

Book 1: Chapter 3 - Polyethylene Material Fundamentals

From the 1941 discovery of low-density polyethylene, through the first production in 1957 of high-density polyethylene using a low-pressure process, polyethylene has developed into a diverse family of materials for packaging, wire and cable jacketing, piping and other applications. Each use demands dedicated polymer engineering to obtain the balance of properties necessary for the application.

Polyethylene materials are engineered for the requirements of the application. Packaging materials are engineered for easy processing, but not for long-term stress. Wire and cable materials are engineered for high electrical and thermal properties. Piping materials must withstand decades of stress and strain from internal pressure, earthloads, and other adverse environmental conditions.

Both short term and long term physical property tests are used to characterize how an “engineered-for-application” polyethylene material may be expected to perform in use. For temporary-use applications like packaging, short-term tests are usually sufficient, but for demanding, long-term applications such as pipe, tests that accurately evaluate long-term property characteristics are essential.

Polymerization

To a large degree, the molecular structure of polyethylene determines its suitability as a piping material. Polyethylene is made by the polymerization of the ethylene monomer, generally with the addition of another alpha-olefin co-monomer such as propylene, butene, hexene, etc. For piping applications, thousands of monomeric units are combined to form polyethylene.

If the ethylene monomer were used exclusively, you would “grow” a very linear polyethylene homopolymer. However, as higher alpha-olefin co-monomers are introduced, the monomer chain lengthens by their inclusion, and short chain or side chain branching occurs. Overall however, co-polymer polyethylene is still considered a linear polymer. See Figure 3-1.

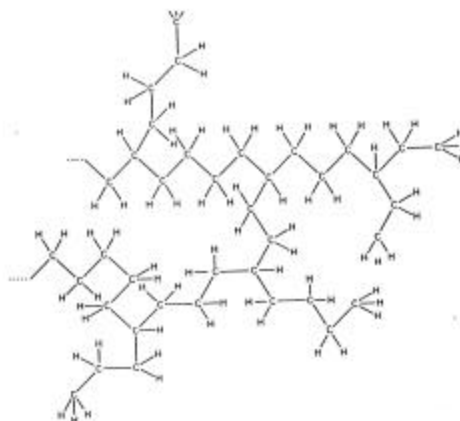
Co-polymer polyethylene materials used for piping are prepared by the polymerization of no less than 85% ethylene, and no less than 95% of total olefins (up to 10% higher alpha-olefin co-monomers) with additional compounding ingredients.

The polymerization reaction process utilizes highly sophisticated catalyst systems that initiate polymerization and propagate the reaction. Resin manufacturers utilize proprietary catalyst technology and specialized reaction processes to control polymer processing. Polymers are engineered for various end uses with catalysts, and combinations of monomer and co-monomer units. Key control indicators for the polymerization process are density, and melt flow rates at several conditions.

Fundamental Characteristics

In the broadest sense, polyethylene resin properties are determined largely by three

Figure 3-1 Branched Polyethylene Molecule



fundamental characteristics: crystallinity (density), molecular weight, and molecular weight distribution.

Crystallinity (Density)

In the solid phase, polyethylene is characterized as a semi-crystalline polymer, that is, it has both crystalline and amorphous regions. Crystalline regions are dense, ordered regions where the molecules are in a regular, ordered structure. Amorphous regions are less dense areas of irregular, random molecular entanglement.

As molten polyethylene cools, nuclei form, and spherulitic crystals of folded molecule chains begin to grow. When a side chain branch is reached, the branch may be accommodated within the fold, or it may disrupt crystal formation and end up in the amorphous region surrounding the crystal, or it may cross over into another crystalline structure. See Figure 3-2.

The density of solid polyethylene resin is dependent upon the rate of cooling from the molten state. Quickly quenched materials have lower density because crystalline structure has had less time to form and grow. Slow cooling from the melt phase allows more time for crystallization, so density is higher. Heavily branched materials have lower density because branching disrupts the crystallization process. Standardized tests that use a specified cooling procedure are used to determine resin density. When polyethylene is re-melted then re-solidified, the density of the re-solidified material may vary from the original resin density if the cooling rate is different.

