

Cycletime Tips – General

Volume 36: High Density Polyethylene

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INTRODUCTION

HIGH DENSITY POLYETHYLENE

Polymer science has made tremendous strides in the last century. From the earliest attempts at synthetic reproduction of natural fibers and rubber to the most technically advanced engineering plastics today, scientists worldwide endeavor to make advancements in stronger, more versatile polymers. Polyethylene is one such polymer whose versatility is proven by thousands of uses and by its position as the largest thermoplastic resin produced by volume, just over 30 billion pounds per year. The subject of this article is High Density Polyethylene (HDPE) whose phenomenal growth proves its versatility.

POLYMER DESIGN CONSIDERATIONS

HDPE is primarily produced today by four processes: slurry reactor with titanium-based catalyst; slurry loop with chromium-based catalyst; gas phase with titanium-based catalyst; and, solution phase with a vanadium-based catalyst. Resin manufacturers can produce a wide variety of HDPE resins. Density, molecular weight, and molecular weight distribution are the three most important characteristics of HDPE resins and they determine the processability and end-use performance characteristics of items made from HDPE.

DENSITY

Density is primarily controlled by the amount of comonomer. High density polyethylene resins typically vary in density from .940 g/cm³ to about .965 g/cm³. HDPE is referred to as a homopolymer if the density is .960 or above while copolymers have densities less than .960. The typical alpha olefins used as comonomers are butene, hexene, and octene. The comonomer used depends upon the polymerization process used and the desired end-use performance characteristics of the resin. Hexene and octene copolymers are reported to be “tougher”; however, butene copolymers are typically less expensive. The design of the catalyst can provide a polymer molecule with controlled side branching allowing the molecules to arrange themselves into compact, crystalline regions. The greater number of crystalline regions, balanced with areas that are characterized by a more random (or amorphous) orientation of molecules, are what differentiate HDPE from its lower density cousins. High density polyethylene may have up to five side branches per thousand carbon atoms (compared to 20 or more for LDPE) allowing for very close alignment of the main chains of adjacent molecules and thus crystallite formation. The highly crystalline nature of HDPE is responsible for its high density and stiffness as well as relative opacity. Stiffness is an important attribute of HDPE allowing parts to be made with thinner walls and thus, offer material savings. Other important properties of HDPE are affected by density as well (see Table 2, page 2).

MOLECULAR WEIGHT

Molecular weight is technically the weight of one mole of molecules but it is also a term that generally indicates the size or length of the molecule. In very general terms, as molecular weight increases, strength increases. On the other hand, processability can become more challenging as molecular weight increases due to the increased viscosity of the resin. HDPE resins are produced in four major molecular weight classes: Low (inj. molding, etc), Medium (blowmolding, film, pipe, sheet, etc), High (large part blowmolding, high-strength thin films, pipe, sheet, etc), and Extra High Molecular Weight (large part blowmolding, pipe, etc). Each class has distinct and appropriate uses for which your General Polymer Sales or Tech Rep. will be happy to provide additional information. The melt index test data can be used to roughly approximate molecular weight, viscosity, and processability of polyethylene resins. For example, a high melt index generally means lower molecular weight and easy flow (low viscosity) while a low melt index means higher molecular weight and stiffer flow (high viscosity). Please see Table 2, page 2, for important properties affected by molecular weight.

Much confusion can exist with the use of such terms as “frac” melt and “HLMI” resins. The term “frac melt” or “fractional melt” resins means that the melt index value is less than 1.0 g/10 minutes using ASTM 1238 Condition E (2.16 kg load). The term “HLMI” (high load melt index) refers to those resins that should properly be called High Molecular Weight resins -- resins with an HLMI of less than 15 g/10 min using ASTM D1238, Cond. F (21.6 kg load). In other words, there are “frac” melt HDPE resins that are called “HLMI” resins but are not true HMW-HDPE resins. For example, a 0.9 melt HDPE is a “frac” melt yet the HLMI (high load melt index) could be as high

as 20-25 g/10 min. Confused? Table 1 below helps by organizing the melt index classifications and their general relationship to molecular weight.

Table 1:
Molecular Weight and Melt Index

Category	# of Carbons	Molecular Weight	MI 2.16 "melt index"	MI-21.6 "HLMI"
Low Molecular Weight	75 - 7,500	1,000 - 100,000	10 - 100	not typically measured
Medium Mol. Weight	7,500 - 12,000	100,000 - 180,000	0.6 - 10	15 - 50
High Molecular Weight	18,000 - 56,000	250,000 - 750,000	0.06 - 0.15	7 - 15
Extra High Mol. Weight	56,000 - 120,000	750,000 - 1,500,000	not typically measured	2 - 7

MOLECULAR WEIGHT DISTRIBUTION

Due to the high viscosity of higher molecular weight resins, molecular weight distribution becomes a very important consideration in the processability of HDPE especially in HMW-HDPE. Resin suppliers today can vary the molecular weight distribution (MWD) by process, catalyst, and plant design. Some plastic processing techniques such as injection molding and oriented monofilaments and tapes may benefit by being produced from resins with narrow molecular weight distributions. Other processes such as blown film, pipe, and blowmolded items may benefit from a broad to very broad distribution. While narrow distribution resins are tougher than broad distribution resins (at equivalent molecular weight), processability becomes easier as the distribution broadens. Recent advancements in polymerization technology have made available HDPE resins with a broad, bi-modal MWD. These resins are touted as being easier to process and tougher than broad, unimodal resins. Table 2 below illustrates the effect that MWD has on processability and important physical properties of end products.

In closing...

Future articles from your BRE Tech Service Team will focus on the specific processes of **Blowmolding**, **Rotational molding**, and **Extrusion** of many polymer types. We hope that our customers will benefit from this and future Tech Tips and that they will create the basis for fruitful discussions both in-plant and with end-users. As always, the General Polymers BRE Sales and Tech Service Team will be there to help you, our valued customer and partner.

Table 2:
Effect of Density, Melt Index and Molecular Wt. On Polyethylene

Property	As Density Increases Property	As Melt Index Increases Property	As Mol. Wt. Distribution Broadens Property
Tensile Strength @ Yield	INCREASES	DECREASES	_____
Stiffness	INCREASES	DECREASES SLIGHTLY	DECREASES SLIGHTLY
Impact Strength	DECREASES	DECREASES	DECREASES
Low Temp Brittleness	GETS WORSE	GETS WORSE	GETS WORSE
Abrasion Resistance	INCREASES	DECREASES	_____
Hardness	INCREASES	DECREASES SLIGHTLY	_____
Softening Point	INCREASES	_____	DECREASES
Stress Crack Resistance	DECREASES	DECREASES	INCREASES
Permeability	DECREASES	INCREASES SLIGHTLY	_____
Chemical Resistance	INCREASES	DECREASES	_____
Melt Strength	_____	DECREASES	INCREASES
Gloss	INCREASES	INCREASES	DECREASES
Haze	DECREASES	DECREASES	_____
Shrinkage	INCREASES	DECREASES	INCREASES
Processability	_____	INCREASES	INCREASES