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Using Melt Flow Rate to Determine Change in Molecular Weight

If there is one key property for polymers, it is molecular weight --- actually it's the presence of the very-high-molecular weight fraction. It's these very long molecules which give the polymer its high elongation, toughness, impact strength, long-term creep resistance and resistance to stress cracking. In semi-crystalline polymers, these long-chain molecules get captured in one or more adjacent crystalline sections and act as links (tie molecules) between the crystallites. In amorphous polymers, the chains are so long that they get severely entangled with the other molecules. Unlike short chains that can easily slip through the entangled mass (a term we define as flow), the long chains are "tied" together such that pulling on one causes all the others to resist the movement. These long chains form the "mortar between the bricks" which gives the strength to the plastic part.

Of course, it's the high molecular weight fraction which is also responsible for high resin viscosity which shows up as low extrusion rates, short injection flow lengths, and poor knit-line strengths. Also, when you "force" the material to flow, these long molecules which are carrying a disproportionate amount of the load, tend to break, therein, slightly reducing the overall molecular weight average.

When there is a failure, one often wants to determine if the molecular weight of the material is the same as that which was specified, or has it been altered during processing or in use. After all, small reductions in average molecular weight can be responsible for significant reduction in tie-molecule density, i.e., performance.

There are a number of methods by which one can determine different average molecular weights --- melt rheology, solution viscosity, membrane osmometry, gel permeation chromatography (also called size exclusion chromatography), and light scattering techniques. Each has its own advantages as well as limitations, however, the one most widely used is also the simplest and often the most sensitive measurement --- melt flow rate.

As discussed earlier, a very small change in molecular weight can result in a very significant alteration of a material's properties. Most of the other methods measure properties of the polymer which are directly proportional to the average molecular weight. Small changes in molecular weight therefore can be lost in the normal variability of the measurements. Melt flow rate, on the other hand, is exponentially related to the average molecular weight of the material:

$$MF \cong M_w^{3.4}$$

The power factor makes melt flow rate an extremely sensitive tool for measuring small changes in molecular weight.

One way to get an indication of molecular weight distribution is to measure the MFR at two or three different conditions. Melt flow rate of polyethylene is generally measured under ASTM D1238 Condition E (190°C/2.16 Kg load) --- commonly called the “melt index”. However, the MFR of polyethylene can also be measured at different conditions like Condition F (190°C/21.6 Kg load) --- the so-called “high load melt index” --- or Condition N (190°C/10.0 Kg load). By monitoring the ratio of the Condition N or F to Condition E, one can develop an index which measures the breadth of the molecular weight distribution --- the higher the ratio the broader the MWD.

Manufacturers generally “tune” their products to fall within a narrow range of melt flow rate. As we all know, MFR is a poor indicator of how the resin will actually “flow” in the machine --- products with the same MFR can result in molding difficulties on the floor. However, by measuring the MFR at these different conditions (effectively at different shear rates), one can measure differences in different batches of resins. With experience, you can set up a specification, within which the resin will be suitable for your molding.

Don’t overlook the power of simplicity.

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