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A Phase Fluctuation Theory of Polymer Viscoelasticity

By

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This report is a theoretical description of time-dependent behavior of amorphous polymers. The theory was developed over many years of ONR-sponsored elastomer development and characterization, but was not a deliverable of any specific program.

14. ABSTRACT

Amorphous polymers are modeled as a heterogeneous network of nanoscale cells. A “cell” is a homogeneous region within the network. Amorphous polymers have time-dependent properties because the phase of the cells is time-dependent. The cells fluctuate between the glass and elastomer phase with a period τ. The values of τ vary from cell to cell over several orders of magnitude, and are a strong function of temperature. Whether a given cell responds as glassy or elastomeric depends on the ratio between its period of phase fluctuation (τ_j) and the period of observation (1/f), where f is the test frequency. We express this ratio as (τ_j x f), and present equations for modulus and energy loss as functions of (τ_j x f). If (τ_j x f) >> 1, the cell will have a glassy modulus. If (τ_j x f) << 1, the cell will have an elastomeric modulus. The condition (τ_j x f) = 1 has special significance. It occurs at the glass transition temperature of the cell, and is the condition of maximum energy loss. Energy stored during glass phase deformation is lost as heat if the cell fluctuates to the elastomer phase. More specifically, the energy is dissipated as the heat of fusion when the cell fluctuates back to the glass phase. The energy loss is a function of strain rate, because strain rate controls the level of stress in glassy cells between phase fluctuations.

15. SUBJECT TERMS

Viscoelasticity, Time-Temperature Superposition, Phase Fluctuation, Glass Transition, Chemical Potential, Energy Loss.

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Abstract

Amorphous polymers are modeled as a heterogeneous network of nanoscale cells. A "cell" is a homogeneous region within the network. Amorphous polymers have time-dependent properties because the phase of the cells is time-dependent. The cells fluctuate between the glass and elastomer phase with a period τ. The values of τ vary from cell to cell over several orders of magnitude, and are a strong function of temperature. Whether a given cell responds as glassy or elastomeric depends on the ratio between its period of phase fluctuation (τ_j) and the period of observation (1/f), where f is the test frequency. We express this ratio as (τ_j x f), and present equations for modulus and energy loss as functions of (τ_j x f). If (τ_j x f) >> 1, the cell will have a glassy modulus. If (τ_j x f) << 1, the cell will have an elastomeric modulus. The condition (τ_j x f) = 1 has special significance. It occurs at the glass transition temperature of the cell, and is the condition of maximum energy loss. Energy stored during glass phase deformation is lost as heat if the cell fluctuates to the elastomer phase. More specifically, the energy is dissipated as the heat of fusion when the cell fluctuates back to the glass phase. The energy loss is a function of strain rate, because strain rate controls the level of stress in glassy cells between phase fluctuations.

Keywords Viscoelasticity, Time-Temperature Superposition, Phase Fluctuation, Glass Transition, Chemical Potential, Energy Loss.

1.0 Introduction

The purpose of this paper is to introduce an explanation for time-dependent behavior of amorphous polymer, one that allows calculation of the modulus and energy loss as a function of test frequency and temperature. We develop a time-dependent structure model for a specific material and show how its parameters are determined for any amorphous polymer. The model proposes that amorphous polymer is heterogeneous, and must be envisioned as a network of cells whose properties vary with time. The properties vary because each cell fluctuates between the solid (glass) and liquid (elastomer) phases. The periods of phase fluctuation are designated τ_j.

Phase fluctuations are detected in viscoelastic polymers because these materials are used in engineering applications, for which time-dependent properties are measured meticulously. Fluctuations cause time-temperature superposition, which is exploited for energy dissipation. In a typical application, a vibration must be damped. Energy loss is maximized when the period of phase fluctuation is equal to the period of vibration.

The phase fluctuation theory of viscoelasticity is an alternative to the legacy theory. The legacy theory proposes that viscoelastic deformation involves an actual viscous flow, and that energy is lost by molecular friction during this flow [1-7]. The legacy theory assumes that polymers are homogeneous, having the same properties in all locations.

