POLYETHYLENE, LOW DENSITY

1. Introduction

Low density polyethylene (LDPE) was the first thermoplastic polyolefin used commercially. It was discovered serendipitously in 1933 and was quickly utilized for electrical cable sheathing for radars during the war. LDPE, along with high density polyethylene (HDPE) and linerar low density polyethylene(LLDPE), offers an unparalleled combination of low cost, ease of fabrication into a variety of end uses, and balance of physical properties. Polyethylene has displaced paper, metal, wood, and other materials of construction. LDPE is unique in its polymerization process. Free-radical-initiated polymerization is used to make LDPE, as compared to transition-metal catalysis for HDPE and LLDPE. The free-radical process leads to the unique molecular structure of LDPE: large amounts of long-chain branching. The long-chain branching imparts unusual rheological behavior in both shear and extension. LDPE is used in a variety of applications, such as film, coating, molding, and wire and cable insulation. One of the reasons for its wide range of utility is its thermal stability and low toxicity.

2. Monomer and Comonomers for LDPE

Ethylene [74-85-1] is the monomer used to make LDPE [9002-88-4]. The predominant method of manufacture of ethylene is high temperature cracking of natural gas or crude oil. Some properties of ethylene are collected in Table 1. The principal method for the industrial preparation of ethylene is thermal cracking of hydrocarbons. Small amounts of comonomers, such as vinyl acetate [108-05-4], methyl acrylate [96-33-3], or ethyl acrylate [108-88-5], can be added to modify the properties of the polymer. Vinyl acetate is made by the oxidative addition of acetic acid to ethylene in the presence of a palladium catalyst. The acrylates can be commercially manufactured from acetylene, but the preferred route is by the oxidation of propylene oxide. A few of the pertinent physical properties of these monomers and more detailed descriptions of their manufacture can be found in the articles on Vinyl Acetal Polymers and Acrylic Ester Polymers and Methacrylic Ester Polymers.

3. Properties of LDPE

3.1. LDPE Homopolymer. LDPE, discovered by ICI in 1933 (1,2), quickly found war-time utility in high frequency cables for ground and airborne radar equipment. After the war, the balance of chemical inertness, thermal and environmental stability, ease of processing, physical properties, stiffness, and optical properties made this polyolefin polymer useful in a variety of applications. A detailed and exhaustive compilation of molecular, physical, and chemical data on LDPE can be found in the *Polymer Data Handbook* (3).

With the commercialization of HDPE in the early 1950s (see article on Ethylene Polymers, HDPE) and LLDPE in the 1960s (see article on Ethylene Polymers, LLDPE), there was cannibalization of LDPE markets and applications by these new polymers. Despite some predictions of the demise of LDPE due to the better properties and lower cost of LLDPE and HDPE, LDPE remains the resin of choice in many applications. The most unique structural difference between LDPE and HDPE/LLDPE is the presence of large amounts of long-chain branching in the molecule (Fig. 1). This branching leads to rheological and property behaviors which cannot be matched by the other polymers. Today, LDPE is still used in a variety of film, coating, wire and cable, and molding applications. The physical and extrusion properties of LDPE depend on the molecular weight, molecular weight distribution (MWD), frequency of short-chain branches, and frequency and length of the long-chain branches. Some typical molecular properties for LDPE are found in Table 1. A comparison of blown film properties between LDPE and LLDPE is found in Table 2. A comparison on injection-molding properties between LDPE and LLDPE is found in Table 3.

3.2. LDPE Copolymers. A variety of comonomers can be added to the polymerization of ethylene to make copolymers. The free-radical polymerization mechanism of LDPE production allows for the copolymerization of polar comonomers. At this time, the incorporation of polar comonomers is unique to LDPE. The transition metals used to catalyze HDPE and LLDPE production are generally poisoned by polar comonomers and therefore, only copolymers containing alpha-olefins like 1-butene, 1-hexene, and 1-octene can be made. Because the polar copolymers can be made only by the LDPE process, they command a premium in the market. The most common comonomers (and their corresponding copolymers) are vinyl acetate (EVA), methyl acrylate (EMA), ethyl acrylate (EEA), and acrylic acid [79-10-7] (EAA). The presence of the comonomer decreases crystallinity and imparts more flexibility and softness to the final articles. Increasing levels of these comonomers imparts better adhesion to other materials. This superior adhesion of LDPE copolymers to other materials like metal, foil, cardboard, and paper is unmatched by other polyolefins and remains a unique property of LDPE. Comonomer contents as high as 20 wt% of EVA, EMA, and EEA can be used in various extrusion and molding applications. Films made from EVA, EMA, or EEA tend to have good low temperature properties and very good sealability. Because of the good sealability and broad sealing latitude, these materials are often used in coextruded structures as a seal layer. Copolymers containing acrylic or methacrylic acid have very good toughness and stress-crack resistance, but impart corrosivity to the polymer. In general, these products are used in coextruded or laminated structures. Comonomer levels from 20 to 40 wt% can also be made in the LDPE process. These copolymers are used in coating and adhesive applications.

3.3. Ionomers. Copolymers of acrylic or methacrylic acid can be converted into the sodium or zinc salts of the acids. These ionomers(qv) show strong ionic bonding, such that the properties are similar to LDPE of very high molecular weight (4). However, the ionic bonds are weakened at extrusion temperatures so that the ionomers process under similar conditions of LDPE homopolymers of normal molecular weight. Because of their polar nature, ionomers are paintable and commonly used to adhere to aluminum and metal or laminate to nylon.

4. Polymerization Reactors

LDPE is also known as “high pressure, low density” or HPLD, because it is exclusively made by the high pressure process. LDPE is produced under high pressures (81–276 MPa) and high temperatures (130–330°C) with a free-radical initiator, such as peroxide or oxygen. The polymerization mechanism is a free-radical reaction that leads to the formation of long-chain branches, which can be as long as the main polymer backbone (5). The free-radical mechanism also leads to the formation of short-chain branches, typically one to five carbon atoms long (6). These short-chain branches normally seen in LDPE include 1,3-diethyl and 2-ethylhexyl side chains as well as the most common butyl branches. LDPE also contains lesser amounts of amyl branches while hexyl branches are rare. Most of the methyl branches occur when propylene is added to the reactor as a chain-transfer agent. The polymerization is carried out in tubular or stirred autoclave reactors (7).

The rate-limiting factor in LDPE production is heat removal from the reactor. The heat of polymerization of ethylene is very high, at about 3.35 kJ/g. For comparison, the heat of reaction of styrene is only about 0.657 kJ/g. There are basically two ways to dissipate the heat during the polymerization: through the walls of the reactors and by the unreacted ethylene, which is cooled and returned to the reactor. Since the LDPE polymerization occurs at very high pressures, the reactor walls must be very thick and external cooling is not very efficient. This is especially true for the autoclave reactor. The tubular reactors can benefit from cooling jackets, which is one of the factors accounting for the fact that only large tubular reactors are being built today. Older small autoclave and tubular reactors of 100–150 kta (kta $= 10^3$ t/year) cannot economically compete with new 400–500 kta low pressure “mega-reactors” being built for HDPE and LLDPE. The new high pressure tubular reactors of 350 kta, which are being installed now, will be able to compete with the HD and LLDPE units as well as offer the unique polymer properties that customers value.

In both the tubular and autoclave reactors, the control of molecular weight can be accomplished by reaction pressure, temperature, or the addition of chain-transfer agents or telogens. However, reaction pressure and temperature also affect the MWD and the amount of short- and long-chain branching. Therefore, it is desirable to use chain-transfer agents for the primary control of molecular weight so that pressure and temperature can be used for MWD and branching control.

There are subtle differences in the structure of the LDPE resins made from the tubular and autoclave reactors. The biggest difference is in the type and level of long-chain branching. As was seen in Figure 1, the autoclave reactor gives rise to shorter, more ‘bushy’ long-chain branching than does the tubular reactor. This is due to the higher level of backmixing in each stage of the reactor. The free radicals have more opportunity to react and terminate with other polymer molecules in the autoclave. In the tubular reactor, there is relatively little backmixing since the reaction flow is carrying the polymer down the tube as it is reacting. Therefore, once a long-chain branch is started, it is likely to continue to grow rather than interact with another polymer molecule to terminate.

The effects of these subtle differences in long-chain branching are difficult to measure (see the section on Analytical and Test Methods). Spectroscopically, the long chains are indistinguishable from the polymer backbone. The differences are also very minor in the rheology of the polymer. There are a few extrusion and physical property differences that are created by the different types of long-chain branching. Autoclave resins tend to have better see-through clarity than tubular reactors, due to the smaller spherulites formed during the crystallization process. Autoclave resins also exhibit better drawdown and neck-in in the extrusion coating process.

4.1. Stirred Autoclave Reactor. The stirred autoclave reactor (Fig. 2) generally has a (proprietary) stirrer running the length of a cylindrical vessel with a length to diameter ratio of 4:1 to 18:1. There are baffles in the reactor to divide it into multiple reactor zones, with independent temperature control and initiator injection points. The stirrer provides backmixing in each stage, but practically no mixing between stages. Product molecular weight, MWD, and branching are controlled by the temperatures in each zone and the placement of the initiator injection. Pressure is held constant by using a modulating valve. Because of the high pressures used, generally about 210 MPa, the reactor walls are very thick and severely limit heat removal from the vessel. Therefore, unreacted ethylene is used to remove the heat of polymerization from the reactor. This limits the conversion per pass of ethylene to about 22%. In some cases, conversion may be even lower, if unusual product characteristics are desired.

