Order–Disorder Transition in Polymer–Diluent Systems: Elastic Constants

T. S. Chow

Xerox Webster Research Center, 800 Phillips Road, 0114-39D, Webster, New York 14580

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ABSTRACT: A new theoretical model is presented to describe the effect of diluent on the elastic constants of polymer–diluent mixtures. Our theory shows the limitation of the traditional composite theories, which are based on the micromechanics and/or strain energy calculations, and points out the important role of molecular parameters. The present result is expressed in terms of both molecular and bulk elastic properties of the two components. As the diluent concentration increases, the elastic modulus decreases very slowly until a critical concentration Φ_c is reached. Beyond Φ_c, the modulus decreases rapidly. This order–disorder transition is related to the crossover between the energy and entropy contributions of the system at the molecular level. The prediction of the theory is in good agreement with experimental data.

Introduction

The effects of a diluent or plasticizer on the physical properties of solid polymers have been a subject of great interest to both scientists and technologists for many years. The main focus of the activities has been on the sorption and diffusion of small molecules, such as gases, vapors, or solvents, in glassy polymers.[1–5] The presence of small molecules is also known to have a strong influence on the glass transition temperature[3,6,7] and on mechanical properties.[8,9] Significant advancement in the understanding of transport coefficients and the glass transition has already been made. However, there is no comparable theoretical development in the study of mechanical properties which are very important nowadays to reduce the development time of new products by establishing methods that predict polymer behavior. It is reasonable to start the investigation by trying the composite theory in the determination of the elastic constants of polymer–diluent systems. The traditional composite theories[9–13] are usually derived on the basis of the micromechanics and/or strain energy calculations. On the other hand, the properties such as the glass transition, sorption, and diffusion originated from the change in entropy due to the introduction of small molecules.

This paper presents a theoretical model to describe the effect of diluent on the elastic constants of polymer–diluent mixtures. We will examine the physics behind the limitation of the composite theory in its application down to the molecular level. The crossover from the energetic to entropic contributions to the elastic constants of plasticized polymers, defined as the order–disorder transition, will be discussed. Finally the theory will be compared with experiment.

Thermodynamics of Deformation

Consider a solid which is deformed under a stress tensor σ_{ij}; the change in deformation is expressed in terms of the change in the strain tensor e_{ij}. The work done by the internal stresses per unit volume of the body is then[14,15]

$$dW = -\sum_{ij} \sigma_{ij}\, de_{ij} \tag{1}$$

We assume that the process of deformation occurs slowly and thermodynamic equilibrium is established in the system at every instant. All thermodynamic quantities such as the entropy S, the internal energy U, etc., are denoted by capital letters and are taken relative to the unit volume of the deformed solid. Hence, the combined equation of the first and second laws of thermodynamics of such a system is

$$T\, dS = dU + dW = dU - \sum_{ij} \sigma_{ij}\, de_{ij} \tag{2}$$

where T is temperature. Introducing the free energy of the body,

$$F = U - TS \tag{3}$$

There is competition between the energy U (which favors order) and entropy (which favors disorder) at the state of thermodynamic equilibrium. Under a constant temperature, a rise in entropy due to the presence of small molecules in the polymer tilts the balance toward disorder which forms the basis of this paper. Combining eqs 2 and 3, we obtain the differential of F to be

$$dF = -S\, dT + \sum_{ij} \sigma_{ij}\, de_{ij} \tag{4}$$

From eq 4, it follows that

$$\sigma_{ij} = \left(\frac{\partial F}{\partial e_{ij}}\right)_{Te'} \tag{5}$$

The fourth-order tensor of elastic constants is determined from

$$C_{ijkl} = \left(\frac{\partial \sigma_{ij}}{\partial e_{kl}}\right)_{e'} = \left(\frac{\partial^2 F}{\partial e_{ij}\, \partial e_{kl}}\right)_{Te'} = \left(\frac{\partial^2 U}{\partial e_{ij}\, \partial e_{kl}}\right)_{Te'} - T\left(\frac{\partial^2 S}{\partial e_{ij}\, \partial e_{kl}}\right)_{Te'} \tag{6}$$