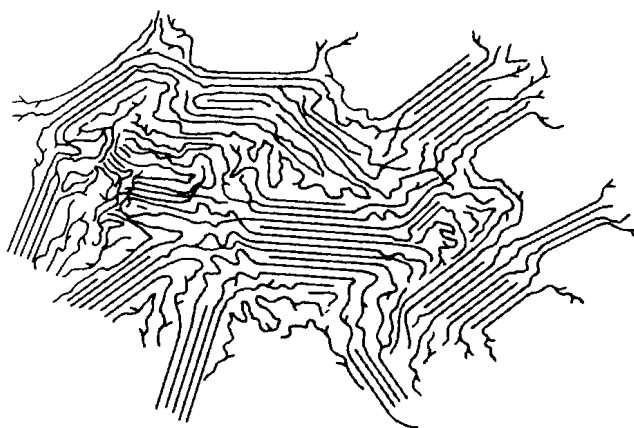
Medium density polyethylene pipe resins typically have average base (unpigmented) resin densities from 0.937 gm/cm³ to 0.940 gm/cm³. High-density pipe resins have densities of 0.941 gm/cm³ and above.

Pigmentation Effects on Density

Pigments and other additives are compounded into polyethylene pipe resins for various reasons; however, these ingredients are a very small percentage of the overall pipe compound. When pigments are compounded into the base resin, the overall density may increase slightly. However, the physical properties of the pigmented compound are set predominantly by the physical properties of the base resin.

Pigmentation may be a color, or inert ingredients such as titanium dioxide or carbon black. In the case of carbon black, density is increased by 0.0044 gm/cm³ per percent carbon. For example, a 0.945 gm/cm³ high-density base resin that is compounded with 2.5% carbon black will have a pigmented density of 0.956 gm/cm³. Although the carbon black has increased the overall density of the compound, the physical properties are still those of the 0.945 gm/cm³ base resin. ASTM D 1505 is a standard for resin density measurement.

Figure 3-2 Crystalline and Amorphous Structure



Molecular Weight

When polymerized, the polyethylene molecule is a linear chain of carbon-carbon single bonds, flanked by hydrogen. See Figure 3-1. The numbers of monomer and comonomer units joined together determine molecular weight in the polyethylene molecule. The molecular weight of each “mer” unit, C_2H_2 , is 26, so a polyethylene molecule with an average molecular weight of 260,000 has 10,000 mer units in the molecule chain.

Analytical methods that directly determine molecular weight include solution viscosity, size exclusion chromatography (SEC), and gel permeation chromatography (GPC). These sophisticated procedures usually involve running a molten resin solution through a series of columns to determine molecular weight.

In the melt state, higher molecular weight materials usually flow less readily than lower molecular weight materials; thus, melt flow rate may provide an indirect reference — *not a direct measure* — of molecular weight. Melt flow rate is significantly affected by the polymerization process, by catalyst technology, by side chain branching, by co-polymer material, and by molecular weight distribution. *Among different polyethylenes, it is incorrect to infer performance relationships on the basis of melt flow rate.*

Melt flow rate is used to compare a sample of a material against specifications for that same material. Melt flow rate is determined using ASTM D 1238. Under set temperature and load conditions, the mass of material extruded through a calibrated orifice in a set time is the melt flow rate of the material.

Per ASTM D 1238, polyethylene melt flow rate is usually tested at 190° C, and under loads of 2.16 kg (melt index, MI), and 21.6 kg (high load melt index, HLMI). Loads of 5 kg, 10 kg, and 15 kg are also used.

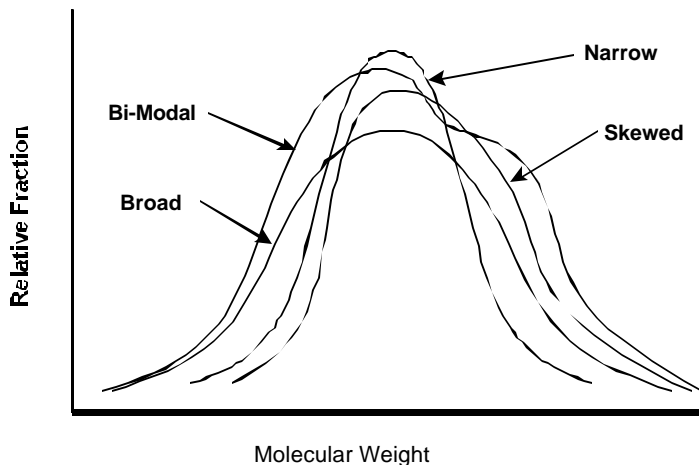
Many properties improve with increasing molecular weight; however the processability of the melted material decreases with increasing molecular weight. Melt processing is important for polyethylene piping materials in extrusion and molding, and in heat fusion joining. Successful medium density and high-density polyethylene piping materials generally have MI's in the range of 0.04 to 0.20 gm/10 min.