4.2. Tubular Reactor. Tubular reactors (Fig. 3) are basically long, thick-walled pipes from 0.5 to 1.5 km long, arranged as elongated coils, with cooling jackets. The use of cooling jackets allows more efficient heat removal than in the autoclave reactor and hence, higher conversion of ethylene per pass. Typical conversion rates for tubular reactors are in the 35% range. In contrast to the autoclave reactor, where reaction pressure is held constant, pressure in the tubular reactor varies. Pressure is controlled by a cycle valve that opens periodically. This generates pressure waves and surges in the reactor. These surges are actually beneficial to the process in that they help keep the walls cleaned of polymer buildup and help optimize heat transfer to the cooling jacket. Ethylene can either be added in the front or in the front with one or more additional side feed entries. Initiators, peroxide or oxygen, can also be introduced in multiple places down the tube. Thus, multiple reaction zones can be created, which can be used to control the properties of the final product.

4.3. Post Reactor Process. Since only a portion of the ethylene fed to the reactor is converted to polyethylene, recovery and recycling of the unreacted ethylene (and other monomers, if present) is necessary to improve the economics of the process. The recycle system generally comprises two sections: a high pressure separator and a low pressure separator. When the polymer first exits the reactor, it is still at very high pressures and temperatures and contains a lot of entrapped ethylene gas. The high pressure separator first partitions the polymer from the gases and low molecular weight waxes. The gases and waxes are then separated and cooled. The cool gas stream is combined with fresh feeds and fed to the secondary compressor.

Meanwhile, the polymer stream from the high pressure separator is fed to the low pressure separator. Although considerable ethylene has already been removed from this stream, further recovery is still possible. This recovered gas is fed to a multiple stage compressor to get it back to feed pressure and then fed to the secondary compressor with the gas from the high pressure separator. Small purges (less than 2%) of the feed from the multiple stage compressor may be taken to control the buildup of inert gases, such as methane and ethane.

The molten polymer coming out of the low pressure separator is then mixed with stabilizers and processing additives and fed to a pelletization process. An extruder or a melt pump can be used to force the polymer through a die with multiple holes. The polymer strands are cut under water and the water/pellet slurry fed to a centrifugal drier. The pellets can be loaded directly into hopper cars or can be stored in silos and loaded at a later time.

5. Polymerization Mechanism

5.1. Initiation. A free radical is generated from the thermal decomposition of a peroxide or by an as-yet unknown mechanism in the case of oxygen. The free radical then reacts with ethylene to start a growing polymer chain.

$$\mathrm{I}\cdot + \mathrm{CH_3} - \mathrm{CH_2} \rightarrow \mathrm{I} - \mathrm{CH_2} - \mathrm{CH_2}\cdot \tag{1}$$

$$R_\mathrm{i} = k_\mathrm{i}[\mathrm{I}] \tag{2}$$

The choice of initiator is made on the basis of the type of reactor, the residence time in each zone, the desired reaction temperature, and initiator cost. A principal factor in choosing an initiator is the half-life. The longer the half-life of the initiator, the higher the degree of polymerization, but the higher the cost of the peroxide. Table 4 gives some common initiators, half-lives, and costs.

5.2. Chain Propagation. Chain propagation proceeds by radical reaction with ethylene or comonomer molecules. In the case of ethylene homopolymerization, the mechanism and kinetics are straightforward.

$$\mathrm{R} - \mathrm{CH_2} - \mathrm{CH_2}\cdot + \mathrm{CH_2} = \mathrm{CH_2} \rightarrow \mathrm{R} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2} - \mathrm{CH_2}\cdot \tag{3}$$

$$R_\mathrm{p} = k_\mathrm{p}[\mathrm{R}\cdot]P_\mathrm{e} \text{ or } R_\mathrm{p}[\mathrm{R}\cdot][\mathrm{E}] \tag{4}$$

where P_e is the ethylene pressure and E is ethylene.

When comonomers are involved, the propagation step becomes more complicated. When comonomer is present, the growing chain can react with an ethylene molecule ($\mathrm{M_1}$) (eq. 5, which is the same as eq. 3 with $\mathrm{M_1}$ representing the ethylene molecule) or a comonomer molecule ($\mathrm{M_2}$) (eq. 6), and those reactions may have very different rate constants. Likewise, if the growing chain does react with a comonomer, the comonomer radical end can now react with another comonomer (eq. 7) or with ethylene (eq. 8).

$$R - CH_2 - CH_2 \cdot + M_1 \rightarrow R - CH_2 - CH_2 - M_1 \cdot \quad (5)$$

$$R - CH_2 - CH_2 \cdot + M_2 \rightarrow R - CH_2 - CH_2 - M_2 \cdot \quad (6)$$

$$R - M_2 \cdot + M_2 \rightarrow R - M_2 - M_2 \cdot \quad (7)$$

$$R - M_2 \cdot + M_1 \rightarrow R - M_2 - M_1 \cdot \quad (8)$$

Each of these reactions has its corresponding rate reaction (eqs. 9–12).

$$R_{11} = k_{11}[\mathrm{R - M_1 \cdot}][\mathrm{M_1}] \quad (9)$$

$$R_{12} = k_{12}[\mathrm{R - M_1 \cdot}][\mathrm{M_2}] \quad (10)$$

$$R_{22} = k_{22}[\mathrm{R - M_2 \cdot}][\mathrm{M_2}] \quad (11)$$

$$R_{21} = k_{21}[\mathrm{R - M_2 \cdot}][\mathrm{M_1}] \quad (12)$$

Determining the individual propagation constants is not easy. However, if one defines reactivity ratios of the propagation constants (eqs. 13 and 14), then the reactivity ratios can be determined by measuring the rates of disappearance of M_1 and M_2 (eq. 15) in a controlled experiment.

$$r_1 = k_{11}/k_{12} \quad (13)$$

$$r_2 = k_{22}/k_{21} \quad (14)$$

$$\mathrm{d}[\mathrm{M_1}]/\mathrm{d}[\mathrm{M_2}] = \{[\mathrm{M_1}]/[\mathrm{M_2}] \times \{(r_1[\mathrm{M_1}] + [\mathrm{M_2}])/([\mathrm{M_1}] + r_2[\mathrm{M_2}])\} \quad (15)$$

Between 1945 and 1970, ethylene was copolymerized with many comonomers and the reactivity ratios measured (8–12). Table 5 lists some common comonomers and their reactivity ratios.

The reactivity ratios can be used to predict how the comonomer will be distributed in the final polymer. If the product of r_1 and r_2 approaches unity, then the monomer and ethylene are randomly distributed. If r_1 equals r_2, then the concentrations of the comonomer and ethylene in the polymer is the same as their concentrations in the feed. If one reactivity ratio is higher than the other, then the copolymer contains more of that comonomer than is in the feed. If the product of r_1 and r_2 is less than one, the monomers tend to alternate along the chain. If r_1 is higher than unity, then the amount of ethylene in the copolymer is greater than in the feed. If both ratios are less than 1, then certain feed compositions yield a copolymer of the same composition. If the product of r_1 and r_2 is greater than unity, then block copolymerization is favored. This has not been established in free-radical polymerization.

For example, in Table 3, it is seen that the r_1 and r_2 ratios for EVA are nearly one. Therefore, the ethylene and EVA are randomly distributed along the polymer chain, and the concentration of EVA in the copolymer is approximately the same as in the feed.

5.3. Short- and Long-Chain Branching.

LDPE is a unique polymer with respect to the high amount of long-chain branching in the polymer. The long-chain branch is a direct result of the free-radical polymerization mechanism. A free radical at the end of a growing polymer chain can abstract a hydrogen from the middle of another polymer chain. This terminates the first polymer molecule and creates a new radical growth point in the middle of the second polymer chain. This is known as intermolecular chain transfer.

$$\mathrm{R'CH_2R^{\sim} + R\cdot \rightarrow RH + R'C \cdot HR^{\sim}} \tag{16}$$

$$R_{\mathrm{trp}} = k_{\mathrm{trp}}[\mathrm{R\cdot}][\mathrm{P}] \tag{17}$$

where P is the polymer.

Short-chain branching is created by intramolecular chain transfer. A free radical at the end of a growing chain can abstract a hydrogen from within the same chain (backbiting) to end up with the free radical on an internal carbon atom. When polymerization continues from that internal radical, a short alkyl branch is formed. Statistically, abstraction of the hydrogen from the fifth carbon atom back is favored, and the resulting branch is a butyl group. However, backbiting can also occur on the third, fourth, and sixth carbon atoms back, forming ethyl, propyl, and amyl branches.

$$\mathrm{RCH_2CH_2CH_2CH_2CH_2\cdot \rightarrow RC\cdot H - C_4H_9} \tag{18}$$

$$\mathrm{RC\cdot H - C_4H_9 + CH_2 = CH_2 \rightarrow (R)(C_4H_9)RHCH_2CH_2\cdot} \tag{19}$$

$$R_{\mathrm{b}} = k_{\mathrm{b}}[\mathrm{R\cdot}] \tag{20}$$

5.4. Termination. There are a variety of competing mechanisms by which the growth of a polymer chain can be stopped. The dominant mechanisms are determined by the polymerization conditions and the concentrations of chain-transfer agents present.