The subscript e' means that all other e_{ij} are to be held constant while differentiating with respect to e_{ij}. The Maxwell equations are obtained by differentiating the dependent variables and by comparing the various derivatives in the form of second derivatives of the state functions. Thus, eqs 4 and 5 give

$$\left(\frac{\partial S}{\partial e_{ij}}\right)_{Te'} = -\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_{e} \tag{7}$$

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Substituting eq 7 into eq 6 yields

$$C_{ijkl} = C_{ijkl}^{(U)} + T\left(\frac{\partial C_{ijkl}}{\partial T}\right)_e \tag{8}$$

For simplicity, we shall consider the tensile (Young's) modulus in this paper. That is

$$E(\Phi) = E_U(\Phi) + T\frac{\partial E(\Phi)}{\partial T} \tag{9}$$

where Φ is the volume fraction of the diluent. The subscript U in eq 9 and the superscript in eq 8 are identified as energy related elastic constants. The second term in the above equation is related to the disorder caused by the presence of small molecules in the polymer. We have dropped e on the partial derivative in eq 9, which will be implied without mentioning in the rest of the paper.

Energy Contribution

The first term, E_U, in eq 9, can be determined from the traditional composite theory. The effective elastic constant is related to the system's change in strain energy as a function of the diluent concentration. The polymer–diluent system can be considered as a disordered solid consisting of randomly distributed liquidlike particles in a solid matrix. The shear modulus of the diluent (μ_d) is always many orders of magnitude smaller than that of the polymer (μ_p), but the magnitudes of the bulk modulus of the diluent (k_d) and of the polymer (k_p) are quite comparable. Thus,

$$\mu_d = 0 \qquad and \qquad k_d \neq 0 \tag{10}$$

When a constant tensile strain is applied to a system at infinity, the perturbed local stress field is not uniform throughout the composite. Due to the structural randomness, the composite as a whole has to be macroscopically homogeneous. The effective tensile modulus can then be calculated from the volume average of the stress field. The interaction between diluent particles in the polymeric matrix is treated by a mean-field approximation.[12] The effective tensile modulus E_U is derived as[13]

$$\frac{E_U(\Phi)}{E_p} = 1 - \frac{1}{3}\left(\frac{1 - k_d/k_p}{B} + \frac{2}{G}\right)\Phi \tag{11}$$

where E_p refers to the tensile modulus of polymer,

$$B = 1 - (1 - k_d/k_p)(1 - \Phi)\frac{1 + \upsilon_p}{3(1 - \upsilon_p)} \tag{12}$$

and

$$G = 1 - 2(1 - \Phi)\frac{4 - 5\upsilon_p}{15(1 - \upsilon_p)} \tag{13}$$

where υ_p is the Poisson ratio of the polymer. For isotropic materials, there are only two independent elastic constants for a given material. E, k, μ, and υ are related to each other by $k = E/3(1 - 2\upsilon)$ and $\mu = E/2(1 + \upsilon)$.

Entropy Contribution

There is significant drop in the tensile modulus for temperatures beyond the glass transition. Small molecules in the polymer serve as softeners. According to eq 9, we introduce the softening temperature

$$T_s = -\frac{E_U}{\partial E/\partial T} > 0 \tag{14}$$

and rewrite eq 9 as

$$E = -\frac{\partial E}{\partial T}(T_s - T) \tag{15}$$

The softening temperature is directly proportional to the glass temperature,[16]

$$T_s(\Phi) = T_g(\Phi) + A \tag{16}$$

where A is a constant independent of Φ and is greater than zero (see eq 20). The theoretical concept of T_s has been found to be very useful in describing other mechanical properties like yield stress, $\sigma_y \sim T_s - T$, quantitatively.[16] T_s is a signature of the onset of large-scale motion of polymer chains which results in vanishing elastic constants and yield stresses.

