

MAKING SENSE OUT OF PE NOMENCLATURE

By R. N. Shroff
Senior Research Scientist
Chemplex Company
and
L. V. Cancio *

* Formerly with Chemplex

Reprinted from



September 1977

HDPE...UHMWPE...HMWPE...

Understanding PE Nomenclature

Having trouble differentiating among high-molecular-weight PE resins and anticipating differences that their molecular weights may cause in blow molding? The authors clarify terminology and discuss how you can predict processing behavior from molecular-weight values.

By R. N. Shroff, Senior Research Scientist, Chemplex Co., Rolling Meadows, Ill., and L. V. Cancio, Clopay Corp., Cincinnati.^a

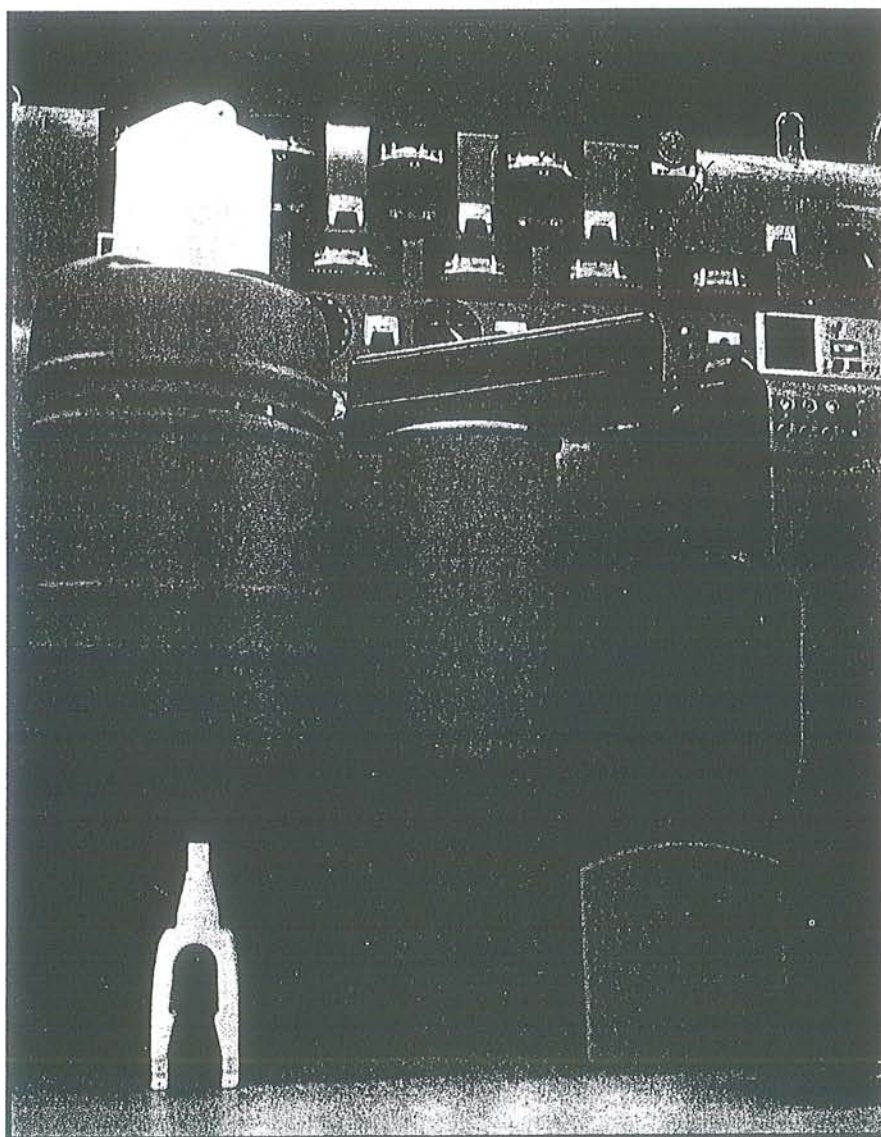
The advent of above-normal molecular weight resins in recent years (and the markets they are opening up) has been of immense interest to many processors; however, a number of questions are frequently being asked.

How high is "high"? What's the difference between high-molecular-weight (HMW) and ultra-high-molecular-weight (UHMW)? What, precisely, is the MW of this or that resin? Some of these questions have simple answers, others not so simple. A little in-depth study of what these characterizing values really mean can shed some needed light on the whole subject.

Defining molecular weight Unlike density and melt-index values that are always provided for every commercial HDPE, molecular weight is seldom stated. Why not, since it is an important property?