Molecular Weight Distribution

During the polymerization process, molecules of different lengths, or weights, will be produced. Molecules will begin to grow at different times during polymerization, so there will be molecules of various lengths when polymerization is completed. Molecular weight distribution denotes the statistical distribution of molecule weights in a material. Molecular weight distributions may be narrow, broad, skewed, or poly-modal.

When molecule weights are

Figure 3-3 Molecular Weight Distribution and Modality



closely grouped around a common (average) molecule weight, the distribution is termed narrow. A greater dispersion of weights around the average indicates a broader distribution. A skewed distribution is an unequal distribution of heavier or lighter molecules to either side of the average. See Figure 3-3.

Modality is an indication that there is more than one concentration of molecular weights in the distribution. Materials with two concentrations are bi-modal, and those with multiple concentrations are multi-modal or poly-modal.

The polymerization process and the catalysts used determine molecular weight distribution. Different polymerization processes and catalysts will produce materials with different melt flow rates, different distributions, and different physical property values. Different materials may have the same average molecular weights, but very different molecular weight distributions.

Between polyethylene materials of like molecular weight, the broad molecular weight distribution material will have a higher melt flow rate compared to the same material with narrow molecular weight distribution.

Understanding Property-Characteristic Interrelationships

Polyethylene piping is specially engineered for piping applications. Reviewing how changes in crystallinity, molecular weight, and molecular weight distribution affect material physical properties can provide a general understanding of how polyethylene piping materials are engineered to provide the necessary balance of strength, toughness, and long-term performance.

A Discussion of Table 3-1

Table 3-1 illustrates some general interrelationships among the fundamental characteristics of polyethylene and the typical effect on physical properties when a fundamental characteristic is changed. Table 3-1 assumes a single, basic polyethylene material having a given crystallinity, molecular weight, and molecular weight distribution. The columns below the fundamental property indicate the relative effect (increase, decrease, or no change) on the physical property when the fundamental property is changed as indicated.

The effects of change are indicated across the rows from left to right, that is, take the base material, and increase its density; take the increased density material and increase its molecular weight; and then take that same material and broaden its molecular weight distribution.

Table 3-1 illustrates that when density is increased, stiffness, hardness, tensile strength and chemical resistance all increase. Increases in these properties are usually considered beneficial for pipe, but increasing density also has a downside. By increasing density, the material becomes less ductile, more sensitive to impact, and more sensitive to cracking under long term stress — generally things that are not so good for pipe.

In the next column, the molecular weight of the higher density material is increased. This offsets some of the negatives that came along with increased density. Impact strength, low temperature toughness, and resistance to cracking from long term stress are all improved by increasing molecular weight. The downside of increased molecular weight is reduced melt processability (melt flow rate), which is important in product manufacture and in heat fusion joining.

Melt processability is improved by broadening the molecular weight distribution. Resistance to slow crack growth — that is, long-term performance — is also improved.

Table 3-1 generally illustrates that successful polyethylene piping materials are the result of an

engineered balance of density, molecular weight, and molecular weight distribution so that strength, toughness, long-term performance, and the ability to manufacture, join, and install are optimized.

Table 3-1 is intended only as a general illustration of influences and interrelationships. Some polyethylene materials may have interactions among properties and characteristics that may deviate significantly from the Table 3-1 illustration.