2.0 Overview

Time-dependent properties are caused by time-dependent structure. Specifically, individual cells of amorphous polymer fluctuate between glass and elastomer phases. A single cell is shown as a function of time, fluctuating with period τ, in Figure 1. Throughout this paper, the glass phase is represented in white, and the elastomer phase in black.

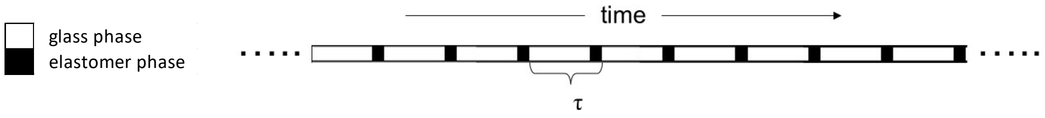
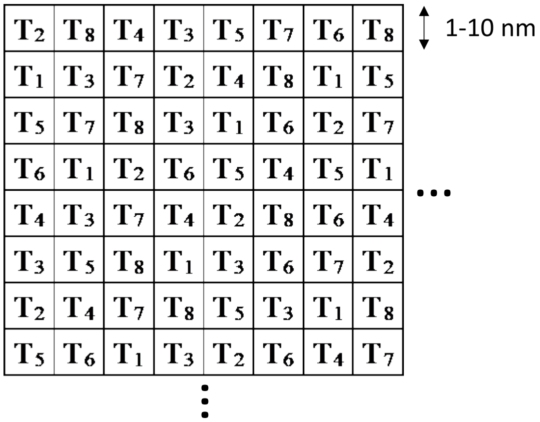


Figure 1. Phase fluctuation in amorphous polymers.

It is proposed herein that phase fluctuations are caused by energy fluctuations. Energy fluctuations occur in all substances, and are typically unnoticed. However, given the small cell size in amorphous polymers, these fluctuations are sufficient to cause phase transitions.

Most substances have crystalline solid phases. Due to crystalline regularity, they are homogeneous, so their structure and properties are the same in all locations. Amorphous polymers are substances that cannot crystallize. As a result, their structure varies from place to place. In this context, "structure" refers to the intermolecular secondary bond network that forms the glass phase and to the chain segment molecular weight and flexibility in the elastomer phase.

Amorphous polymer must be understood as a heterogeneous network of nanoscale cells. In Figure 2 we depict a small section of the microcellular network. Since the cells differ in structure, we introduce a nomenclature to characterize them: a "cell" is defined as a region of amorphous polymer that has a uniform chemical potential (μ) in both the glass phase and elastomer phase. Stated another way, a cell is a homogeneous region within the heterogeneous network. The transition temperature of a cell occurs when the μ values of the two phases are equal. We have therefore chosen to designate a cell by its observed transition temperature, T_j. However, since the phase of each cell fluctuates, the measured value of T_j depends on the period of observation. Therefore, the designation T_j represents cell types. Further, the heterogeneous structure of amorphous polymers is quantified by the distribution in T_j. For this paper, we have modeled a specific polyurethane elastomer into eight different cell structures, T_1 - T_8, as indicated in the figure. (The cell T_j locations were randomly assigned. They are depicted in equal volume fractions, which, as discussed later, is not the case.)



T_2	T_8	T_4	T_3	T_5	T_7	T_6	T_8
T_1	T_3	T_7	T_2	T_4	T_8	T_1	T_5
T_5	T_7	T_8	T_3	T_1	T_6	T_2	T_7
T_6	T_1	T_2	T_6	T_5	T_4	T_5	T_1
T_4	T_3	T_7	T_4	T_2	T_8	T_6	T_4
T_3	T_5	T_8	T_1	T_3	T_6	T_7	T_2
T_2	T_4	T_7	T_8	T_5	T_3	T_1	T_8
T_5	T_6	T_1	T_3	T_2	T_6	T_4	T_7

Figure 2. Amorphous polymer is a network of cells of varying structure and properties.