Termination by Coupling. Two growing polymer chains can react together to form one long polymer molecule or can disproportionate to form two inert chains.

$$\mathrm{R - CH_2 - CH_2\cdot + R - CH_2\cdot \rightarrow R - CH_2 - CH_2 - CH_2{-}R \text{ or } RCH_3 + R - CH = CH_2} \tag{21}$$

$$R_{\mathrm{t}} = k_{\mathrm{t}}[\mathrm{R\cdot}]^2 \tag{22}$$

Termination by Chain Transfer with Ethylene. The growing polymer chain can react with ethylene, and instead of the ethylene inserting into the growing chain, a radical transfer reaction can take place to form vinyl end group.

$$\mathrm{RCH_2CH_2\cdot + CH_2 = CH_2 \rightarrow RCH = CH_2 + CH_3CH_2\cdot \text{ or } RCH_2CH_3 + CH_2 = CH_2\cdot} \tag{23}$$

$$R_{\mathrm{tre}} = k_{\mathrm{tre}}[\mathrm{R\cdot}]P_{\mathrm{e}} \tag{24}$$

Termination by Chain Transfer with Chain-Transfer Agents or Solvents. Polyethylene radicals are very reactive and will react with solvents or other trace contaminants in the reactor to terminate one chain and begin another. Chain-transfer agents or telogens, such as propane, propylene, hydrogen, and isobutylene, can be added to the reaction to facilitate control of molecular weight.

$$\mathrm{RCH_2CH_2 \cdot + SH \rightarrow RCH_2CH_3 + SH\cdot} \tag{25}$$

$$R_{\mathrm{trs}} = k_{\mathrm{trs}}[\mathrm{R\cdot}][\mathrm{S}] \tag{26}$$

Chain-transfer constants for some common chain-transfer agents, as well as impurities found in feedstocks, are found in Table 6. As resin producers are striving to increase production rates and aim-grade polymer yield, reaction models are being used to predict polymer properties and accelerate transitions. Analytical devices are being used to measure the impurities in the incoming and recycled ethylene streams and the corresponding chain-transfer constants applied to calculate the molecular weights being made in the reactor. Therefore, these chain-transfer constants are more than just of academic interest.

Termination by β-Scission of Polymer Radicals. Internal polymer radicals, formed by either intra-or intermolecular chain transfer (see eqs. 16 and 18), can undergo chain cleavage to form a terminated polymer chain and a new radical.

$$\mathrm{RCH_2C^{\bullet}R'CH_2R'' \rightarrow R^{\bullet} + CH_2 = CR'CH_2R''} \text{ or } \mathrm{R''^{\bullet} + RCH_2CR' = CH_2} \tag{27}$$

$$R_{\beta} = k_{\beta}[\mathrm{R\cdot}] \tag{28}$$

5.5. Kinetics. The average molecular weight of LDPE can be expressed as the degree of polymerization(DP). The DP is equal to the rate of propagation (eq. 4) divided by the sum of all the rates of termination (eqs. 22,24,26, and 28).

$$\mathrm{DP} = k_{\mathrm{p}}[\mathrm{R\cdot}]P_{\mathrm{e}}/\{R_t = k_t[\mathrm{R\cdot}]^2 + k_{\mathrm{tre}}[\mathrm{R\cdot}]P_{\mathrm{e}} + k_{\mathrm{trs}}[\mathrm{R\cdot}][\mathrm{S}] + k_{\beta}\mathrm{R\cdot}]\} \tag{29}$$

If one makes the simplifying assumption that, at steady state, the rate of initiation for a polymer radical is the same as the rate of termination (eq. 30), then one can solve for the value of [R·].

$$k_{\mathrm{i}}[\mathrm{I}] = k_{\mathrm{t}}[\mathrm{R\cdot}]^2 \tag{30}$$

$$[\mathrm{R\cdot}] = k_{\mathrm{i}}^{1/2}[\mathrm{I}]^{1/2}/k_{\mathrm{t}}^{1/2} \tag{31}$$

Substituting for [R·] in equation 29, one gets the following:

$$\mathrm{DP} = \{k_{\mathrm{p}}P_{\mathrm{e}}/k_{\mathrm{t}}k_{\mathrm{i}}[\mathrm{I}]\} + \{k_{\mathrm{p}}/k_{\mathrm{tre}}\} + \{k_{\mathrm{p}}P_{\mathrm{e}}/k_{\mathrm{trs}}[\mathrm{S}]\} + \{k_{\mathrm{p}}P_{\mathrm{e}}/k_{\beta}\} \tag{32}$$

These factors can be either measured directly or calculated from other known relationships.

6. Processing of Polymers

LDPE can be processed by most standard plastics processes. In fact, since LDPE was the first large volume polyolefin commercialized, many plastics fabrication processes were designed around the rheological properties of LDPE. For example, blown film lines were developed to accommodate the shear thinning of LDPE during melting and extrusion and the strain hardening of LDPE in the bubble forming parts of the process (19). Therefore, when LLDPE was introduced to the film market in the late 1970s, significant retrofitting of blown film lines was necessary to handle the very different rheology of LLDPE.

Shear thinning and strain hardening are rheological phenomena that occur during extrusion and extensional deformation, respectively (20). The long-chain branching in LDPE affects these two behaviors significantly. The differences between LDPE and LLDPE in shear thinning and strain hardening are illustrated in Figures 4 and 5. *Shear thinning* is the term used to describe the flow behavior of a polymer in a melt-extrusion process. Shear thinning polymers exhibit a decrease in viscosity as the output rate is increased or as they are forced through narrower die gaps. The presence of long-chain branching, and in some cases, the broader molecular weight distribution of LDPE versus LLDPE both contribute to a greater degree of shear thinning for LDPE. The result is that under extrusion conditions, the viscosity of an LDPE resin is much lower than that of an LLDPE resin of the same molecular weight. The commonly accepted reason for the difference in melt viscosity is that the LDPE molecule, containing long-chain branches, is much more compact and ‘spherical’ in nature than the LLDPE molecule of the same weight. The LDPE molecules flow past each other more easily than the linear, entangled LLDPE molecules. This means that the LDPE resin will extrude at lower temperatures and requires less power per pound of resin. As a result of this extrusion behavior, film extruders designed for LDPE were commonly underpowered for LLDPE extrusion and larger motors had to be added to convert them to efficiently extrude LLDPE.

The strain hardening effect is most clearly seen in blown film extrusion. A polymer that exhibits strain hardening will become more rigid as it is drawn to a greater extent or drawn at faster rates. An LDPE resin typically strain hardens to a greater degree than an LLDPE resin. As the polymer melt is formed into a bubble and drawn down to its final thickness, the strain hardening behavior of LDPE gives the bubble rigidity and stability to withstand the cooling air being blown on it. LLDPE, on the other hand, has a much ‘softer’ bubble, which is easily deformed by cooling air. The difference in extensional behavior is analogous to the difference between pulling on a rubber band versus pulling on bubble gum. The rubber band will extend and pull, but the more you pull it, the more resistance is felt. Bubble gum can be easily pulled; it develops very little resistance to the stretching force. Because of the highly stable bubble, gauge uniformity is excellent with LDPE. On the other hand, the softer LLDPE bubble can be drawn to thinner gauges and is more forgiving of imperfections and gels that would cause the LDPE bubble to tear off or break. It is commonly accepted that the strain hardening behavior of LDPE is the result of long-chain branches.

The common methods of processing LDPE are blown and cast film extrusion and coextrusion, extrusion coating, blow molding, injection molding, rotomolding, and wire extrusion. Explanations for these processes can be found in other articles in the Encyclopedia.

7. Economic Aspects

Despite threats from other polyolefins, such as HDPE, LLDPE, and *m*-LLDPE, LDPE remains a viable, high volume polymer (Table 7) (21). During the 1980s, no new LDPE capacity was added because of the assumption that low cost LLDPE would replace LDPE in most applications. However, while LLDPE did displace LDPE in many areas and did absorb most of the overall growth in the North American film market, LDPE remains the resin of choice in some applications and markets (Table 8) (21,22). The overall growth of LDPE demand remains very low (0–1% annually), and there is relatively little growth in LDPE capacity. The picture for LDPE in the rest of the world is not much different in terms of growth (Table 9) (21,23,24). LLDPE took longer to be accepted by the rest of the world because the supply was mainly located in North America for several years while LDPE was locally available. LDPE is still favored in many areas of the world because of its easy film processing. In many countries, film blowing equipment is old and has been designed to handle the rheology of LDPE. Substituting LLDPE causes significant production rate penalties on film lines. Many film fabricators had resorted to blends of LDPE with small amounts of LLDPE to improve film toughness without sacrificing extrusion rates.

Looking forward, continued substitution of LLDPE and HDPE for LDPE will take place. As older film extrusion equipment is replaced or retrofitted to handle LLDPE, the consumption of LDPE will decrease. The two attributes of LDPE which, as of today, have not been satisfactorily met with LLDPE are the long-chain branching and the flexibility and properties of polar comonomer containing copolymers. But even these attributes are under attack with new technology. Some metallocene catalysts, which give very narrow molecular weight and narrow comonomer distribution LLDPE, also show the presence of long-chain branching (25). When the type and level of long-chain branching can be controlled by these catalysts, applications such as extrusion coating will be vulnerable to LLDPE substitution. Another category of new polyethylene catalysts is based on late transition metals, such as Fe and Ni. These catalyst systems give the promise of the ability to incorporate polar comonomers (26).

Pricing in the polyethylene market is extremely volatile. Because of the significant economies of scale, when new ethylene and polyethylene capacity is added, it is in very large increments. This overwhelms the regular, but modest, growth in consumption so that a large imbalance in supply versus demand occurs when the new plant starts up. When there is an overabundance of supply, prices are very low as all producers struggle to keep their facilities sold out. This condition lasts a few years until the demand catches up to the supply and prices start to rise. However, as soon as prices start increasing, new capacity is announced and the cycle starts all over. Typical low density pricing in North America will vary from US$600/ton to over US$1100/ton through the cycle (27).

8. Specifications and Standards

There are about 10 manufacturers of LDPE in North America. The top six include Equistar Chemicals, LP, The Dow Chemical Co., Exxon Mobil Corp., Chevron Phillips Chemical Co., DuPont, and Westlake Polymer Corp. Each company has their own trade names and specific grade slates for various applications. Data sheets and MSDSs are available from each supplier and many have them available on their web sites. A typical product data sheet will cover resin characteristics such as melt index and density, as well as 'typical' final product properties, such as film tear and tensile and impact strength. The tests will identify the ASTM test methods and the data sheet will usually have the conditions under which the test samples were made. There will also be an indication of the FDA and food contact status of the resin and the applications for which the resin is suited.