The reasons are best understood by first taking a look at the nature of density and MI measurements. Both are direct evaluations of specific properties, readily performed with relatively simple equipment. There is a high degree of confidence that results obtained by several analysts will differ by no more than a small experimental error.

A molecular-weight determination is another matter altogether. First, there is no such thing as the MW of a resin.



HDPE, like many other plastics, is not made up of molecules of the same MW, but of a collection of molecules of many different MW's. A plot of weight fraction (the fraction of the total number of molecules) vs. the logarithm of MW would give a curve similar to that in Fig. 1. There will be many molecules clustered around a central point, with fewer and fewer molecules present as

the distance from the central point increases.

So, at best, an average MW value can be stated, but difficulties arise for several reasons:

- There is more than one kind of average MW.
- There is more than one technique by which to measure average MW.
- There is experimental error in-

^aFormerly with Chemplex.

volved in these techniques.

The net result is that there can be confusion in reporting and understanding MW data. It is evident that results obtained in two laboratories using different methods might be so unlike as to appear to describe totally different resins, when in fact the same material was under test.

Setting aside the matter of precision and which test provides the "true" value, what does average MW mean for two HDPE's whose MWD's are as shown in Fig. 2? Here, if all molecules were counted and their weights added up, and this total divided by the number of all molecules, then the two resins could turn out to have identical average MW's. Yet the suspicion would remain that something is amiss—there must be differences in processibility or properties or both.

To clarify such matters, even though further complicating things, several kinds of average MW values have been defined, the most commonly used being number-average molecular weight, M_n , and weight-average molecular weight, M_w .

M_n is the result of simple arithmetical averaging of the weights of all the molecules, as described above, and the value would be the same for the two resins. M_w is determined by more complex calculations (which need not be described here), which give an average MW value that's more influenced by the heavier molecules in the MW distribution. Thus M_w would reflect the greater number of higher MW molecules present in Resin B than in Resin A, would recognize that these heavy molecules have an effect out of proportion to their number, and would calculate a higher M_w for Resin B.

For example, taking a totally fictitious resin consisting of equal numbers of molecules of 50,000 and 100,000 MW, calculation would yield $M_n=75,000$ and $M_w=83,000$.

Taking a second material having equal numbers of molecules of 20,000 and 130,000 MW, then $M_n=75,000$ as before, but $M_w=115,000$.

In the case of the resins shown in Fig. 2, M_n and M_w for Resin A are 19,100 and 170,000, respectively; for Resin B, they are 19,100 and 215,000.

In these examples, as well as in the case of the complex mixtures of molecules that make up real polymers, M_w is always greater in value than M_n . Only when all molecules are of the same size will $M_n=M_w$.

Importance of MW distribution These MW values can be a useful tool to a

polymer scientist investigating reactor conditions or studying new catalysts, but they are difficult to use in any practical way in the field.

For example, in blow molding, low-shear viscosity—desirably high for good melt strength in the parison—is largely a function of M_w . But high-shear viscosity—desirably low for easy processing—is more a function of M_n .

The ratio M_w/M_n can be used to describe the breadth of molecular-weight

distribution, a broad-MWD resin generally having better processibility than a narrow one.

Both M_n and M_w also relate to physical properties. All else being equal (same M_w), a resin with a narrow MWD will provide better physical properties than one with a broad MWD. This runs counter to conditions for good processibility, so compromise is necessary.