Each of the eight T_j cell types is associated with a period of phase fluctuation, τ_j. For our model polyurethane elastomer, the τ_j values (in seconds) are provided in Figure 3. The values of τ_j vary from cell to cell over several orders of magnitude at any given temperature.

	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8
T (°C)	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8
-80	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}	10^{7}	10^{8}
-70	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}	10^{7}
-60	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}
-50	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}
-40	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}
-30	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}
-20	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}
-10	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}
0	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}
10	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
20	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}
30	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}

Figure 3. Values of τ_j (in seconds) for the model polyurethane elastomer as a function of temperature and T_j.

The cells of common T_j are present in certain volume fractions, γ_j, which are readily estimated. The values of τ_j and γ_j, together with the values of glassy modulus (E_g) and elastomeric modulus (E_e), can be used to predict dynamic properties over a wide range of frequency and temperature.

An expression for the modulus as a function of τ_j and f (the frequency of cyclic strain) is given in Equation 1. E_g is the Young's modulus of the glass phase. It is a measure of resistance to energy increase caused by changes in length and angle of intermolecular secondary bonds. We demonstrate in the paper that E_g dominates the properties of a cell when the values of τ are long with respect to the period of observation (1/f). E_e is the Young's modulus of the elastomer phase. Elastomers deform by covalent bond rotation. E_e is a measure of the resistance to entropy decrease as the imposed deformation reduces the number of permissible conformations. E_e dominates the cell response when the values of τ are short with respect to (1/f). The material modulus is expressed as a rule of mixtures average of the eight individual cell moduli.

Equation 1 can be used to calculate the modulus as a function of frequency by selecting the values of τ_j (in Figure 3) at any temperature of interest. Alternatively, it can be used to calculate the modulus as a function of temperature at any frequency of interest.

$$\text{Modulus} = \sum_{j=1}^{8} \gamma_j \left(E_g \left(\frac{(\tau_j \text{ x } f)}{(\tau_j \text{ x } f) + 100} \right) + E_e \left(\frac{100}{(\tau_j \text{ x } f) + 100} \right) \right)$$

Equation 1. Modulus of a viscoelastic polymer.

Equation 2 can be used to calculate the maximum energy loss as a function of frequency by selecting the appropriate τ_j values for any temperature of interest.

$$\text{Energy Loss} = \sum_{j=1}^{8} \gamma_j \left(\tfrac{1}{2} E_g \sin^2(2\pi \, (\tau_j \text{ x } f)) \right)$$

Equation 2. Energy loss of a viscoelastic polymer.

3.0 Heterogeneity of Amorphous Polymers

The vast majority of solids are crystalline. Within a crystal lattice, all like constituents have the same bond length and near neighbor environment. The homogeneity of unit cell structure results in a uniform chemical potential (μ), and the melting point therefore occurs at a distinct temperature. Sharp melting temperatures do not indicate crystallinity, since thermodynamic theory makes no assumptions regarding the nature of the assembly of constituents that form the solid. Instead, sharp transition temperatures indicate a uniform chemical potential.

Many synthetic polymers have irregular chain segments that will not fit into a lattice. Because the material cannot solidify with a uniform bonding arrangement, it vitrifies into an amorphous "glass" with a range of structures. The first cells to vitrify will have high order, but we would expect a decrease in order upon further cooling as ideal arrangements become less available. The chemical potential of both the glass phase (μ_g) and the elastomer phase (μ_e) vary from cell to cell.