A majority of the LDPE used in North America is shipped in 82-ton rail cars. Other common forms of shipment are 18-ton bulk trucks, 500-kg boxes, and 25-kg bags. In general, no special safety labels are needed for LDPE products. In other parts of the world, the most common mode of shipment is in 25-kg bags.

9. Analytical and Test Methods

The most important tests for LDPE are those that measure the molecular characteristics of the resin: molecular weight, molecular weight distribution, and density. Since long-chain branching is unique to LDPE, a short description of the analytical test methods used to measure it is given. However, because of the difficulty and lack of precision of the tests, measurement of long-chain branching is not commonly done as a quality control test. The measurement and reporting of gels, or film imperfections, are covered.

9.1. Melt Index. The melt index of a polymer is a measurement that is inversely related to molecular weight. ASTM D1238 is typically used for this test. A small amount (less than 10 g) of LDPE is melted and forced through a small orifice under constant load. The weight of polymer extruded in 10 min under 298 kPa pressure at 190°C is called the melt index. If a pressure of 2982 kPa is used, the measurement is called the flow rate (FR) or melt-flow rate (MFR). Typical LDPE melt indices range from 0.2 to over 100 g/10 min. In general, the lower melt index resins are used for film and blow molding and wire and cable applications while the higher melt index resins are used for extrusion coating and injection-molding applications. Low melt index resins have higher molecular weight than high melt index resins. The higher the molecular weight, the better the strength properties of the final products, but the more difficult the extrusion behavior (Fig. 6).

9.2. Flow Rate Ratio. The FR ratio is used as a rough estimate of the MWD of a resin. Molecular weight distribution can be measured directly by gel permeation chromatography, but this is a time-consuming, technically challenging measurement that is not commonly found in quality control laboratories.

Melt-flow ratio measurements are easily done, since the MFR of a resin is the flow index of the sample divided by the melt index of the sample.

Melt-flow ratios for LDPE resins can range from very narrow [20] to very broad [100], and can be controlled by reactor conditions and reactor type. Resins with narrow MWD give stronger products but are more difficult to extrude than resins with broad MWD.

9.3. Density.

ASTM D1505 is used to measure polymer density. A small sample (1–5 g) of powder or pellet is molded in a carefully prescribed manner and dropped into columns with alcohol/water gradients of different viscosities. The position of the sample in the column is compared with standards of known density, and the density of the test sample is determined.

Density is a measure of the crystallinity of the polymer. Polymer crystallinity affects such product properties as stiffness, rigidity, environmental stress-crack resistance (ESCR), and barrier properties (Fig. 7). The lower the crystallinity, and hence the density, the more limp and flexible the material is. A 0.918-g/cm^3 density LDPE product has better ESCR and worse barrier properties than a product with a density of 0.930 g/cm^3.

9.4. Long-Chain Branching.

The number of long-chain branches per 1000 carbon atoms on the main backbone of LDPE can range from 0.4 to over 10. Long-chain branching has been a very difficult feature to quantify. The variations in the lengths and locations and branch points for the long-chain branches make comparison of data and standardization of samples difficult. Qualitatively, the presence of long-chain branching can be surmised by looking at intrinsic viscosity as a function of molecular weight. Linear polymers give a linear response of intrinsic viscosity as a function of molecular weight. If the intrinsic viscosity of a resin with long-chain branching is plotted on this same graph, it will fall below the line for the linear polymers. However, the quantitative information on the amount and length of the long-chain branching has been difficult to extract from this method. The ^{13}C nmr analysis has been used to quantify the number of long-chain branches (28,29); however, there are some limitations to this method as well. In ^{13}C nmr, any branch longer than six carbon atoms is considered a long branch (30). Combinations of methods, such as ^{13}C nmr plus sec (size exclusion chromatography) (31,32) and sec plus intrinsic viscosity (33), are being developed to overcome the deficiencies of single-method determinations.

9.5. Gels.

While gels are neither a physical property nor a reported attribute of LDPE, the gel level is a critical quality variable for LDPE film resins. Gels are physical defects which can affect the appearance, but more importantly, the performance of LDPE film. There are many forms of gels, ranging from arrowheads, pinpoint gels, black specks, and fish-eyes. Gels can be caused by many factors. Gels can be formed in the reactor by poor mixing in a reactor zone. If polymer builds up on the reactor wall, it can cross-link to form high molecular weight gels or even black specks. The compounding or pelletizing step can also cause cross-linking and gels if not cleaned and operated properly. Most resin manufacturers will run a film quality test on LDPE resin to ensure that the gel level is low in the product before certifying it as prime material.

However, gels can be caused in the material after it has left the resin producer. Extraneous materials, like dirt, fibers, or contamination with other polymers, can occur during shipment or unloading at the fabricator. In addition, gels can be created during extrusion into film by improper film blowing conditions or inadequate maintenance and cleaning of film blowing equipment.

Gels can be analyzed by a variety of techniques to determine their origin. A simple melting point can determine if the gel is polymeric or cross-linked. Infrared spectroscopy can determine the nature of the polymer to determine if cross-contamination with another material has occurred. Conducting the melting point under a microscope can reveal if there is a solid core to the gel which might indicate a foreign contaminant. Electron microscopy can hone in on the gel and measure the presence of any metal that might indicate barrel or screw wear or totally foreign materials like bolts or nails. Because gels are an important quality issue and can be caused by a variety of mechanisms, resin producers have developed sophisticated analytical methods to identify the gels so that improvements can be made in resin production and handling to prevent them.

The reason gels are a critical quality factor with LDPE film is that they can cause problems in film extrusion and in film performance. If the gels are large enough, they can actually cause the bubble to break during the blown film process. “Bubble tear-offs” are a serious problem for the film fabricator because it causes down time and loss of product quality. If the gels are not large enough to cause problems during the extrusion process, they can still cause problems for film quality. In extrusion coating, for example, the presence of small gels in the very thin layer of polyethylene can cause pinhole leaks in the coating and destroy the barrier performance of the material. In wire and cable applications, the gel can form a weak spot in the wire coating, which will be the initiation point for electrical failure.

10. Health and Safety Factors

The majority of homo- and copolymer LDPE is supplied in small pellet form and is consider a material with low toxicity, low reactivity, and low flammability. However, during movement of the pellets in a conveying system, fines and dust can be created as the pellets come in contact with the piping system. If these fines build up in the system, the potential for a dust explosion exists. In addition, polyolefin powders are supplied for certain applications, such as rotomolding or coating. These polyolefin powders also pose fire and explosion safety concerns. Polyolefin dust is defined as a combustible material in the “Standard for the Prevention of Dust Explosions in the Plastics Industry” (NFPA 654). Concentrations of polyolefin powder as low as 0.02 kg/m^3 can burn, releasing sufficient heat to produce a self-propagating reaction that can result in an explosion (34). This explosive concentration is dependent on the particle size of the powder and also on the type and concentration of any additives used in the polymer. The material supplier should always be consulted for advice on handling dust and powders from LDPE.

Polyolefin dust is currently classified as a nuisance material. Polyolefin materials have a long history of safe use and are not thought to produce irreversible change in lung tissue or produce significant disease or toxic effects when exposure is kept under reasonable control. The Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental

Industrial Hygienists (ACGIH) have established permissible exposure limits of 15 and 10 mg/m^3 of air, respectively, for total nuisance dust, and 5 mg/m^3 for the respirable fraction.

10.1. Food Contact.

Homopolymer LDPE is a relatively inert, nontoxic and benign polymer, which is used extensively in a variety of food contact and medical applications. Copolymers containing EEA, EMA, EVA, and other comonomers can also be used selectively in food contact applications. The resin supplier should be asked for specific information on FDA compliance for each particular resin, as the type of polymer, the amount of comonomer, and the type and level of additives and stabilizers all play a part in determining the FDA compliance of a specific resin.

10.2. Environmental Impact.

In recent years, there has been quite a bit of adverse publicity around the use of plastics and the impact of plastic litter on the environment. The decision of fast food restaurants to discontinue the use of expanded polystyrene clamshell hamburger containers is one example of how plastics growth and use can be changed by public opinion. Many states have considered or passed regulations specifying the amount of recycled plastic that must be incorporated into new plastic articles. This has had a direct impact on the polyethylene industry, including LDPE, because polyethylene is one of the more recyclable plastics being used today. However, the recycling effort has been hampered by the higher cost of collecting, separating, and cleaning the polyethylene containers compared to the cost of virgin polymer.

Photo- and biodegradable plastics have been offered as possible solutions to the litter problem. LDPE copolymers containing carbon monoxide have been produced by Union Carbide Chemical and Plastics Co., Inc. (35) and The Dow Chemical Co. These photodegradable copolymers have been used to make beverage can carriers or rings but have not been widely used in other commodity applications because of the unique physical properties. Currently, the search for biodegradable LDPE has not led to a commercially successful product. Blends of LDPE and starch-like fillers improve the biodegradation of LDPE, but at a significant sacrifice of physical properties (36). A new degradable/compostable technology has been developed, such that the degradability can be triggered by heat, light, and/or stress. Products made by this technology are being currently marketed in Europe and South America (37).

Plastic pellets inadvertently lost from plastic production and warehouse facilities pose a threat to fish and wildlife. Therefore, the U.S. EPA (Environmental Protection Agency) has classified plastic pellets as “significant materials.”. The finding of even one pellet in a storm water run-off without a permit is now subject to federal regulatory action with the potential for substantial fines and penalties. As a result, the plastics industry has launched Operation Clean Sweep, an initiative to prevent the accidental release of pellets into the environment. Specific recommendations for handling polyolefins to prevent resin loss into the environment have been developed by the Society for the Plastics Industry (38).