Many properties—for example, im-

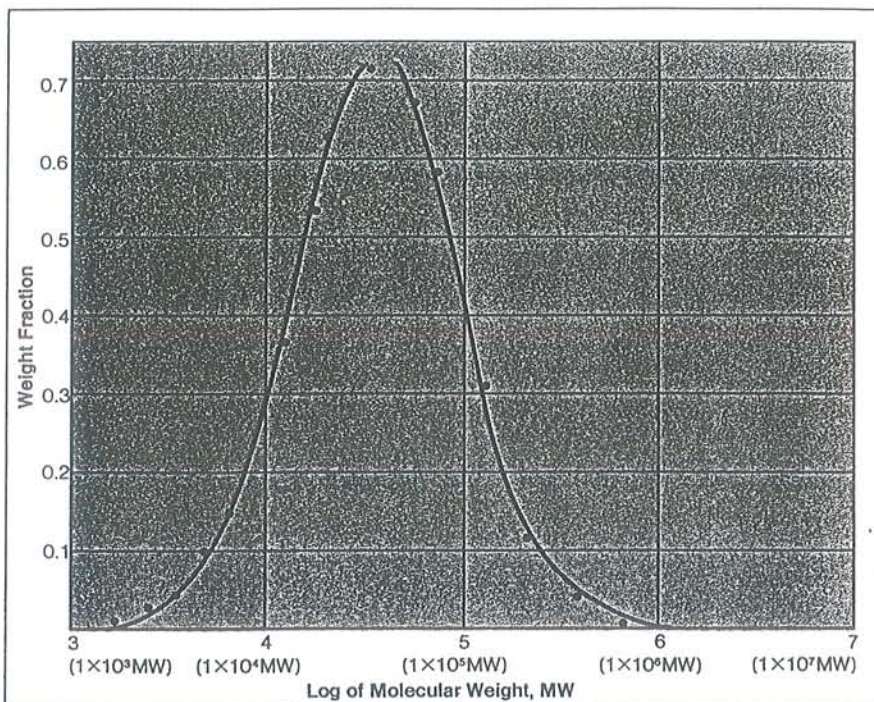


Fig. 1—High-density PE molecules (represented here by points) have many different molecular weights (MW) that are clustered together at a central point, as this plot of weight fraction vs. the logarithm of MW shows.

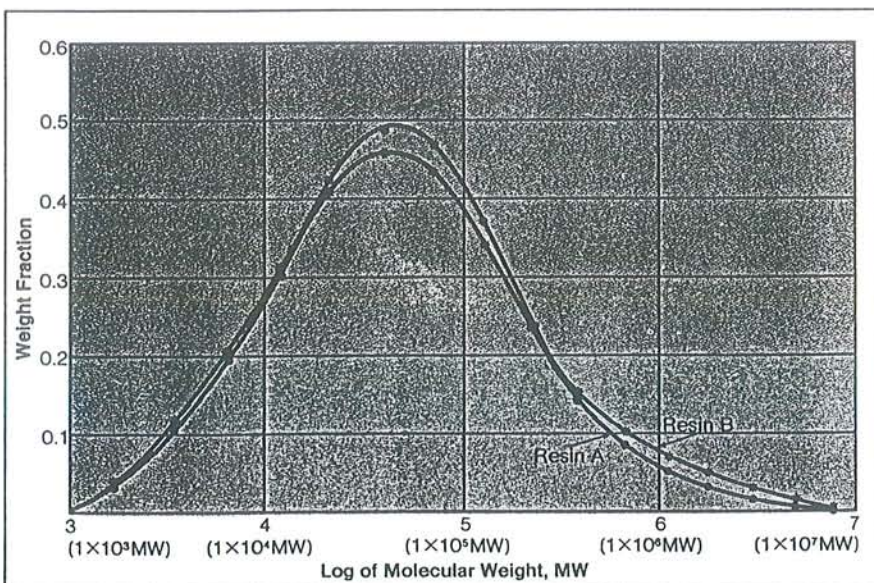


Fig. 2—The molecular-weight-distribution (MWD) curves of two HDPE resins indicate a similar average MW for both materials, but further calculation shows that resin B has the greater amount of higher MW molecules with an effect out of proportion to their number.

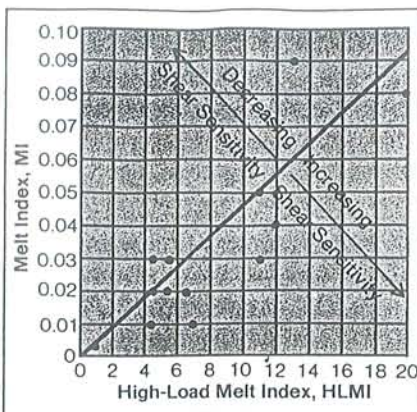


Fig. 3—For a group of high MW resins (points on the graph), a high HLMI indicates good shear sensitivity, while a low MI implies that the resin has a high MW.

compact strength—depend on MW (however defined); in most cases, the property value increases with increasing MW. This is true until very high MW levels are reached, at which point dependence becomes less sensitive, and a plot of property vs. MW (again referring to MW in a general sense) will begin to flatten out.

Melt index is the most commonly accepted indicator of processability for normal-MW PE—higher values normally mean easier processing. Lower values usually mean more difficult processing but better product properties. Again, compromise is needed.

MI also happens to be an indicator—although not a good one—of MW. The lowest MI applicable to normal-MW resins is generally accepted as being 0.1 gm/10 min. Any value below 0.1 designates an HMW PE. This is an arbitrary standard. At this level it is not possible to measure MI under practical conditions, 0.1 gm of extrudate being a very small quantity to take off a die face after a wait of 10 min and measure accurately.

In the MI test, the pressure applied to the melt to force it through a small die orifice is 43.25 psi; in the high-load melt-index (HLMI) test, the pressure is 10 times as great, or 432.5 psi, and is considerably more successful in extruding a weighable sample.