In particular, different polymerization reaction processes, catalysts, and co-monomers will produce different polymers. Polyethylene made using one polymerization process, or set of catalysts, or co-monomer should not be directly compared to materials made using different processes, catalysts, or co-monomers. Polymerization processes and catalyst technologies can impart distinctive characteristics to the material that may enhance or diminish a property or characteristic, and how it interacts with another. Table 3-1 does not address the possible effects of different polymerization processes, catalyst technologies, or co-monomers on materials.

Table 3-1 Physical Property Changes due to Fundamental Characteristic Changes

<i>Material Property</i>	<i>Fundamental Characteristic (change)</i>		
	<i>Crystallinity (increase)</i>	<i>Molecular Weight (increase)</i>	<i>Molecular Weight Distribution (broaden)</i>
<i>Stiffness</i>	Increases	–	–
<i>Tensile Strength at Yield</i>	Increases	–	–
<i>Tensile Strength at Break</i>	Increases	Increases, then levels off	–
<i>Tensile Elongation at Break (Ductility)</i>	Decreases	–	–
<i>Softening Temperature</i>	Increases	Increases	Increases
<i>Impact Strength</i>	Decreases	Increases, then levels off	–
<i>Low Temperature Toughness</i>	Decreases	Increases	Increases
<i>Permeation Resistance</i>	Increases	–	–
<i>Chemical Resistance</i>	Increases	–	–
<i>Resistance to Slow Crack Growth</i>	Decreases	Increases	Increases
<i>Weatherability</i>	–	Increases	–
<i>Melt Flow Rate Processability</i>	–	Decreases	Increases
<i>Hardness</i>	Increases	–	–

Interrelationships among characteristics and properties may alter these effects. See the text discussions.

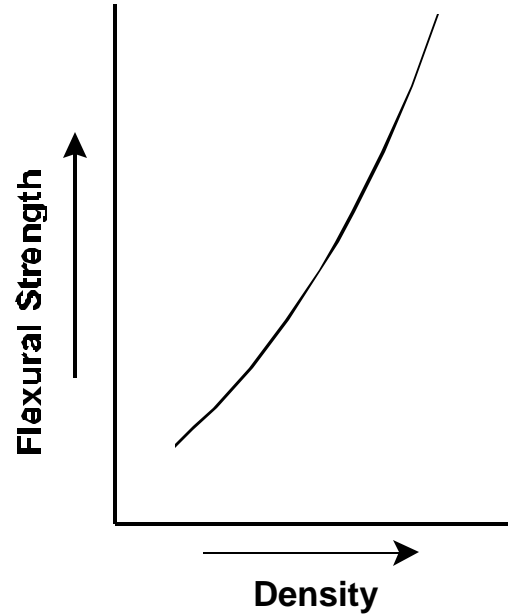
Graphical Illustrations of Interrelationships

The following figures further illustrate some interrelationships among various physical properties and fundamental characteristics. For all of the figures, the relationships are for polyethylene base resin (unpigmented) as typically used in compound formulations for piping applications.

Stiffness

Stiffness increases directly with increasing crystallinity (increasing density). See Figure 3-4.