From a polymerization process standpoint, fugitive hydrocarbon emissions, mainly ethylene, are the biggest environmental concern. Much progress has been made in controlling these emissions by recovering and recycling gas from various points in the process. Using advanced process control software and better instrumentation, runaway reactions or “decomps” have been significantly reduced. These “decomps” are typically vented to the atmosphere and so this improved control has resulted in fewer hydrocarbons being released. On a positive side, many polymerization units capture the heat of polymerization from the reaction and use that to generate low pressure steam. This reduces the need for electrical power to run the process.

11. Uses

11.1. Film and Sheet. The film and sheet market is the largest application for low density polyethylene, consuming about 50% of the total North American demand (Table 8). Packaging applications include pallet and shrink wrapping, heavy-duty sacks, and food packaging. Nonpackaging applications comprise refuse bags, storage bags, agricultural film, and industrial sheeting. The film market has been the primary focus of LLDPE manufacturers, and LLDPE now accounts for over 50% of the low density film market (Table 7). At one time, garbage bags, grocery sacks, garment bags, stretch film, and food packaging films were made from 100% LDPE, but because of the outstanding physical properties of LLDPE, these markets have largely been converted to LLDPE or LLDPE-rich blends of LDPE. There are still a few film applications where LDPE remains the resin of choice: shrink wrap, clarity films, etc. The advantages of LDPE in film are ease of extrusion, clarity, and low taste and odor. Typical resins used for film have melt indices from 0.2 to 6 and densities from 0.917 to 0.930 (Tables 10–12).

11.2. Extrusion Coating. In extrusion coating, LDPE is used as a thin coating on another material, such as paper, aluminum foil, paperboard, or another polymeric material. The final structure is used for snack food packaging, juice boxes, milk, or other food containers. The LDPE can serve as an adhesive, moisture barrier, seal layer, printing surface, or barrier to tearing. Typically, resins with melt indices from 4 to 10 and densities from 0.920 to 0.930 are used in this application (Tables 13–15). This is one market where LLDPE has not made significant penetration. The unique long-chain branching characteristics of LDPE, especially that produced in autoclave reactors, has not been duplicated by LLDPE manufacturers. This long-chain branching gives LDPE the combination of neck-in and drawdown necessary for successful high speed extrusion coating.

11.3. Wire and Cable. Radar sheathing cable was one of the first commercial uses for LDPE. Currently, about 10% of LDPE production is used in wire and cable applications. The cleanliness of LDPE insofar as its lack of gels or inorganic catalyst residues is a key advantage in high energy wire sheathing. The ease of extrusion is also another advantage of LDPE, as wire coating lines run at very high speeds. Many resin producers offer wire and cable resin, which has been pre-compounded with a variety of colors, including black (Table 16). Some wire and cable manufacturers prefer to add color themselves. Typical resins used for wire and cable are very similar to film resins in the melt index and density ranges employed (Table 17).

11.4. Injection Molding. This market, which includes lids, buckets, toys, freezer containers, has seen significant penetration by LLDPE. LLDPE offers advantages in product properties such that higher melt index products can be used without sacrificing product performance. The use of the higher melt indices allows the fabricator to increase production speed and reduce costs. The markets where LDPE is still used are those in which some clarity is desired, such as caps and closures (Table 18).

11.5. Blow Molding. HDPE is the preferred resin for blow molding because of its combination of rigidity and barrier properties. LDPE is less commonly used, but does offer advantages in applications where clarity, flexibility, and excellent ESCR are required. Typically, low melt index resins are used for blow molding applications (Table 19).

BIBLIOGRAPHY

"High Pressure (Low and Intermediate Density) Polyethylene" in *ECT* 2nd ed., under "Olefin Polymers," Vol. 14, pp. 217–241, by P. L. Clegg, Imperial Chemical Industries Ltd.; in *ECT* 3rd ed., under "Olefin Polymers," Vol. 16, pp. 402–420, by R. L. Boysen, Union Carbide Corp.; "Low Density Polyethylene"; in *ECT* 4th ed., under "Olefin Polymers," Vol. 17, pp. 707–723, by Lloyd W. Pebsworth, Polyethylene Technology; "Polyethylene, Low Density" in *ECT* (online), posting date: December 4, 2000, by Lloyd W. Pebsworth, Polyethylene Technology.

1. Brit. Pat. 471590 (Sept. 6, 1937), E. W. Fawcett and co-workers(to Imperial Chemical Industries, Ltd.).
2. U.S. Pat. 2153553 (Apr. 11, 1939), E. W. Fawcett(to ICI, Ltd.).
3. A. Prasad,in J. E. Mark, ed., *Polymer Data Handbook*, Oxford University Press, New York, 1999, p. 518.
4. H. K. Loveless, in R. Raff and K. W. Roak, ed.,*Crystalline Olefins Polymers, Part II*, John Wiley & Sons, Inc., New York, 1964, p. 70.
5. P. J. Flory, *J. Am. Chem. Soc.* **59**, 241(1937); P. J. Flory, *J. Amer. Chem. Soc.* **69**, 2893 (1947).
6. M. J. Roedel, *J. Am. Chem. Soc.* **75**, 6110 (1953).
7. K. W. Doak and A. Schrage, in R. A. V. Raff and K. W. Doak, eds., *Crystalline Olefin Polymers*, Part 1 Wiley-Interscience, New York, 1965, Chapt. "8".
8. G. Luft, H. Bitsch, and H. Seidl, *J. Macromol. Sci. Chem.* **11**, 1089 (1977).
9. H. Siedl and G. Luft, *J. Macromol. Sci. Chem.* **15** (1), 1 (1981).
10. P. Ehrlich and G. A. Mortimer, *Adv. Polym. Sci.* **7**, 386 (1970).
11. L. Bogetich, G. A. Mortimer, and G. W. Daues, *J. Polym. Sci.* **61**, 3 (1962).
12. G. A. Mortimer, *J. Polym. Sci., Part B* **3**, 343 (1965).
13. R. D. Burkhart and N. L. Zutty, *J. Polym. Sci., Part A* **1**, 1137 (1963).
14. D. D. Coffman and co-workers, *J. Am. Chem. Soc.* **74**, 3391 (1952).
15. G. A. Mortimer, *J. Polym. Sci., Part A1* **4**, 881 (1966).
16. P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci., Part A1* **8**, 1549 (1970).
17. G. A. Mortimer, *J. Polym. Sci., Part A1* **8**, 1513 (1970).
18. G. A. Mortimer, *J. Polym. Sci., Part A1* **10**, 163 (1972).
19. L. A. Utracki, *Adv. Polym. Technol.* **5**, 41 (1985).
20. J. M. Dealy and K. F. Wissbrun, *Melt Rheology and Its Role in Plastics Processing*, Van Nostrand Reinhold Co., Inc., New York, 1990.

21. *Modern Plastics* **77** (2), 74 (Feb. 2000).
22. *Modern Plastics* **75** (1), 74 (Jan. 1998).
23. *Modern Plastics* **78** (2), 42 (Feb. 2001).
24. *Chem Systems, Polyolefins Planning Service, POPS 2000*, Report 2: Global Commercial Analysis, Dec. 2000.
25. U.S. Pat. 5272236 (Dec. 21, 1993), S. Lai and co-workers(to The Dow Chemical Company).
26. U.S. Pat. 5866663 (Feb. 2, 1999), M. S. Brookhart and co-workers(to E. I. du Pont de Nemours & Co., Inc., and University of North Carolina).
27. *Data from Equistar Chemicals, LP.*
28. D. E. Axelson, G. C. Levy, and L. Mandelkern, *Macromolecules* **12**, 41 (1979).
29. J. C. Randall, *J.M.S. Part C: Rev. Macromol. Chem. Phys.* **29**, 201–317 (1989).
30. F. A. Bovey and co-workers, *Macromolecules* **9**, 76 (1976).
31. D. C. Bugada and A. Rudin, *J. Appl. Polym. Sci.* **33**, 87 (1987).
32. D. C. Bugada and A. Rudin, *Eur. Polym. J.* **23**, 847 (1987).
33. F. M. Mirabella Jr. and L. Wild, *Advances in Chemistry Series No. 227: Polymer Characterization: Physical Property, Spectroscopy, and Chromatographic Methods*, American Chemical Society, Washington, 1990, p. 23, Chapt. “2”.
34. *Handling and Storage of Equistar Polymers, published by Equistar Chemicals, LP.*
35. Brit. Pat. 915240 (Jan. 9, 1963), G. Madgwick and co-workers (to Union Carbide Corp.)
36. F. Otey and W. Done, *in Proceedings of the Symposium on Degradation of Plastis*,-Society of the Plastics Industry, Inc. Washington, D.C., June 10, 1987.
37. U.S. Pat. 5854304 (Dec. 29, 1998), R. A. Garcia and J. G. Gho (to EPI Environmental Products Inc.).
38. *Operation Clean Sweep—Pellet Loss Prevention Program, SPI, Literature Sales Department, 1801 K St., NW #600, Washington, DC 20006-1301.*

GENERAL REFERENCES

L. W. Pebsworth, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., vol. 17, Wiley-Interscience, New York, 1997, pp. 707–723.

R. A. V. Raff and J. B. Allison, *Polyethylene*, Interscience Publishers, New York, 1956.

A. Renfrew and P. Morgan, eds., *Polythene*, Interscience Publishers, New York, 1957.

H. D. Anspon, in W. M. Smith, ed., *Manufacture of Plastics*, Vol. 1, Reinhold Publishing Corp., New York, 1964, pp. 66–193, Chapt. “2”.

