11.5 Material Properties and Applications

At this point you may well ask what this business of polymer geometry, size distributions and average molecular weights has to do with real materials. We did touch briefly upon some of these connections earlier, when we noted that mechanical properties of polymers do depend on the size of the molecules and on the material's crystallinity, which itself depends on the geometry of the molecules. Here we will fill a few more details of interest.

11.5.1 Molecular Weight Effects

The first point to note is that a wide variety of polymers show a universal qualitative behavior of certain mechanical properties with respect to the size and size distribution of the molecules in the material.

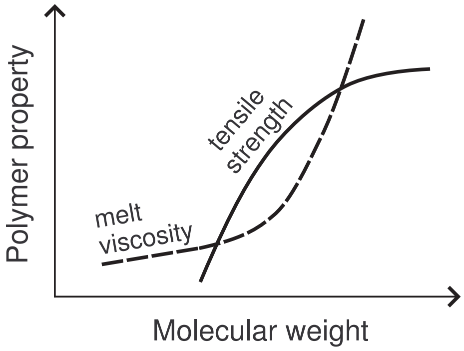

Figure 11.10: Qualitative dependence of mechanical property parameters on average molecular weight.

Properties such as the elastic modulus and the tensile strength tend to show a marked increase in a certain range of intermediate molecular weights and level off at very large $\overline{M_n}$. On the other hand, the melt viscosity measured at low strain rate increases only modestly at low molecular weights, but more rapidly above a certain threshold value of $\overline{M_n}$.

This behavior has immediate practical consequences for polymer processing. A lot of this requires flow and forming operations of the material at elevated temperature, where the viscosity is an important parameter. The figure suggests that the larger $\overline{M_n}$, the more difficult a material will be to process. In addition, when it comes to parameters related to material strength, it appears that there is a point beyond which increasing $\overline{M_n}$ brings little benefit.

The curve of viscosity η vs M_n has an interesting shape in itself. For many different polymers it has been found that there is a critical value M_n such that

$$\eta = K M_n \quad \text{for} \quad M_n < M_c \tag{11.7}$$
$$\eta = K' {M_n}^{3.4} \quad \text{for} \quad M_n > M_c \tag{11.8}$$

In other words, below M_c the viscosity η varies linearly with M_n, and above M_c as a power law with an exponent of 3.4. (This work usually involved material with a narrow size distribution, so that $M_n = \overline{M_n}$).

The physical reason for this behavior is that the rapid rise of tensile strength and η are due to strong entanglement of the polymer chains. Entanglement limits the motion of polymer chains relative to each other, and in order for entanglement to take place to an appreciable extent, the chains have to have a certain minimum length.

Another parameter which shows interesting behavior as a function of molecular weight is the glass transition temperature T_g. This should not come as a surprise, since T_g is also related to the ease of chain motion, and below T_g such motion is not possible. Data of two investigative groups for polystyrene are displayed in the figure below:

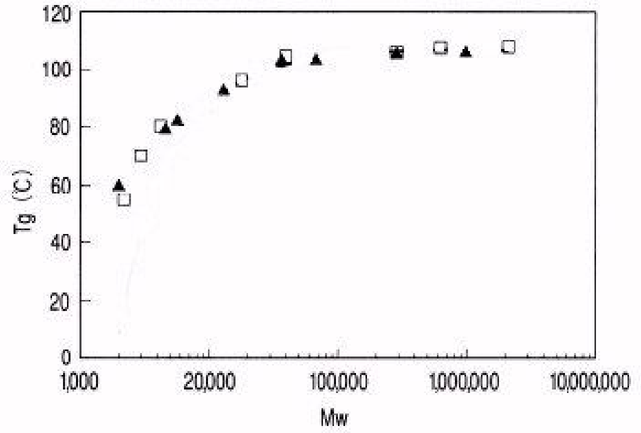

Figure 11.11: T_g of polystyrene as a function of molecular weight.

The data are for practically monodisperse polymer samples, with a PDI of around 1.1. Note the logarithmic scale for M_w, which under these conditions is essentially the same as $\overline{M_w}$ and $\overline{M_n}$. The function $T_g(M_w)$ has the same shape as the mechanical strength properties in Fig. 11.10 above: T_g rises in the low-M_w range and levels off at high M_w.