The chemical potential controls the phase transition behavior of substances. With an increase in temperature, a glass phase cell in an amorphous polymer will change to elastomer when the values of μ_g and μ_e become equal. The cell selects whichever phase has a lower value of μ. The transition of a general T_j cell is shown in the left graph in Figure 4. During heating from below T_j, the cell is a glass and follows the solid line. At temperature T_j, the elastomer phase has a lower μ, so the material in this cell changes phase and follows the dashed line. This is a typical first order transition, with a latent heat and a discontinuity in molar volume, not fundamentally different from a melting point (except that the cells are nanoscale). Amorphous polymers, having a range of μ values in both glass and elastomer phases, transition over a range of temperature (the glass transition). To be clear, each cell has a sharp transition temperature. This is shown in the right graph of Figure 4. An amorphous polymer would have innumerable glass-to-elastomer intersecting μ curves during the glass transition. To allow calculation of modulus and loss, the elastomer was modeled with only eight cells, four of which are indicated in the figure. T_1 cells have the lowest transition temperature and T_8 cells have the highest.

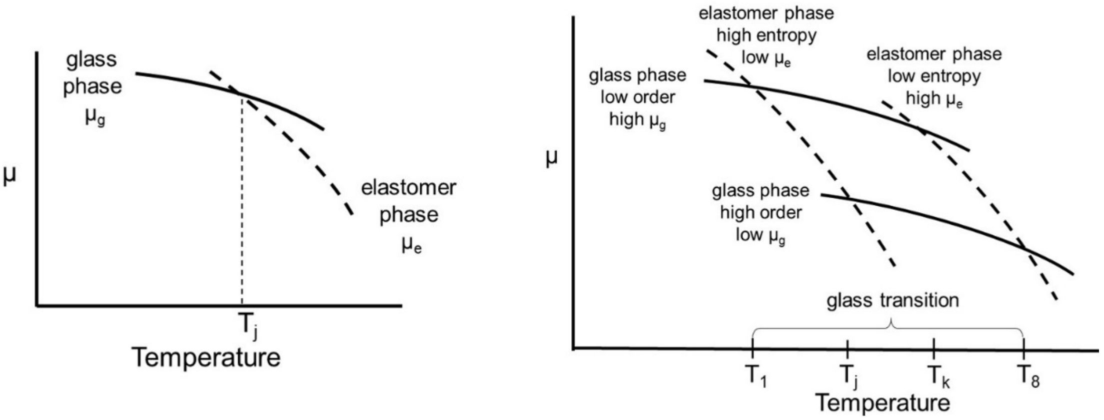


Figure 4. A phase transition occurs when the values of μ for the two competing phases are equal.

Solid (glass) phase polymer is heterogeneous because the molar bond enthalpy varies from cell to cell. The distribution in order results in a distribution in glass phase chemical potential. The value of μ_g decreases as the order increases. Liquid (elastomer) phase is heterogeneous because the molar entropy varies from cell to cell. The distribution in entropy results in a distribution in elastomer phase chemical potential. The value of μ_e decreases as entropy increases. Entropy increases with segment molecular weight and with the flexibility of the polymer chain. (Flexibility in this context refers to the ease of covalent bond rotation. The model polymer has a hydrocarbon ether backbone, among the most flexible of polymers.)

Since glass phase enthalpy and elastomer phase entropy both contribute to the common value of μ at the phase transition, this common value of μ cannot be used to designate the cell type (as evident by inspection of Figure 4.) For this reason, cell types are represented by the observed transition temperatures, T_j.

In summary, amorphous polymers are viscoelastic and have a broad glass transition because they are composed of innumerable small cells of varying chemical potential.

4.0 The Deborah Number, D_e

The Deborah number, D_e, is typically defined as the ratio between the relaxation time and the timescale of the deformation [7]. In the phase fluctuation theory of viscoelasticity, we do not attribute time-dependent behavior to a relaxation time. Instead, the Deborah number relates a time-dependent *structure* to a time-dependent test. Specifically, D_e is defined herein as the ratio of the period of phase fluctuation (τ) to the period of deformation (1/f), given in Equation 3.

$$D_e = \left(\frac{\tau}{1/f}\right) = (\tau \text{ x } f)$$

Equation 3. An expression for the Deborah number, D_e.