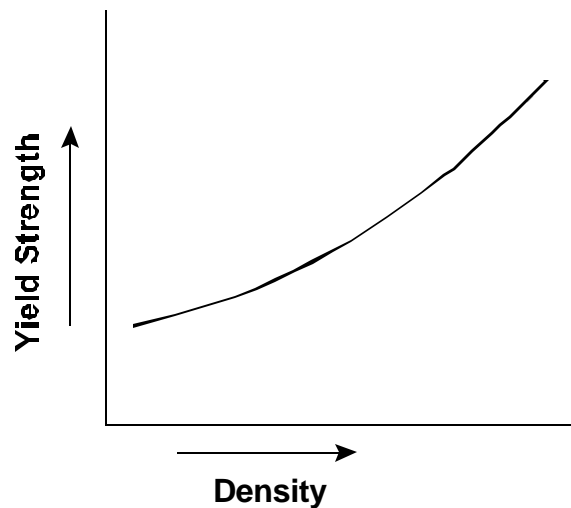
Figure 3-4 Stiffness



Tensile Strength, Impact & Melt Viscosity

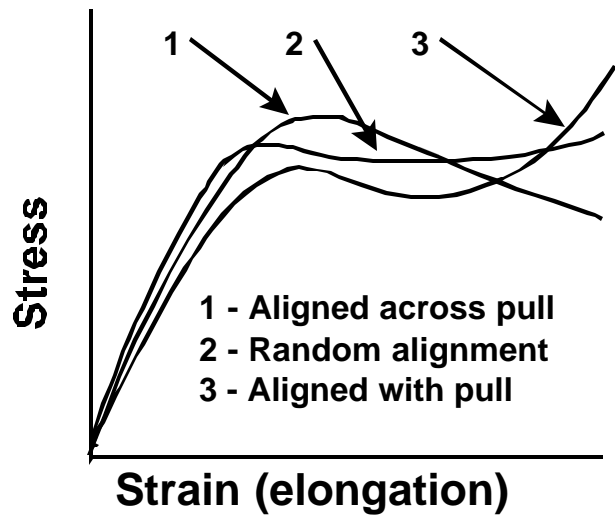
Tensile yield strength increases directly with increasing density (crystallinity), and increases then levels off with increasing molecular weight. See Figure 3-5.

Figure 3-5 Yield Strength



Tensile yield, break, and elongation are affected by specimen preparation and molecular orientation. Slow cooling maximizes density and yield strength, and minimizes elongation at break. Break strength is typically higher than yield strength when molecules are aligned with the strain (tensile pull) direction; break is lower than yield when alignment is across the strain direction. When there is little or no molecular orientation, break and yield strengths are about the same. See Figure 3-6.

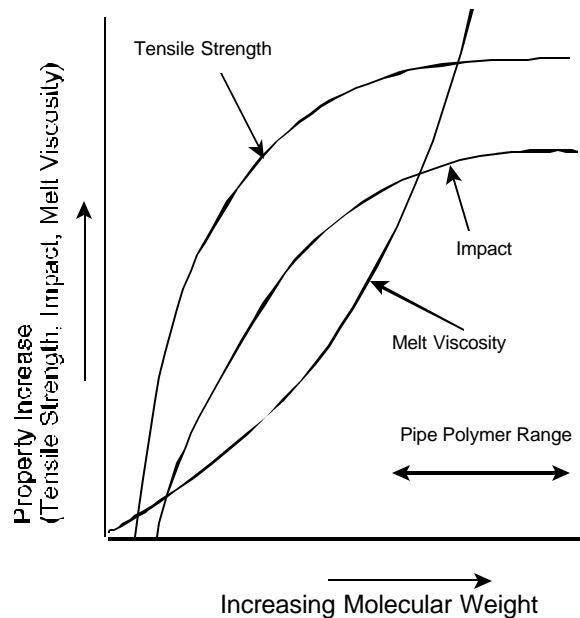
Figure 3-6 Tensile Strength vs. Molecular Orientation



Impact resistance decreases with increasing density, increases then levels off with increasing molecular weight, and increases with broadening molecular weight, but to a lesser extent.

Melt viscosity is the inverse of melt flow rate; that is, higher viscosity results in a lower melt flow rate. Melt viscosity increases (melt flow rate decreases) with increasing molecular weight. Melt viscosity decreases (melt flow rate increases) with broadening molecular weight distribution. See Figure 3-7.

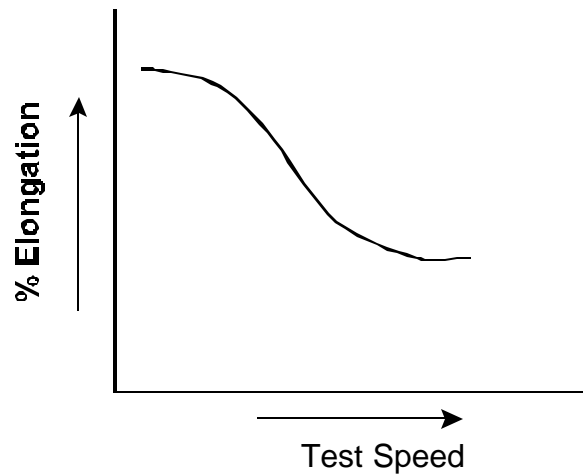
Figure 3-7 Property Change vs. Molecular Weight



Tensile Elongation

Tensile elongation is inversely related to density, and is sensitive to strain rate (pulling speed). At a set strain rate, tensile elongation decreases with increasing density. For a given density, tensile elongation is reduced at higher pulling speeds (higher strain rates). See Figure 3-8.