J. H. DuBois and F. W. John, *Plastics*, Van Nostrand Reinhold Co., Inc., New York, 1981.

T. O. J. Kresser, *Polyethylene*, Reinhold Publishing Corp., New York, 1961.

S. L. Aggarwal and O. J. Sweeting, *Chem. Rev.* **57**, 665 (1957).

W. Hollar and P. Ehrlich, *Chem. Eng. Comm.* **24**, 57–70 (1983).

D. Stoiljkovich and S. Javanovich, *Makromol. Chem.* **182**, 2811–2820 (1981).

H. Oosterwijk and H. Van Der Bend, *Akzo Chemie America Bulletin*, Initiations Seminar, New York, 1980, p. 87.

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Table 1. **Typical Properties of LDPE**[a]

Property	Value	Method
molecular weight	70,000–120,000	gpc
melt index, g/10 min	0.2–50	ASTM D1238
density at 20°C, MPa g/cm^3	0.920–0.935	ASTM D1505
Vicat softening point	80–96°C	ASTM D1525
tensile strength, MPa[b]	9–15	ASTM D638
tensile elongation at rupture, %	150–800	ASTM D638
hardness, Shore D	40–60	ASTM D676
dielectric constant at 1 MHz	2.3	ASTM D1531
dissipation factor at 1 MHz	0.0001	ASTM D1531
low temperature brittleness F_{50}, °C	< -76	ASTM D746

[a] Data supplied courtesy of Equistar Chemicals, LP.

[b] To convert MPa to psi, multiply by 145.

Table 2. **Blown Film Property Comparison[a] between HP-LDPE and LLDPE**

Property	ASTM test method	HP-LDPE	HP-LDPE	LLDPE	LLDPE	LLDPE
melt index, g/10 min	D1238	2.5	0.2	1.0	1.0	1.0
density, g/cm^3	D1505	0.921	0.923	0.918	0.918	0.918
comonomer		None	None	Butene	Hexene	Octene
Dart drop, N/mm (=dyn/cm)	D1709	29	71	39	77	97
puncture energy, kJ/m[b]		27	22	71	76	–
Elmendorf tear, N/mm (=dyn/cm)	D1922					
MD		62	35	54	131	143
XD		43	39	131	226	309
tensile strength, MPa[c]	D882					
MD		20	19	35	36	45
XD		19	21	26	32	35
haze, %	D1003	6	25	17	20	12
gloss, 45°	D2457	70	30	53	50	60

[a] All properties measured on 38-μm film produced at a 2:1 blow-up ratio.

[b] To convert hJ/m to ft·lbf/in., multiply by 18.73.

[c] To convert MPa to psi, multiply by 145.

Table 3. **Injection Molded Property Comparison of LDPE and LLDPE**

Property	ASTM test method	LDPE	LDPE	LLDPE	LLDPE
melt index, g/10 min	D1238	24	38	21	105
density, g/cm^3	D1505	0.923	0.923	0.924	0.929
tensile strength, MPa[a]	D638	8.3	8.9	8.3	12.5
dishpan impact[b] at −20°C, J		12	7	41	4
failure mode		Brittle	Brittle	Ductile	Ductile
low temperature brittleness[c] F_{50}, °C	D746	−39	−25	< -76	−58
ESCR[d] F_{50}, h	D1693	<1	–	150	<2

[a] To convert Mpa to psi, multiply by 145.

[b] Industry test done on standard molded plastic dishpan. Parts of various weights dropped on dishpan until failure.

[c] Test method has been found useful for specification purposes, but does not necessarily indicate the lowest temperature at which the material may be used.

[d] At 50°C, 100% Igepal, no slit.

Table 4. **Peroxide Initiators for LDPE Polymerization**

Peroxide	CAS No.	Half-life (1 min) temperature[a], °C	Cost[b] \$/gram
t-butyl peroxypivalate	[927-07-1]	123	
dioctanoyl peroxide	[762-16-3]	127	
t-butyl peroxyisobutyrate	[109-13-7]	130	
dibenzoyl peroxide	[96-36-0]		0.084
t-butyl peroxyisopropylcarbonate	[2372-21-6]		0.141
t-butyl peroxybenzoate	[614-45-9]	170	0.075
dicumyl peroxide	[80-43-3]		0.101
di-*t*-butyl peroxide	[110-05-4]	191	0.084
t-butyl hydroperoxide	[75-91-2]	260	0.205

[a] Refs. 8 and 9.

[b] Aldrich Catalog, 2000–2001 Edition.

Table 5. **Reactivity Ratios for Comonomers with Ethylene**

Comonomer	r_1	r_2	Pressure, MPa[a]	Temperature, °C	Reference
propylene	3.1 ± 0.2	0.77 ± 0.05	103–172	130–220	10, 11
1-octene	3.1 ± 0.1	NA[b]	138	130	10, 11
vinyl acetate	1.07 ± 0.06	1.09 ± 0.2	101	90	12, 13
vinyl chloride	0.24 ± 0.07	3.6 ± 0.3	101	90	12, 13
methyl acrylate	0.042 ± 0.004	5.5 ± 1.5	138	130–152	12
methyl methacrylate	0.2	NA	207	160–220	12
carbon monoxide	0.15	0.0	92	130	14

[a] To convert Mpa to psi, multiply by 145.

[b] NA = not available.

Table 6. **Common Chain-Transfer Agents and Their Constants**

Agent	Transfer constant	Reference
methane	0.0002	15
ethane	0.0006	15
propane	0.0030	16
ethanol	0.0075	17
propylene	0.0122	17
hydrogen	0.0159	17
acetone	0.0168	17
isobutylene	0.021	15
2-butene	0.038	17
1-butene	0.047	17
propionaldehyde	0.33	18

Table 7. **Comparison of Markets for LDPE, LLDPE, and HDPE (1999)[a] North America, 10^3 t**

Market area	LDPE	LLDPE	HDPE
extrusion			
packaging film	1022	1180	164
nonpackaging film	506	1010	753
coating	420	13	–
sheet	56	18	333
pipe and extrusion	–	–	710
injection molding	150	277	1177
blow molding	29	9	2066
rotomolding	58	191	65
resellers and compounders	39	–	84
other domestic	666	819	–
export	707	750	718
Total	*3610*	*4268*	*6968*

[a] Ref. 21.

Table 8. **Low Density PE Volumes by Market Area (1999) North America, 10^3 t**

Market area	1996[a]	1997[a]	1998[b]	1999[b]
extrusion				
packaging film				
food	497	459	490	502
nonfood	416	382	328	366
stretch/shrink	168	157	148	153
nonpackaging film				
carryout bags	63	49	54	56
trash, can liners	48	29	45	55
other	335	399	394	394
coating	397	430	414	420
sheet	66	59	51	56
injection molding	135	134	128	150
blow molding	36	31	31	29
rotomolding	45	44	53	58
resellers and compounders	395	392	40	39
other domestic	–	–	702	666
export	671	636	671	707
Total	*3580*	*3544*	*3507*	*3610*

[a] Ref. 22 (United States only).

[b] Ref. 21 (United States and Canada).

Table 9. **LDPE Supply/Demand by Region, 10^3 t**

	Consumption		Production	
Region	1998[a]	1999[a]	2000[b]	2000[c]
North America	2,843	2,909	2,710	4,050
Western Europe	4,688	4,719	4,635	5,843
Japan	954	1,059	NA	1,355
China	1,445	1,583	1,630	714
India	238	244	254	175
All Other			7,119[c]	6,488
Global Total			*16,348*[c]	*18,625*

[a] Ref. 21.

[b] Ref. 23.

[c] Ref. 38.

Table 10. **Low Density Resin for Film Applications**[a]

Physical Properties	ASTM test method	LDPE heavy duty grades[b]	LDPE garment grade[c]
density, g/cm^3	D1505	0.926	0.920
melt index, g/10 min	D1238	0.25	6.5
vinyl acetate incorporated, %		4.5	0
Vicat softening point, °C	D1525	88	85
film properties			
haze, %	D1003		12.0
gloss, 45^0	D2457		50
tensile strength at break, MPa[d]	D882		
MD		22.1	17.3
TD		20.7	14.0
elongation at break, %	D882		
MD		370	225
TD		550	450
1% secant modulus, MPa	D882		
MD		131	146
TD		159	166
dart drop impact strength F_{50}, g	D 1709	320	60
Elmendorf tear strength, g	D1922		
MD		150	350
TD		250	150
key properties		High impact strength	Good drawdown
applications		Ice bags, frozen food, packaging	Garment bags

[a] Data courtesy of Equistar Chemicals, LP.

[b] Data obtained on film produced from Petrothene® NA 480 on an 89-mm blown film line, 203-mm die, at 221°C melt temperature, 2:1 BUR, at 51-μm thickness.

[c] Data obtained on film produced from Petrothene® NA 336 on an 89-mm blown film line, 203-mm die, at 163°C melt temperature, 1.2:1 BUR, at 32-μm thickness. Petrothene is a registered trademark of Equistar Chemicals, LP.

[d] To convert MPa to psi, multiply by 145.

Table 11. **Low Density Resin for Film Applications**[a]

Physical properties	ASTM test method	LDPE clarity grades	LDPE industrial clarity grades
density, g/cm^3	D1505	0.926	0.921
melt index, g/10 min	D1238	1.0	2.0
vinyl acetate incorporated, %		4.0	–
vicat softening point, °C	D1525	90	93
film data[b]			
haze, %	D1003	4.0	6.0
gloss, 45°	D2457	75	70
tensile strength at break, MPa[c]	D882		
MD		25.5	23.5
TD		21.4	17.3
elongation at break, %	D882		
MD		340	300
TD		500	500
1% secant modulus, MPa[c]	D882		
MD		145	193
TD		166	221
dart drop impact strength, F_{50}, g	D1709	100	90
Elmendorf tear strength, g	D1922		
MD		180	380
TD		250	200
key properties		good clarity, excellent impact	good processability and clarity
applications		bags and special film applications	stiff liners

[a] Data courtesy of Equistar Chemicals, LP.