The Deborah number (which is not single-valued as in legacy theory, but instead varies over several orders of magnitude from cell to cell) is the number of strain cycles imposed on the glass phase for every emergence of the elastomer phase. It is for this reason that a cell will respond as a glassy polymer when $(\tau \text{ x } f) >> 1$. The same cell will respond as an elastomer at lower frequency or higher temperature, under any conditions in which $(\tau \text{ x } f) << 1$. As discussed at length in this paper, energy is lost when $(\tau \text{ x } f) = 0.1\text{-}10$.

Three values of τ are depicted in Figure 5, a decade apart. The three values could either represent a single cell at three different temperatures (with the temperature increasing from the upper depiction to the lower), or three consecutive T_j cells (for example, T_3, T_4, and T_5 from lower to upper) at the same temperature.

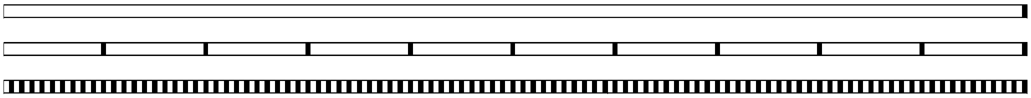


Figure 5. Phase fluctuation, with glass phase shown in white and elastomer phase in black.

It is difficult to illustrate phase fluctuation over more than two orders of magnitude of τ. However, the Deborah number can be illustrated over several orders of magnitude by changing the scale of the test frequency plots, as in Figure 6. Each diagram shows the relationship between the period of phase fluctuation and the frequency of test. The diagrams can represent a cell tested at constant temperature, with frequency increasing from the lower pair to the upper, or they can represent a cell tested at constant frequency, with temperature increasing from upper to lower.

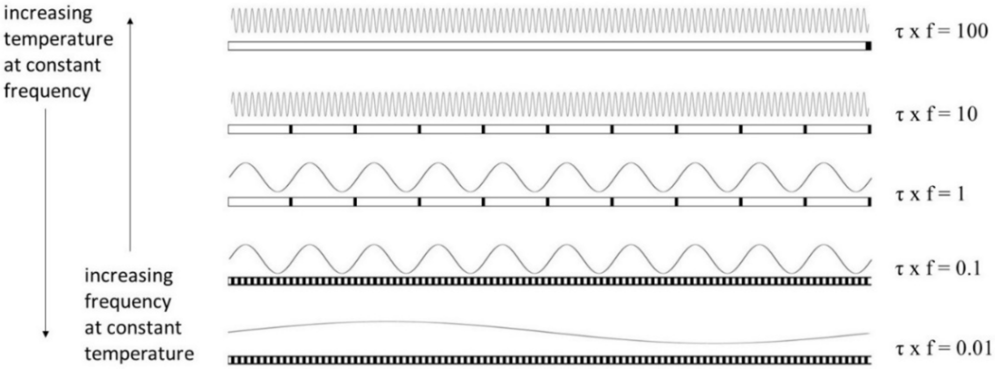


Figure 6. Illustrations of the Deborah number, (τ x f).

4.1 Determination of the Spectrum of τ_j

The modulus vs. temperature curve for the model polyurethane elastomer is given in Figure 7. This curve was measured at 1 Hz on a TA Instruments Q800 Dynamic Mechanical Analyzer.

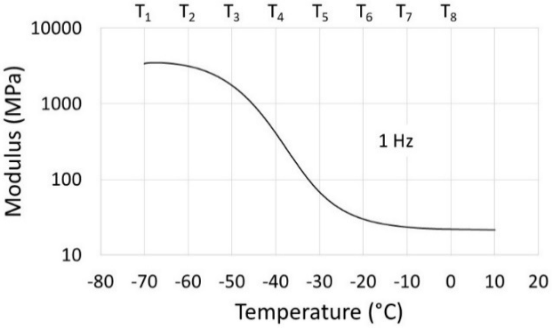


Figure 7. Modulus vs. temperature for the model elastomer at 1 Hz.