For materials with a narrow size distribution, Fox and Flory showed that the behavior of $T_g(M_n)$ data was described quite well by a simple expression, which is now known as the Fox-Flory law:

$$T_g = T_{g,\infty} - k/M_n \tag{11.9}$$

In Eq. 11.9 the parameter k is an empirical constant characteristic of a particular material, and $T_{g,\infty}$ is the limiting value of the glass transition temperature for very large M_n. (You will figure out in a homework how good this expression is.)

11.5.2 Material Properties and Uses

Polyethylene

We begin by examining some properties of polyethylene, the simplest polymer. This material is produced in different grades. The two main ones are: **LDPE** for low-density polyethylene, and **HDPE** for high-density polyethylene. LDPE consists of shorter polymer chains with a considerable amount of branches which themselves may be branched; HDPE consists of longer chains with almost no branching. There is also LLDPE, which stands for linear low-density polyethylene, with much shorter branches than LDPE, as well as UHMW-PE, which stands for ultra-high molecular weight polyethylene.

A summary of their mechanical properties is given in Table 11.3 below:

Table 11.3: Material parameters of different types of polyethylene

Material	$\overline{M_n}$ (a.u.)	ρ (g/cm^3)	E (GPa)	T.S. (MPa)	ϵ_f	Izod (kJ/m)
LDPE	20-50k	0.92	0.25	10	4	no break
LLDPE	20-100k	0.93	0.3	20	5	>1
HDPE	200-500k	0.96	1.2	30	1.5	0.1
UHMW-PE	2-5M	0.975	0.55	40	3	no break

The parameters in Table 11.3 are mostly the usual ones for mechanical properties: E is the elastic modulus, T.S. the tensile strength, and ϵ_f the elongation at fracture. Izod refers to the so-called Izod impact strength from a test measuring toughness under impact conditions. The Izod test is similar to the Charpy test described in Chapter 9: Izod also uses a notched sample of fixed dimensions, but with a different geometry than Charpy.

The data in the table have been assembled from several industrial sources. It should be clear that the numbers for each type of polyethylene are representative averages. The numbers for $\overline{M_n}$ are to be taken as broad ranges without sharply defined boundaries. The variation in reported values of other parameters seems to be fairly large, especially for impact strength. Some sources report an Izod strength for LDPE and UHMW-PE of >1kJ/m.

Thus the numbers should be used only for rough correlations. What we do know is that they will depend on material details such as the degree of polymerization, the molecular weight distribution, and the processing of a material. For example, it is important whether a material has been cast into block form, extruded into a more complex shape, or drawn into a film or fiber.

Table 11.4. lists a few of the common uses of the various types of polyethylene. It is understood that the list could be twice as long.

Table 11.4: Common uses of polyethylene

Material	Common uses
LDPE	bags, food and textile packaging, electrical insulation
LLDPE	packaging, containers, pipes, tubing
HDPE	milk bottles, food packaging, containers
UHMW-PE	bottles, containers, gears, guides, dump trailer linings

Additional properties of interest for polyethylene are: good flexibility to temperatures as low as -73 °C, excellent corrosion resistance, excellent electrical insulation, low permeability for water.

Polypropylene, Poly(vinyl chloride), and Polystyrene

The next group of polymer materials we will discuss is the one originating from compounds with the formula $CH_2{=}CHR$, yielding the mer $CH_2{-}CHR$, where R is not an H atom but something else. Here R can be either a methyl group (CH_3) for polypropylene, or a Cl atom for poly(vinyl chloride), or a phenyl group (C_6H_5, essentially a benzene ring) for polystyrene. We will use the abbreviations PP, PVC, and PS for them.

In comparison to polyethylene, one can say that all four materials consist of the the same kind of polymer chain, but the latter three have a side group, something sticking out to the side. Side groups in a polymer chain will inhibit bond rotation and thus will render the chain effectively stiffer. In addition, polymer chains will not uncoil or slide passed each other as easily. These molecular characteristics are reflected in the mechanical properties of the materials in Table 11.5 below.

Again, the values for the mechanical parameters should be taken as broad averages, give or take 25 % for E and T.S., a factor 2 for ϵ_f, and even more for the Izod impact strength. These three materials are available commercially in different grades, differing in average molecular weight, but $\overline{M_n}$ or $\overline{M_W}$ are usually not specified.