[b] Data obtained on film produced from Petrothene® NA 340 and NA 143 on an 89-mm blown film line, 203-mm die, at 191°C melt temperature, 2:1 BUR, at 32-μm film thickness.

[c] To convert MPa to psi, multiply by 145.

Table 12. **Low Density Resin for Sheet and Profile Extrusion**[a]

Typical properties	ASTM test method	LDPE resin (NA 967-000)
density, g/cm^3	D1505	0.919
melt index, g/10 min	D1238	1.5
tensile strength at break, MPa[b]	D638	10.4
elongation at break, %	D638	600
low temperature brittleness F_{50}, °C	D 746	< -76
Vicat softening point, °C	D1525	90
hardness, Shore D	D2240	51
environmental stress-crack resistance F_{50}, h	D1693	
	D2561	
FDA sanction		21 CFR 177.1520
key properties		Excellent, toughness
applications		Sheet/profile extrusion, foamed sheet/profiles

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[a] Data on Petrothene® NA 967-000, courtesy of Equistar Chemicals, LP.

[b] To convert MPa to psi, multiply by 145.

Table 13. **Low Density Resin for Extrusion Coating**[a]

Properties	ASTM test method	LDPE resins	
		NA 204-000	NA 206-000
density, g/cm^3	D1505	0.918	0.918
melt index, g/10 min	D1238	7.0	13
nominal melt temperature range, °F		575–625	575–625
FDA sanction		21 CFR 177.1520, 176.170	21 CFR 177.1520, 176.170
key properties		excellent adhesion and heat seal, good neck-in, high drawdown	formulated for high line speeds and low coating weights
applications		general purpose flexible packaging and laminating	sugar pouches, industrial and multiwall bags

[a] Data on Petrothene® NA 204-000 and Petrothene® NA 206-000, courtesy of Equistar Chemicals, LP.

Table 14. **Low Density Resin for Extrusion Coating**[a]

Properties	ASTM test method	LDPE resins	
		NA 216-000	NA 219-000
density, g/cm^3	D1505	0.923	0.923
melt index, g/10 min	D1238	3.7	10
nominal melt temperature range, °F		575–625	575–625
FDA sanction		21 CFR 177.1520, 176.170	21 CFR 177.1520
key properties		formulated for heavy and medium weight coatings	formulated for high line speed, lightweight coatings
applications		flexible packaging, milk cartons, and food boards	flexible packaging paperboard, and industrial papers

[a] Data on Petrothene® NA 216-000 and Petrothene® NA 219-000, courtesy of Equistar Chemicals, LP.

Table 15. **Low Density Copolymer Resins for Extrusion Coating**[a]

Properties	ASTM test method	EVA copolymers	
		UE 652-249	UE 635-000
melt index, g/10 min	D1238	32	9
vinyl acetate incorporated, %	D638	19	9
nominal melt temperature range		not to exceed 450°F	not to exceed 450°F
FDA sanction		21 CFR 177.1350, 175.105	21 CFR 177.1350, 175.105
key properties		good heat seal response, good clarity	good heat seal response, good clarity
applications		formulated for cheese wrap	coatings on PET and polypropylene film

[a] Data on Ultrathene® UE 652−249 and Ultrathene® UE 635-000, courtesy of Equistar Chemicals, LP. Ultrathene is a registered trademark of Equistar Chemicals, LP.

Table 16. **Low Density Resin for Wire and Cable**[a]

Property	ASTM test method	LDPE compound
nominal unaged physical properties Density, g/cm^3	D1505	0.925
melt index, g/10 min	D1238	0.2
tensile strength at break, MPa[b]	D638	15.9
elongation at break, %	D638	650
hardness, Shore D	D2240	50
environmental stress-crack resistance, 10% Igepal	D1693	F_0 at 168 h
low temperature brittleness F_{50}, °C	D746	< -76
nominal electrical properties		
dielectric constant at 1 MHz	D1531	2.36
dissipation factor at 1 MHz	D1531	0.00060
volume resistivity, Ω·cm	D257	2.5×10^{17}
color		Black
applications		Cable jacketing, line wire insulation
specifications		ASTM D1248, Type I, class C, Category 5, Grades E5 and J3; Federal LP390C, Type III, Class L, Category 5, Grades 2–4; RUS 7CFR, 1755.390

[a] Data on PE 130 courtesy of Equistar Chemicals, LP.

[b] To convert MPa to psi, multiply by 145.

Table 17. **Low Density Resin for Wire and Cable**[a]

Property	ASTM test method	LDPE resin	
		NA 520-024	NA 951-080
nominal unaged physical properties			
density, g/cm^3	D1505	0.918	0.919
melt index, g/10 min	D1238	0.25	2.2
tensile strength at break	D638		
psi		2100	1700
MPa	D638	14.5	11.7
elongation at break, %	D638	550	600
hardness, Shore D	D2240	44	55
environmental stress-crack resistance, 10% Igepal	D1693	F_0 at 168 h	N/A
low temperature brittleness F_{50}, °C	D746	< -76	< -76
nominal electrical properties			
dielectric constant at 1 MHz	D1531	2.28	2.27
dissipation factor at 1 MHz	D1531	0.00010	0.00008
volume resistivity, Ω·cm	D257	1×10^{18}	2×10^{18}
color		natural	natural
applications		primary insulation, compounding base resin	primary insulation, coaxial and electronic cables, compounding base resin
specifications		ASTM D1248, Type 1, Class A, Category 5, Grades E4 and E5; Federal LP390C, Type 1, Class L, Category 5, Grade 2	ASTM D1248, Type 1, Class A, Category 3, Grade E3; Federal LP390C, Type 1, Class L, Category 3, Grade 2

[a] Data on Petrothene® NA 520-024 and Petrothene® NA 951-080 courtesy of Equistar Chemicals, LP. Igepal is a registered trademark of the Rhone-Poulenc Co., Inc.

Table 18. **Low Density Resin for Injection Molding**[a]

Physical properties[b]	ASTM test method	LDPE grades	
		H-2324	NA 820-000
density, g/cm^3	D1505	0.923	0.918
melt index, g/10 min	D1238	24.0	2.0
tensile strength at break, MPa[c]	D638	8.3	11.7
tensile strength at yield, %	D638	1800	1500
elongation at yield, %	D638	13	16
1% secant modulus, MPa[c]	D790	297	255
2% secant modulus, MPa[c]	D790	221	235
Vicat softening point, °C	D1525	88	85
hardness, Shore D	D2280	55	48
low temperature brittleness F_{50}, °C	D746	−39	−70

[a] Data on Petrothene® H-2324 and Petrothene® NA 820-000, courtesy of Equistar Chemicals, LP.

[b] All molded properties use compression molded samples.

[c] To convert MPa to psi, multiply by 145.

Table 19. **Low Density Resin for Blow Molding**[a]

Typical properties	ASTM test method	LDPE homopolymer resins	
		NA 940	NA 820
ASTM Type, Class, Category	D1248	I, A, 5	I, A, 3
density, g/cm^3	D1505	0.918	0.918
melt index, g/10 min	D1238	0.25	2.0
tensile strength at break, MPa[b]	D638	14.4	9.7
elongation at break, %	D638	>600	>600
flexural modulus, MPa	D790	235	228
low temperature brittleness F_{50}, °C	D746	< -76	< -76
Vicat softening point, °C	D1525	90	88
hardness, Shore D	D2240	50	48
FDA status		21 CFR 177.1520	21 CFR 177.1520
key properties		good clarity, excellent toughness, fair processability	good clarity, fair toughness, good processability
applications		flexible containers, squeeze bottles, toys	flexible containers, squeeze bottles, toys

[a] Data on Petrothene NA 940 and Petrothene NA 820 courtesy of Equistar Chemicals, LP.

[b] To convert MPa to psi, multiply by 145.

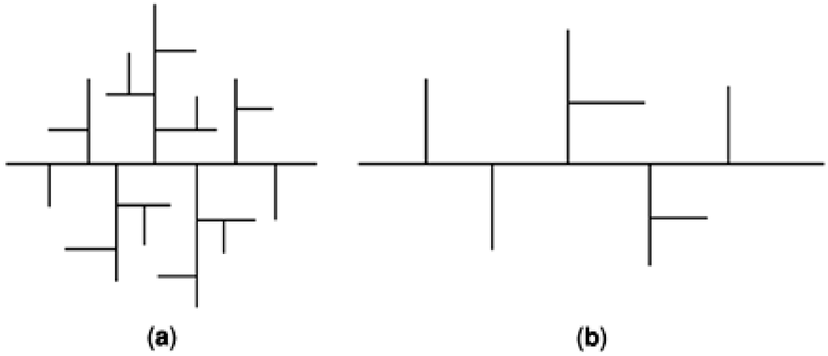

Fig. 1. Long-chain branching in fractions with M_n 200,000 from polyethylenes with melt index 1.7 and density 0.918–0.919 g/cm^3: (**a**) autoclave product with 20 long branches; (**b**) tubular product with 7 long branches. Short-chain branches are not shown.