Figure 3-8 Tensile Elongation vs. Pulling Speed



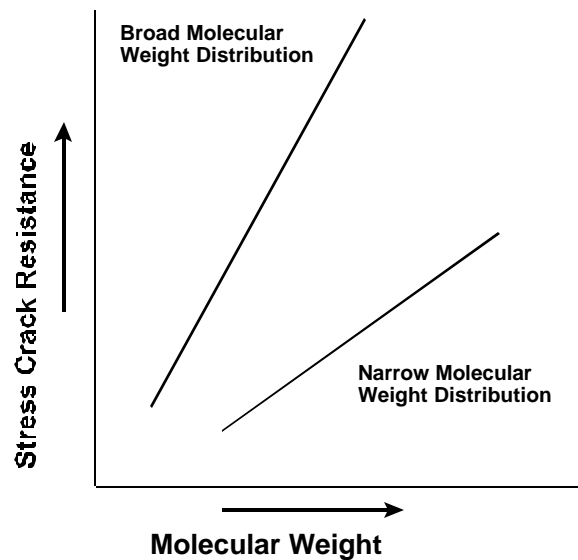
Resistance to Slow Crack Growth

Polyethylene piping is generally intended for long-term service where resistance to failure from long-term stress and strain is required. Tests that simulate conditions of long-term stress or strain show that materials typically fail from cracks that initiate on the surface, then grow slowly through the pipe wall, that is, slow crack growth (SCG). Polyethylene piping materials are engineered for superior resistance to SCG failure.

Early SCG tests typically involved subjecting a specimen to a constant deformation, in an aggressive chemical at an elevated temperature. However, under these early environmental stress crack resistance (ESCR) tests, modern polyethylene piping materials commonly resist cracking failure almost indefinitely.

The newer generations of SCG tests introduce a sharp notch initiation site, and at elevated temperature, apply a tensile load across the notch. The testing conditions for notch, load, and elevated temperature are designed using fracture mechanics principles so that in a few days of laboratory testing, a representative indication of tens of years of field service may be obtained. Resistance to SCG failure decreases with increasing density, increases with higher molecular weight, and increases with broader molecular weight distribution. See Figure 3-9.

Figure 3-9 Resistance to Slow Crack Growth



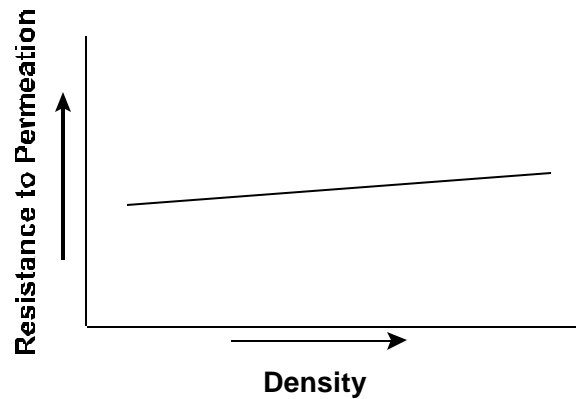
Permeation

The rate of permeation or activated diffusion of gasses is dependent upon polyethylene density (crystallinity) and the molecular weight of the permeating gas. Permeation by solvating chemicals (such as liquid hydrocarbons) is generally greater at elevated temperatures, and when chemical concentrations are higher.

In most circumstances, permeating (solvating) chemicals do not physically injure the polyethylene material. Gasses diffuse very slowly through the pipe wall, resulting in a slight loss of gas from within the pipe. The volume of gas that may permeate through polyethylene pipe is low. For example, methane permeation through a mile of DR 11 pipe at 60 psi is as low as 0.27 ft³ per day.

Caution — Solvating liquids will permeate the pipe wall, which may reduce long-term strength, and may preclude the use of heat fusion joining.

Figure 3-10 Resistance to Permeation



Hardness

Hardness is tested against the Shore D scale using a spring-loaded penetrometer. The procedure is similar to hardness testing of metals, although plastics are generally much softer than metals.

Figure 3-11 Hardness

