

The Elastic Modulus of Isotropic Semicrystalline Polymers

For a number of years, an empirical curve or equation has proved very useful for estimating the degree of crystallinity of a polymer from a simple measurement of the shear modulus.¹ This equation is

$$\log_{10} G \doteq 6.763 + 4.77 w_c \tag{1}$$

where G is the shear modulus in dynes/cm² and w_c is the degree of crystallinity. This equation is one form of the logarithmic rule of mixtures as shown by rearrangement of the equation to give² the following:

$$\log_{10} G \doteq w_a \log G_a + w_c \log G_c. \tag{2}$$

In this equation, w_a is the fraction of the amorphous phase which has an apparent shear modulus of $G_a = 5.8 \times 10^6$. The apparent modulus of the crystalline phase $G_c = 3.4 \times 10^{11}$ dynes/cm². These equations are known to predict moduli which are too high at high degrees of crystallinity. The logarithmic rule of mixtures has been found empirically to be useful for predicting the moduli of block copolymers and polyblends when both polymeric phases are continuous

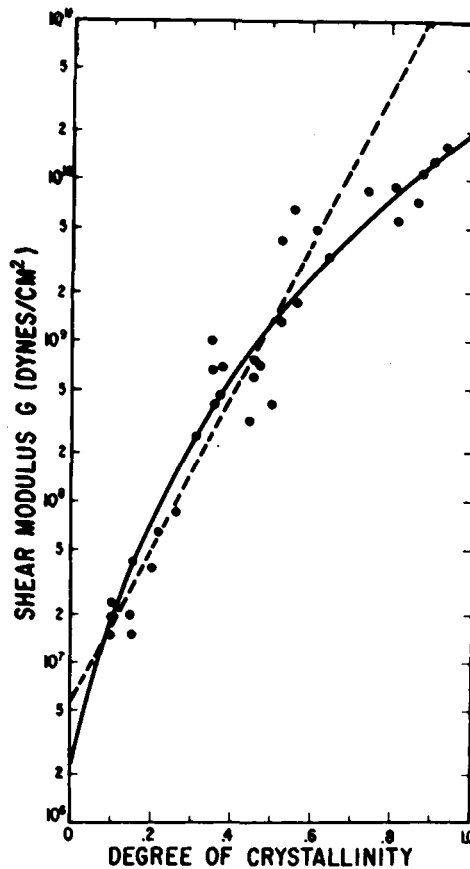


Fig. 1. Shear modulus as a function of degree of crystallinity: (—) eq. (4); (---) eq. (1); (●) experimental values for polymers and copolymers.

phases.^{2,3} Thus, eqs. (1) and (2) imply that crystalline polymers behave mechanically as if both the crystalline and amorphous phases are continuous. This would agree with theories of crystalline polymers in which an isotropic random lamellar structure exists, for instance.

Davies^{4,5} has theoretically derived equations which are applicable when both phases are continuous in contrast to the usual theories in which one phase is assumed to be dispersed.⁸⁻¹⁰ His equations are specific examples of the very general mixing equation

$$G^n = \phi_1 G_1^n + \phi_2 G_2^n; \quad -1 \leq n \leq 1 \quad (3)$$

where ϕ_1 and ϕ_2 are the volume fractions of phases 1 and 2, respectively. Equation (3) becomes the logarithmic rule of mixtures when $n = 0$. As a special case, Davies' equation for the shear modulus of systems containing two continuous phases is

$$G^{1/5} \doteq w_a G_a^{1/5} + w_c G_c^{1/5}. \quad (4)$$

Equation (4) fits many experimental data on crystalline polymers and approximates eq. (1) over a wide range of crystallinities if $G_a = 2 \times 10^8$ and $G_c = 2 \times 10^{10}$ dynes/cm². This is shown in Figure 1. The experimental points include polyethylene, ethylene copolymers, and other polymers at various temperatures above the glass transition temperature. The scatter around the curve is quite large, and in a few cases (not plotted) the deviations are very large. However, in general, eq. (4) can be used to quickly and easily estimate the degree of crystallinity of a polymer. This implies that by far the largest factor in determining the elastic modulus of a crystalline polymer is its degree of crystallinity. Chemical structure and morphology must play a secondary role. This is in line with what has already been found for polyblends and block polymers. Morphology is very important when one phase is dispersed, but it is much less important when both phases are continuous.³ Unfortunately, no one has developed a theory relating the variation in n of eq. (3) to morphology. On the other hand, the morphology of systems containing one continuous phase can generally be incorporated into the theoretical equations.^{2,8-10} Elastic moduli may be as high as 10^{12} dynes/cm² when stresses are applied along covalent bonds or if ionic bonds are involved. However, when van der Waals' types of bonds are involved, the elastic moduli are of the order of 10^{10} dynes/cm².¹¹ Thus, a value of the effective modulus of organic polymeric crystals of 2×10^{10} appears reasonable although the value must vary somewhat from polymer to polymer.

Some of the data points in Figure 1 were supplied by Dr. Thomas B. Lewis and by David Hemmerly.

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