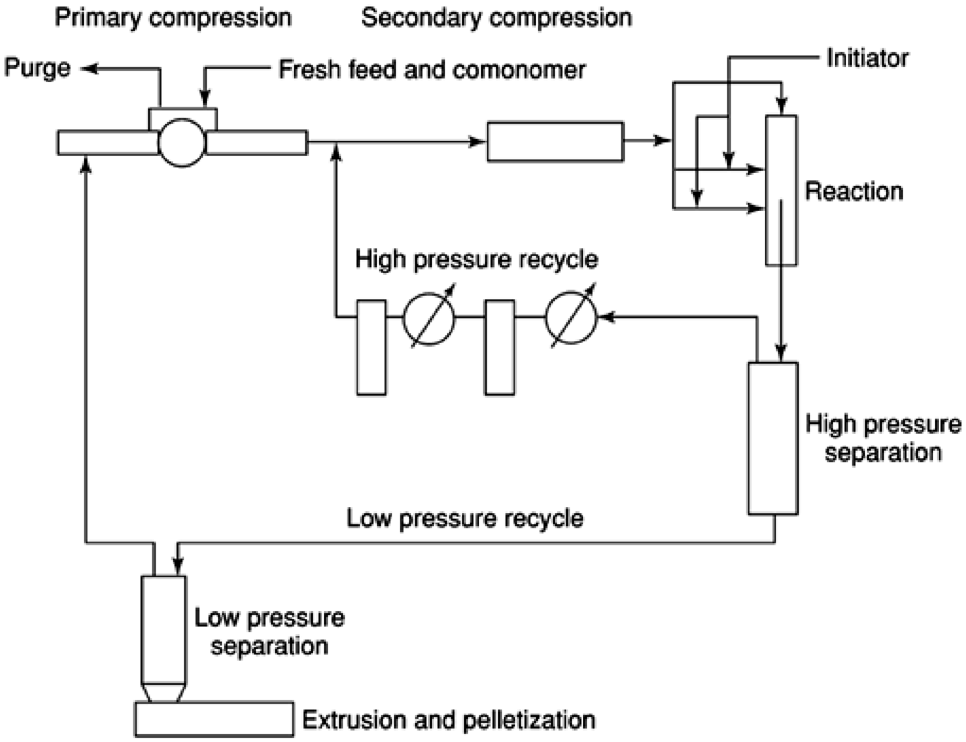

Fig. 2. Autoclave reaction process and recycle system.

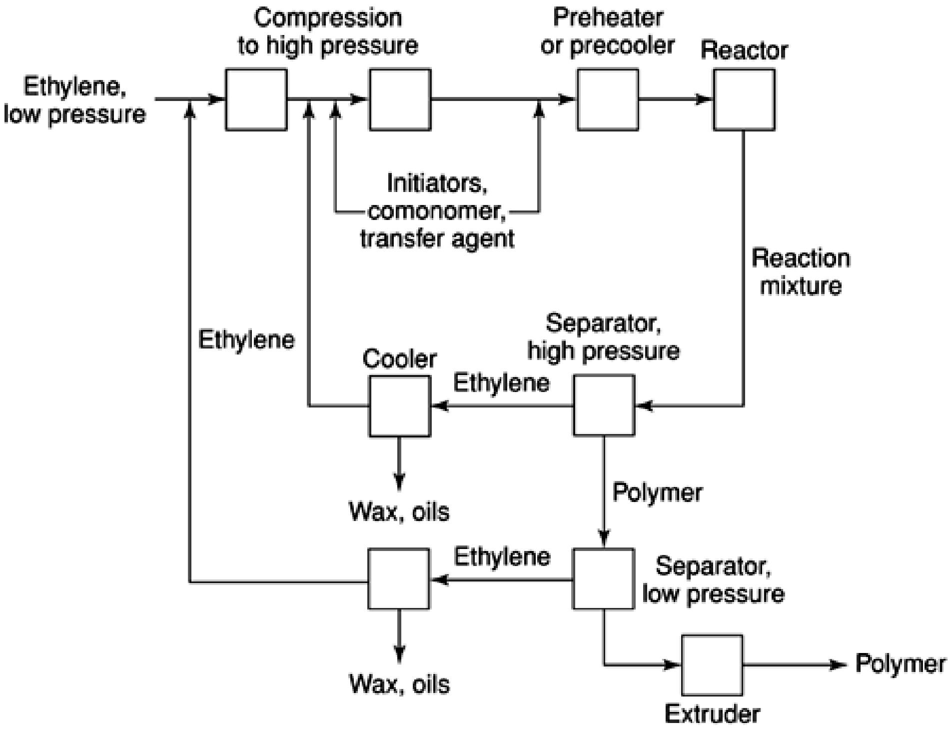

Fig. 3. Tubular reaction process.

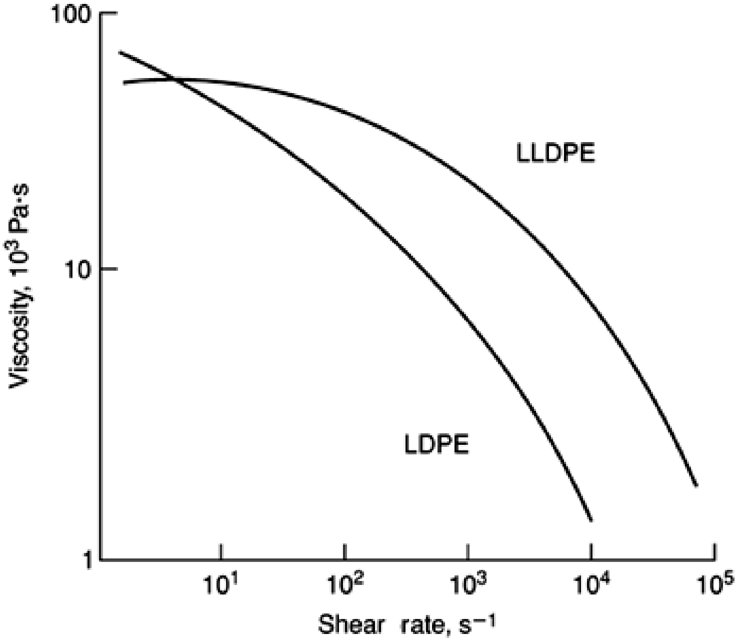

Fig. 4. Viscosity behavior under shear for LDPE and LLDPE.

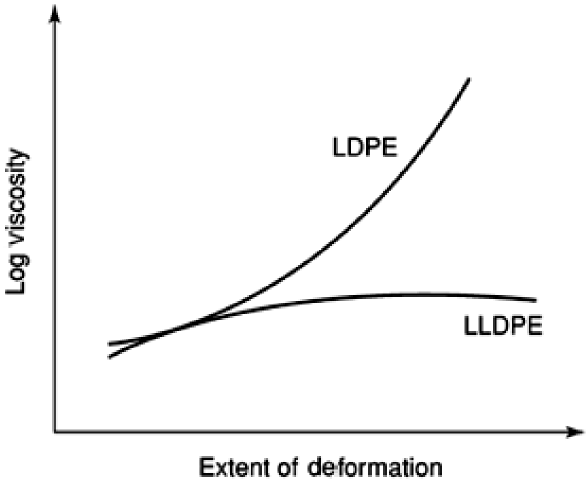

Fig. 5. Viscosity behavior under extension for LDPE and LLDPE.

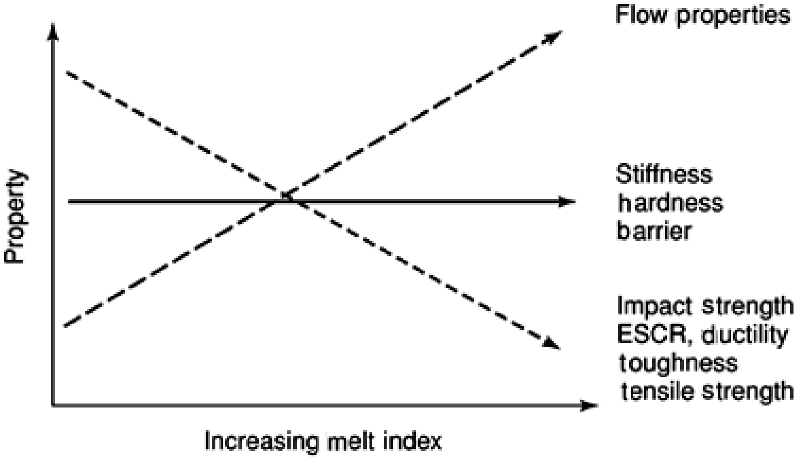

Fig. 6. Effect of molecular weight on LDPE properties.

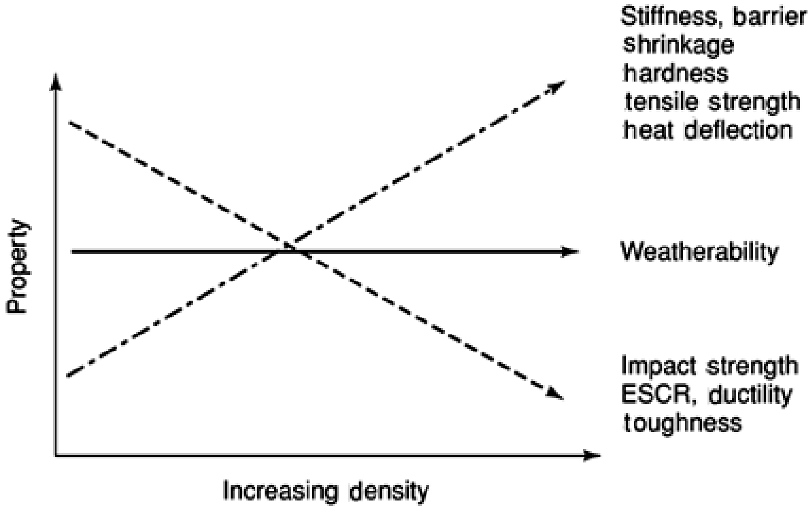

Fig. 7. Effect of density on LDPE properties.