on a variety of extruder screw designs, including both single-flighted and barrier screws.

Some general suggestions for LDPE processability include the following:

1. The extruder L/D can range from 18:1 to 32:1. Typically this would be 24:1 depending upon the need for output, melt temperature control, dispersion of additives and pigments, and melt uniformity.

2. Screw compression ratio will vary from 2.5 to 4.5. If the equipment is also required to run LLDPE polymers ~ the lower compression ratio would be better. For high clarity or excellent melt uniformity, the higher compression ratios work well.

3. For high specific screw output at low melt temperature, barrier screws have been successful in reducing the shear input in the extrusion process.

4. Mixing sections have been successful in providing barriers to unmelt polymer passing through the extruder and dispersing additive concentrates and blends.

5. Die flow channels should be designed for the viscosity of the polymers at the expected flow rates. Streamlined designs will reduce product changeover times.
and eliminate polymer hang-up which could cause degradation problems. High-pressure dies generally will provide better gauge uniformity at the expense of maximum output. Moderate and low-pressure die will maximum output but gauge uniformity might suffer.

The extruder, screw, and die design should be designed as a system. Improper design in any part of the equipment might cause problems throughout the rest of the process. Operating parameters must be carefully controlled to assure good quality film production.

The major fabrication variables influencing LDPE film properties are as follows:

1. Melt temperature.

2. BUR (blown), neck-in (cast).

3. Specific output rate.

4. Die gap and film thickness (DDR).

5. Frostline height (blown), air gap (cast).

6. Quench method (blown), chill roll temperature (cast).

The influence of these fabrication variables can be seen in both the mechanical properties as well as the optical properties. These fabrication variables influence the orientation of the LDPE molecules in all cases and the film density in some cases. Polymer molecules are oriented when strain is applied during the cooling process. Strain is applied as the molten polymer is pulled in the machine direction causing a thinning of the molten polymer flow. In blown film, strain (orientation) is also found as the bubble is expanded beyond the die diameter. The quench rate influences the orientation and the crystallinity of the film.

The influence of orientation on mechanical properties is usually complex nonlinear responses. The response of the mechanical and optical properties are summarized as follows:

**Melt Temperature**

Increasing the melt temperature will usually improve the surface defects thus increasing the optical properties. If quenching rates are increased, film crystallinity is reduced, thus improving impact strength. Higher melt temperatures can increase cross-direction orientation by increasing molecular relaxation, thus reducing machine direction orientation.

**BUR**

Increasing BUR will increase cross-direction orientation, which should then improve impact strength, CD tensile strength, MD elongation, and MD tear strength. Optical properties will typically improve to an optimum and then decrease with BUR.
Die Gap

Increasing die gap will increase machine direction orientation which then results in lower MD tear strength, lower MD elongation, improved CD tear strength, and improved MD tensile strength.

Output

Increasing output typically results in higher machine direction orientation which then results in higher MD tensiles, increased impact strength and improved optical properties if melt temperature is increased and quench rates do not induce defects from frozen-in surface irregularities.

Frostline Height

Increasing the frost line height will decrease machine direction orientation with slower quenching rates resulting in higher film crystallinity. Optical properties will reach an optimum then start to decrease.

Figure 8 shows the response surface of tensile strength (MD and CD) as a function of increasing BUR and increasing output. The MD tensile is more sensitive to BUR. Highest MD tensile properties are obtained at low BUR’s. CD tensile are shown to be less sensitive to either BUR or output rate.
Figure 29-8  Response Surface of Tensile Strength of LDPE

Response surface of tensile strength of LDPE (4.0, 0.925) with BUR and output @ FLH of 14 in.

Figure 29-9 shows the response of impact strength to increasing BUR and output rate. Maximum impact strength is obtained at higher BUR and output rates where MD and CD orientation are maximized.
Figure 29-9  Response Surface of Impact Strength of LDPE

Response surface of impact strength of LDPE \((4.0, 0.925)\) with BUR and output @ FLH of 14 in.

Figure 29-10 shows the influence of BUR and output on tear strength. The increase in MD orientation with increasing BUR’s noted by a reduction of MD tear strength. The influence on CD tear strength with BUR ratio improves bubble cooling, thus reducing surface defects. The higher output either BUR or output is slight.
Response surface of tear strength of LDPE (4.0, 0.925) with BUR and output @ FLH of 14

The influence on optical properties such as haze is shown in Figure 29-11. The higher BUR ratio improves bubble cooling, thus reducing surface defects. The higher output results in higher melt temperatures, which will improve optical properties.
Figure 29-11  Response Surface of Haze of LDPE

Response surface of haze of LDPE 
(4.0, 0.925) with BUR and output @ FLH of 14 in.

Film fabrication has been shown to influence the orientation of the polymer molecules in LDPE. Controlling the fabrication variables reduces the variation in properties obtained. The selection of the proper fabrication conditions can be used to obtain specific performance properties.

Many of these variables are interacting and therefore must be balanced to obtain optimal overall performance properties. The final film properties are the result of a combination of the resin characteristics, the extrusion equipment design, and the operating procedures used to produce the film.
Bibliography