On the basis of statistical thermodynamics, we have analyzed the possible configurations of diluent molecules on polymer lattice sites and have determined the system's change in configurational entropy. This leads to a theoretical expression[7] for $T_g(\Phi)$:

$$\ln\left[\frac{T_g(\Phi)}{T_g(0)}\right] = -\frac{1}{\Delta C_p}[S^{\text{liquid}}(\Phi) - S^{\text{liquid}}(0)] = \frac{zR}{M_p\Delta C_p}[(1 - \theta)\ln(1 - \theta) + \theta \ln \theta] \tag{17}$$

Here, z is the lattice coordinate number, R is the gas constant, M_p is the monomer molecular weight, ΔC_p is the excess isobaric specific heat of the polymer at $T_g(0)$, and

$$\theta = \frac{M_p}{zM_d}\frac{\omega}{1 - \omega} = \frac{V_p}{zV_d}\frac{\Phi}{1 - \Phi} \tag{18}$$

where ω is the mass (or weight) fraction of the diluent and V is the molar volume. The subscripts d and p identify the diluent and polymer, respectively. Equation 17 describes $T_g(\Phi)$ in terms of molecular parameters, and it does not require the glass transition temperature of small molecules, which cannot be determined easily.

Equation 17 clearly reveals that the presence of small molecules in the polymer has strong effect on the configurational entropy and $T_g(\Phi)$ of the polymer–diluent system. However, the elastic constants depend also on the internal strain energy. We, therefore, expect a crossover from the strain energy dominated to configurational entropy dominated $E(\Phi)$. This order–disorder transition can best be described in terms of Φ_c. The critical concentration Φ_c is defined by

$$T_s(\Phi_c) = T_g(0) \tag{19}$$

Equations 16 and 19 give

$$A = T_g(0) - T_g(\Phi_c) \tag{20}$$

For $\Phi > \Phi_c$, the mechanical properties are no longer determined only by the local rearrangements of molecular segments. Cooperative motion of polymer chains related to the entropic change of a system becomes important. This results in a further drop in the tensile modulus. In practical applications, the volume fraction of plasticizer is usually small. Therefore, it is reasonable to assume that

$$\frac{\partial E(\Phi)}{\partial T} \simeq \frac{\partial E(\Phi_c)}{\partial T} \tag{21}$$

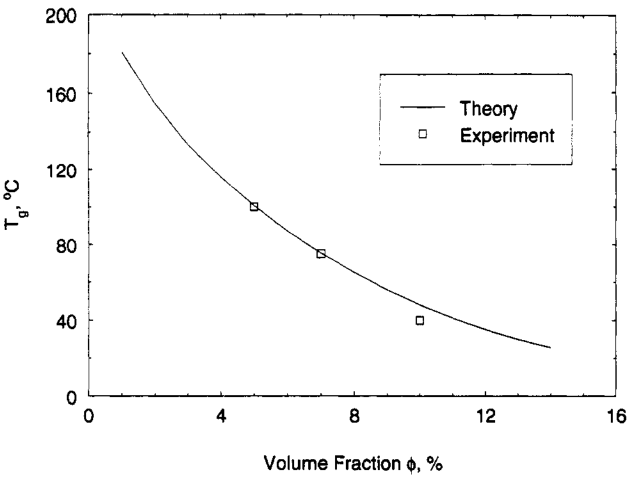

Figure 1. Comparison of the calculated and measured[8] depression of the glass transition temperature of cellulose by moisture (H_2O).

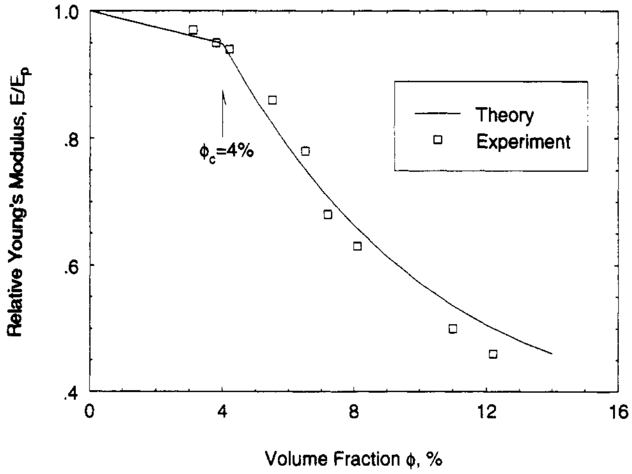

Figure 2. Comparison of the calculated and measured[8] tensile (Young's) modulus of the cellulose–H_2O system at room temperature (T = 296 K).