By taking extraordinary precautions, MI values below 0.1 gm/10 min can be secured, although the effort, expense and inaccuracies do not make this viable for routine purposes. MI is plotted against HLMI for a group of HMW resins in Fig. 3.

HLMI is a less useful indicator of MW than MI, but it has a fair value as an indicator of processability—the higher the HLMI, the easier the resin will process.

With MI relating to MW and HLMI to processability, the data in Fig. 3

point up some interesting facts. At a constant MI of 0.03, for example, three resins here have HLMI values ranging from a low of 4.5 to a high of 11. Thus, equal MI by no means suggests equal HLMI nor equal processability.

Conversely, the two resins with an HLMI of 11, suggesting equal processability, have MI values of 0.03 and 0.05, implying considerable difference in MW.

Obviously, MI cannot be used to predict HLMI, nor vice versa. The reason is shear sensitivity. The three resins mentioned above that have an MI of 0.03 will exhibit similar melt-strength characteristics, for example, in the parison, where shear is essentially zero. But exposed to the high shear rates in the extruder, they will perform very differently. The resin with an HLMI of 4.5 has poor shear sensitivity and will require increased power to process. That with an HLMI of 11 has good shear sensitivity, will have low viscosity at high shear rates, and will be an easy-processing resin.

HMW and UHMW—a big difference
Molecular weight-viscosity relationships can be used to clarify the matter

of HMW vs. UHMW and eliminate some confusion which has occurred in the blow molding field.

In Fig. 4, M_w is plotted against intrinsic viscosity (η), the latter being a viscosity measurement made on dilute solutions of PE in a solvent. The correlation is perfect for the simple reason that M_w is calculated from η , using previously established relationships.

While the whole line plots the theoretical M_w - η relationship, only the sections of heavy lines depict the real world of HMW and UHMW PE. Thus, PE can be produced with M_w values from any low level up to a maximum of about 300,000. The normal-MW blow molding resins fall in the range of about 140,000-200,000, corresponding to an MI range of 1.0 down to 0.1. HMW resins then range from about 200,000 to about 300,000, corresponding to an HLMI range of 25 down to 1.0.

As for UHMW resins, these stand well removed from the HMW materials, falling in the range of about 2-million to 6-million M_w . With viscosities many times greater than those of the HMW resins (aptly described in one literature reference as having a

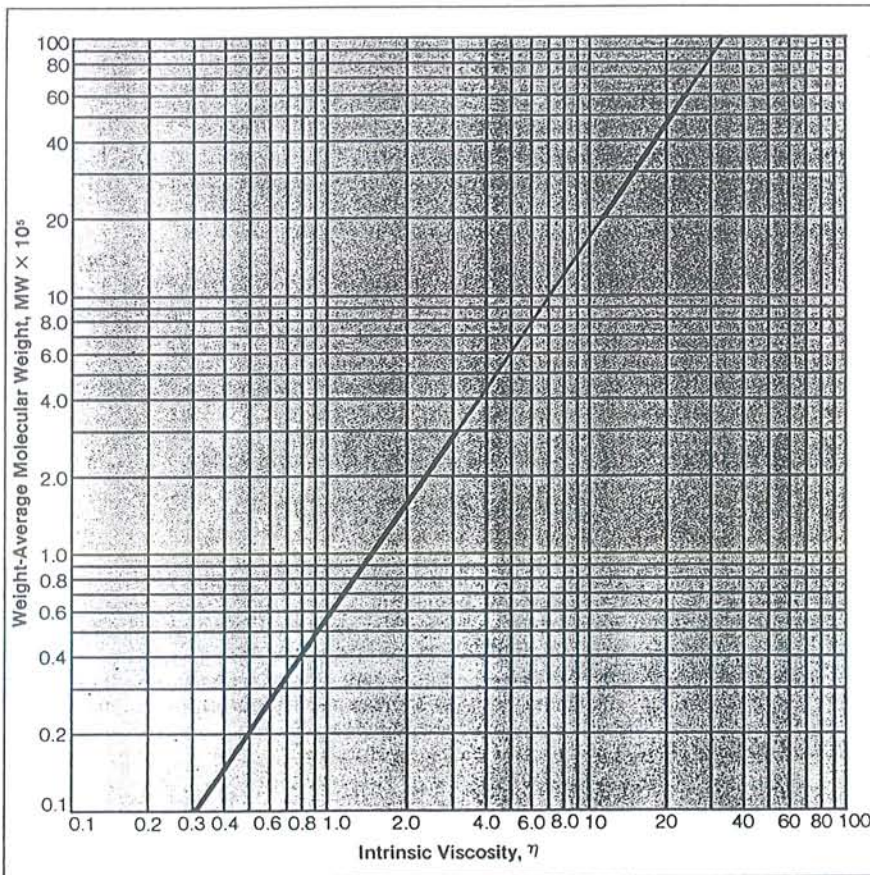


Fig. 4—On a plot of M_w vs. η , the shaded lines indicate the areas where actual PE resins now exist, with increasing MW and viscosity shown by the line as it rises to the right.

