INTRODUCTION

Any predictive method for polymer properties is complicated by effects absent from most small molecule systems such as molecular weight, thermal history and non ideal structure. Therefore most predictive methods for polymer properties limit the problem by assuming a reference for these effects and focusing on the fundamental effect of polymer structure. Typically these methods assume a well annealed monodisperse infinite molecular weight system, with no branching or structural variation. However, since the models are derived from experimental measurements that qualitatively approach these limits they do contain some inherent error due to these effects.

Four basic methods can be used to estimate mechanical properties as a function of polymer structure:

(i) Molecular Modeling
(ii) Group Additivity Methods
(iii) Basic Structural methods
(iv) Graph Theory Methods.

Glassy polymers are simply polymer solids below the glass transition temperature (Tg). They are solids frozen in a state of amorphous or liquid-like order. This means that many of their thermodynamic properties can be modeled as a function of the average interactions of their various components. Therefore, the final three of the aforementioned methods, which are based on average contributions of local structure, are particularly effective. While molecular modeling (see also Monte Carlo Techniques) can provide insight into the connection between structure and properties it is often more time consuming than the experimental characterization of the polymer. Therefore the other three methods are more practical in the prediction of mechanical properties in amorphous polymers.

Mechanical properties characterize the connection between the stress, or force per unit area, applied to a polymer sample (σ) and the relative deformation (ε) in the polymer sample. Most engineering applications of glassy polymers are concerned with small strain behavior. This behavior can be described by a simple linear model in which a proportionality constant, called a modulus, is used to describe the ratio of the stress to the strain (see Stress and Strain). We will concentrate on the prediction of these moduli. No accurate structure-property relationships currently exist that account for the time dependence of this relationship, and the large strain behavior is addressed in the article Structure-Property Relationships: Large Strain Behavior. The stress may be applied in a uniaxial, isotropic or shearing mode and is related to strain by the Young’s
(E), Bulk (B), or Shear (G) modulus respectively as seen in Figure 1. One additional parameter is the Poisson's ratio (v), which is the relative contraction of the sample in the normal directions in response to uniaxial deformation. Poisson's ratio typically varies between 0.3 and 0.4 for glassy polymers, and is slightly below the constant volume limit of 0.5 for rubbery polymers. In the limit of amorphous structure the mechanical properties of a glassy polymer can be completely described by two of these four parameters. These parameters are related by

\[ E = 3B(1-2v) = 2G(1+v). \]  

Which means that any predictive structure-property method must only predict two of these four parameters to be useful for glassy polymers.

\[ \sigma_x = E \varepsilon_x, \quad \varepsilon_x = \Delta x/x \]
\[ \nu = -\frac{\Delta \varepsilon_y}{\Delta \varepsilon_x} = -\frac{\Delta \varepsilon_z}{\Delta \varepsilon_x} \]
\[ P = -B(\Delta V/V) \]
\[ \sigma_y = \sigma_z = \sigma_x = -P \]
\[ \sigma_{yx} = G \varepsilon_{yx} \]
\[ \varepsilon_{yx} = \Delta x/y \]

Figure 1: Various modes of elastic response

GROUP ADDITIVITY METHODS

These methods are based on the fundamental assumption that a property may be expressed as a sum of individual molar contributions for each structural group contained in the polymer repeat unit. This assumes that these contributions are relatively independent of each other. Unfortunately not all polymer properties possess this characteristic of molar additivity, and these properties must be derived using fundamental or empirical relationships from those properties that do. The most comprehensive work on these methods is that of Van Krevelen. Although mechanical moduli do not appear to possess molar additivity, Van Krevelen has deduced that the product of the molar volume and the cube root of the velocity of sound through a material does. Group additivity contributions for this quantity called the Rao function or molar sound velocity function \( (U_R) \) were tabulated for a number of organic structural groups by Van Krevelen (reference 2, chapter 14). Given the proportionality of the