Equations 15 and 21 lead to

$$\frac{E(\Phi)}{E_U(\Phi)} \simeq \frac{T_g(\Phi)-T}{T_g(\Phi_c)-T}, \quad \text{for } \Phi \geq \Phi_c \qquad (22)$$

Because $T < T_g(\Phi) < T_g(\Phi_c)$ in accordance with eqs 16, 19, and 20, the tensile modulus $E(\Phi)$ is always less than $E_U(\Phi_c)$ for $\Phi > \Phi_c$. Equation 22 clearly reveals that $E(\Phi_c) = E_U(\Phi_c)$ at $\Phi = \Phi_c$. Finally, we obtain

$$E(\Phi) = E_U(\Phi)\, \Gamma(\Phi,T) \qquad (23)$$

where

$$\Gamma(\Phi,T) = 1, \quad \text{for } \Phi \leq \Phi_c \qquad (24a)$$

$$= \frac{T_g(\Phi) + A - T}{T_g(0) - T}, \quad \text{for } \Phi \geq \Phi_c \qquad (24b)$$

Here, $E_U(\Phi)$ is given by eqs 11–13, $T_g(\Phi)$ by eqs 17 and 18, and the constant A by eq 20. The concentration and molecular weight of the diluent are combined with the number of sites and the monomer molecular weight of the polymer into a single parameter θ. Both $T_g(\Phi)$ and $E(\Phi)$ are sensitive to the nondimensional parameter θ. The lowering of $T_g(\Phi)$ and $E(\Phi)$ is a measure of the efficiency of plasticizers. When the size of the diluent is small, it is more likely for the molecule to interact with polymer segments and to affect the chain configuration. Our analysis reveals that a smaller molecule, measured in terms of the ratio V_p/zV_d, is a more efficient plasticizer.

Results and Discussion

We have derived the concentration-dependent tensile modulus, $E(\Phi)$, of polymer–diluent mixtures and have established its relationship with the glass transition temperature. $E(\Phi)$ is expressed in terms of both molecular and bulk elastic properties of the two components: diluent and polymer.

As an example for illustration, we consider the cellulose–H_2O system. The lowering of the glass transition temperature is shown in Figure 1. Values of

$$M_p = 162, \quad M_d = 18, \quad z = 4,$$
$$T_g(0) = 493 \text{ K}, \quad \text{and} \quad M_p \Delta C_p = 10.48 \text{ cal/mol·K} \qquad (25)$$

are used to calculate the solid curve from eqs 17 and 18. The only adjusting parameter here is z. The points in Figure 1 are experimental data.[8] The water molecule is serving as a softener, and its presence results in the change in the configurational entropy at the molecular level.

On the basis of eqs 23 and 24, a comparison between the theoretical and experimental[8] tensile modulus at T = 296 K is illustrated in Figure 2. In addition to eq 25, the bulk properties[17]

$$k_d = 2.22 \text{ GPa}, \quad k_p = 2.76 \text{ GPa}, \quad \text{and} \quad \upsilon_p = {}^1/_3 \qquad (26)$$

are also needed to determine $E(\Phi)$. For $\Phi < \Phi_c$, the tensile modulus changes very little in accordance with the composite theory. Beyond Φ_c, the modulus decreases rapidly. In contrast to $T_g(\Phi)$ shown in Figure 1, there is a competition between the internal energy and configurational entropy for $E(\Phi)$. This order–disorder transition occurs at Φ_c = 0.04. The present theory shows the limitation of the composite theory and points out the important role of molecular parameters.

References and Notes

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