

Polymer Properties



Thermoforming involves stretching of rubbery solid plastic sheet. When force is applied to any material, it stretches or elongates. The amount that it stretches depends on the amount of force per unit area, or "stress," applied to the sheet, the nature of the material and its temperature. The amount that the material stretches

is elongation or "strain." For most metals, ceramics and many polymers below their glass transition temperatures, the amount of strain in the material is proportional to the amount of stress applied to the material. The proportionality is referred to as the material "modulus." The modulus of a given polymer depends on the molecular make-up of the polymer, the nature and level of the additives in the polymer and the temperature of the polymer. For example, according to *Modern Plastics Encyclopedia*, the ASTM D638 range in modulus of PS at room temperature [77°F or 25°C] is 330,000 to 475,000 psi.

For many polymers, the stress-strain curve is not linear, but is curved. The room temperature modulus for LDPE, for example, is given in *Modern Plastics Encyclopedia* as 25,000 to 41,000 psi. But at room temperature, LDPE is far above its glass transition temperature of -25°C. Therefore, reported modulus is the slope of the stress-strain curve at zero strain. Furthermore, as the polymer is heated above its glass transition temperature, the stress-strain curve remains curved but flattens. The modulus, being the slope of the curve at zero strain, also decreases with increasing temperature. In addition, the elongation at break increases with increasing temperature.

The decreasing modulus, the flattening of the stress-strain curve, and the increasing elongation at break of a given polymer or polymer recipe with increasing temperature are all important in thermoforming, because the sheet must be stretched into the deepest recesses of a mold. Two other aspects of the stress-strain char-

acteristics of a given polymer are also important, however. If the softening range of the polymer is too narrow, that is, the polymer goes from being very stiff to extremely soft over a very narrow temperature range, the thermoforming window will be very narrow. This is the case with most grades of nylon 6, for example. And if the stress or force per unit area needed to stretch the polymer is always very high, regardless of the polymer temperature, traditional vacuum forming and even normal pressure forming pressures may be insufficient to stretch the polymeric sheet to the farthest reaches of the mold. This is the case for many classes of highly filled and fiber-reinforced polymers.

Again, thermoforming focuses on the solid properties of a polymer, such as stress-strain. Nevertheless the fluid properties of the polymer are important as well. After all, the polymer must be extruded into sheet. Fluid properties of polymers are related to the polymer liquid resistance to applied stress. The polymer liquid resistance is given as "rate of strain" and "viscosity" is the slope of the stress-rate of strain curve. As with solid polymer stress-strain curves, liquid polymer stress-rate of strain curves are temperature dependent, with polymer viscosity decreasing with increasing temperature. Very high viscosity, being a measure of the polymer liquid resistance to applied stress, can lead to

sheet extrusion problems. So can very low viscosity. Unwanted orientation and internal stresses in sheet can be traced back to the viscosity of the polymer at the time of extrusion.

Frequently thermoformers are told to use a polymer with a given "melt index." The melt index test was established years ago as a quick check of the flowability of polyethylene melt. Basically it is the amount of molten plastic, in grams, at a prescribed temperature that can be squeezed through a hole of a given diameter in ten minutes. Ten grams of a polyethylene with a melt index of 10, say, will extrude through the hole in ten minutes, whereas only 1 gram of a polyethylene with a melt index of 1 will extrude through the same hole in the same period of time. Thus, the polymer with the greater melt index value will flow more rapidly at the same stress level and therefore, will have a lower viscosity. For a given type of polymer, a lower viscosity usually means a lower molecular weight. Extruders prefer polymers with relatively high melt indexes.

Keep in mind, however, that melt index gives very little information about temperature- and shear rate-dependent nature of the viscosity of a given polymer. And extending the concept of melt index beyond polyethylenes and polypropylenes is risky, at best.

Keywords: modulus, viscosity, stress, strain, stress-strain curve, stress-rate of strain curve, melt index



Polymer Properties II



In addition to stress-strain and stress-rate of strain characteristics of polymers, thermoformers need to know about the thermal properties of polymers.

"Heat capacity" is a measure of the amount of energy required to elevate the polymer temperature. Heat capacity is sometimes called

"specific heat." The field of study that focuses on energy uptake of materials is called "Thermodynamics." In thermodynamics, one of the fundamental measures of energy uptake is "enthalpy." Enthalpy increases with increasing temperature. When a material goes through a characteristic change such as melting, the temperature-dependent enthalpic curve changes dramatically. When a material goes through a characteristic change such as glass-to-rubber transition, the temperature-dependent enthalpic curve changes subtly if at all. As expected, it takes far more energy to heat a crystalline polymer from room temperature, say, to above its melt temperature than to heat an amorphous polymer from room temperature to the same temperature. For example, it takes more than twice as much energy to heat polyethylene, a crystalline polymer, to 360°F than it does to heat polystyrene to the same temperature. And since the formed shape must be cooled, twice as much energy must be removed to cool polyethylene to a given temperature than to cool polystyrene to the same temperature. A single value of specific heat is frequently given for a specific polymer. These values are determined by dividing the enthalpy difference by the temperature difference. Such values are acceptable for amorphous polymers but care must be taken with a crystalline polymer, since the slope of the temperature-dependent enthalpy curve, and hence the specific heat, changes dramatically as the temperature ap-

proaches the melt temperature of the polymer.

"Thermal conductivity" is the measure of energy transmission through a material. The thermal conductivity values of organics, in general, are substantially lower, by orders of magnitude, than, say, metals. In other words, polymers are thermal insulators. As an example, the thermal conductivity of aluminum, a common metal for thermoforming molds, is one-thousand times greater than the thermal conductivity of, say, polystyrene. During thermoforming, thermal conductivity is a measure of energy transmission through the polymer sheet. Even though the thermal conductivities of polymers are low, there are differences in values among polymers. For instance, the thermal conductivity of HDPE is about four times higher than polystyrene or ABS. Thermal conductivity and its companion property, thermal diffusivity, discussed below, are quite important when forming very thick sheets, because the rate of energy transfer into the sheet governs, to a large extent, the formability of the sheet. Although thermal conductivity typically decreases slightly with increasing temperature, for all intents, the value can be considered constant.

Polymer density decreases and its reciprocal, "specific volume," increases with increasing

temperature. In the vicinity of the glass transition temperature, the slope of the temperature-dependent specific volume curve changes perceptively. In the vicinity of the melt temperature, the slope changes dramatically. Typically, the density of an amorphous polymer at its forming temperature is about 10% to 15% less than that at room temperature. The density of a crystalline polymer at its forming temperature may be as much as 25% less than that at room temperature. Obviously as the polymer cools from its forming temperature, its density will increase, its volume will decrease, the final part dimensions will decrease and the part will exhibit shrinkage. This point will be amplified in later articles.

"Thermal diffusivity" is a polymer property that is a combination of other polymer properties. Thermal diffusivity is divided by its density and specific heat, and is the fundamental polymer property in time-dependent heat transfer to materials.

Because of the unique bundling of temperature-dependent characteristics of the polymer properties, thermal diffusivity is nearly independent of temperature for nearly all polymers.

Keywords: Heat capacity, specific heat, enthalpy, thermal conductivity, specific volume, thermal diffusivity