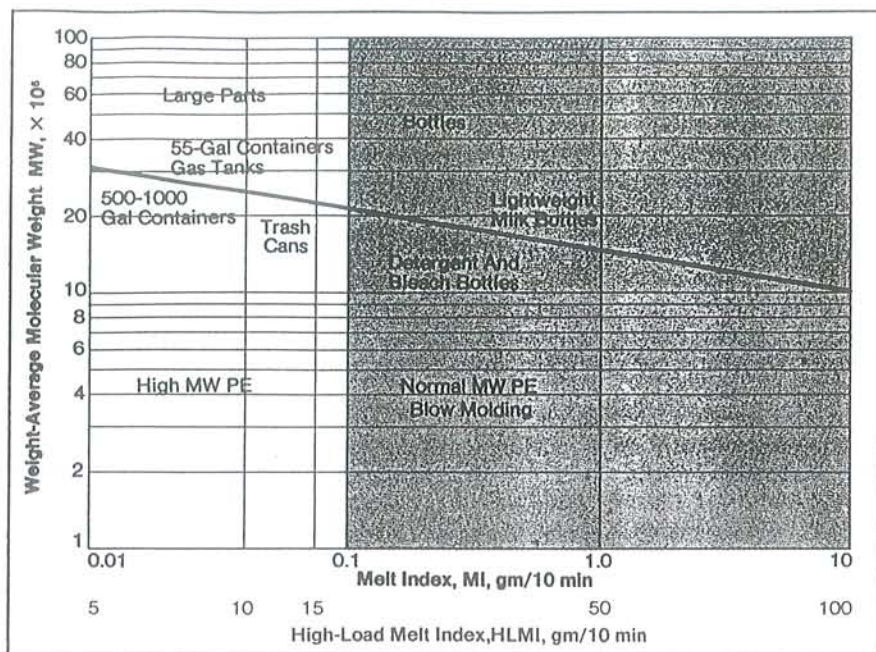


Fig. 5—Using the MW, MI and HLMI of commercially available resins (points on the graph), this graph helps to pinpoint what blow molding application would be most appropriate for a given type of resin.

“gel-like viscosity”), the UHMW resins can under no circumstances be blow molded on existing equipment. And no manufacturer of UHMW resins that we are aware of so much as suggests such a possibility.

One of the UHMW resins at the lower end of the UHMW range is said to be extrudable as pipe under high melt pressure; processing of the other available UHMW resins is confined to such high-force methods as ram extrusion, compression molding and forging of preforms.

The absence of resins along the section of the curve from about 300,000 to 2-million MW is due to the fact that MW depends on various reactor conditions, but chiefly on the choice of catalyst for the polymerization. For

any given catalyst, MW can be varied over some range by varying reactor conditions; for example, MW increases with decreasing reaction temperature. But a limit is imposed since at too low a temperature, the reaction simply stops.

Catalysts for the production of resins that would fall in these blank areas either do not exist, or if they do, products made with them have not emerged into view.

MW and blow molding applications To put matters of MW, MI and HLMI into perspective with respect to applications, Fig. 5 will provide a rough visual interpretation—rough because MI cannot be precisely correlated with HLMI, and neither can be precisely related to MW.

Points on the curve represent the locations of HDPE resins—both homopolymers and copolymers—that are (or have recently been) offered commercially as blow molding materials. Current technology would permit the production of a resin at any point along this curve.

At MI levels below but near 1.0, thin-walled bottles can be produced at high production rates. Approaching the arbitrary cutoff point of 0.1 MI for normal-MW resins (and the upper limit of MW) are resins chosen for high melt strength required for heavy parisons, and for good environmental stress-crack resistance needed in liquid-detergent and chemical applications. (These are normally copolymers.)

In the lower range of HMW PE's, resins are found with high melt strength and toughness, impact strength and other qualities that suit them for large industrial containers and tanks, and for trash cans. In the mid-MW range are resins from which 55-gal containers can be produced that will meet the drop tests and other stringent DOT requirements, as well as gas tanks for automotive applications.

At the highest level of MW are resins being processed in special equipment to produce very large tanks. □ □