In the phase fluctuation theory of viscoelasticity, if the modulus changes with temperature or frequency, only cells with (τ x f) = 0.1-10 change how they respond to an imposed strain. These are the "transition cells", as identified in Figure 7. For example, using the τ_j values in Figure 3, if the material is at -40 °C and the temperature is increased during a 1 Hz cyclic strain, changes in response of the T_4 cells dominates the observed modulus reduction. All remaining cells continue to respond either as glassy or elastomeric. The response of the material changes cell-by-cell as (τ x f) assumes a value in the 0.1-10 range.

At -80 °C, all the cells respond with a glassy modulus, so $(\tau \times f) \geq 10$. Since the frequency is 1 Hz, the value of τ for all cells must be ≥ 10 seconds. As the temperature increases to -70 °C, there is a slight modulus reduction. The cells with the lowest transition temperature, designated T_1, begin to strain while in the elastomer phase. Therefore, in Figure 8, we set τ_1 = 1 second at -70 °C for T_1 cells, such that (τ x f) = 1. The remaining cells continue to spend most of their time in the glass phase. (For example, the T_8 cells fluctuate to the elastomer phase only once every 4 months at -70 °C.)

With an increase in temperature to -60 °C, the T_2 cells begin to test as elastomeric, resulting in further drop in modulus. Since the T_2 cells are the transition cells at -60 °C, τ_2 = 1 second at this temperature. This process is continued until at 0 °C, all cells are elastomeric at 1 Hz. Values of

τ_j as a function of temperature are thus determined for each of the eight T_j cells, based on how the material responds to deformation within a one-second period of observation. These are shown outlined on the diagonal in Figure 8.

	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8
T (°C)	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	τ_7	τ_8
-80	10^1	10^2	10^3	10^4	10^5	10^6	10^7	10^8
-70	10^0	10^1	10^2	10^3	10^4	10^5	10^6	10^7
-60	10^{-1}	10^0	10^1	10^2	10^3	10^4	10^5	10^6
-50	10^{-2}	10^{-1}	10^0	10^1	10^2	10^3	10^4	10^5
-40	10^{-3}	10^{-2}	10^{-1}	10^0	10^1	10^2	10^3	10^4
-30	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^0	10^1	10^2	10^3
-20	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^0	10^1	10^2
-10	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^0	10^1
0	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^0
10	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}
20	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}
30	10^{-10}	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	10^{-4}	10^{-3}

Figure 8. The values of τ_j (in seconds) for the representative polyurethane elastomer.

On the right in Figure 9 we show the "master curve", a prediction of modulus as a function of frequency. The master curve is plotted adjacent to modulus vs. temperature to highlight time-temperature superposition (TTS). Actual dynamic mechanical analysis (DMA) testing was done over a range of frequency between 0.1-20 Hz from -50 °C to 50 °C in increments of 10 °C. These data are shifted to lower and higher frequencies, at a reference temperature of 10 °C, using the well-known TTS protocol [8]. At low frequencies, 10^{-3}-10^0 Hz, every cell can respond as an elastomer. However, beginning at 10^1 Hz, the modulus begins to increase. We can therefore associate 10^1 Hz and 10 °C with the highly ordered T_8 cells, fluctuating at $\tau = 0.1$ seconds such that $D_e = (\tau \times f) = 1$. Further, at 10^2 Hz, the T_7 cells begin to exhibit a glassy response and become the transition cells. So, at 10 °C, $\tau_7 = 0.01$ seconds. This trend continues until at 10^8 Hz, the value of τ for T_1 cells is estimated at 10^{-8} seconds. Thus, the temperature dependence of τ causes time-temperature superposition: properties of T_1 cells at -70 °C and 1 Hz are equivalent to those at 10 °C and 10^8 Hz because the value of $(\tau \times f)$ is the same. The values of τ at 10 °C are outlined with a double line in Figure 8. The remaining values are then estimated by extrapolation, as indicated.

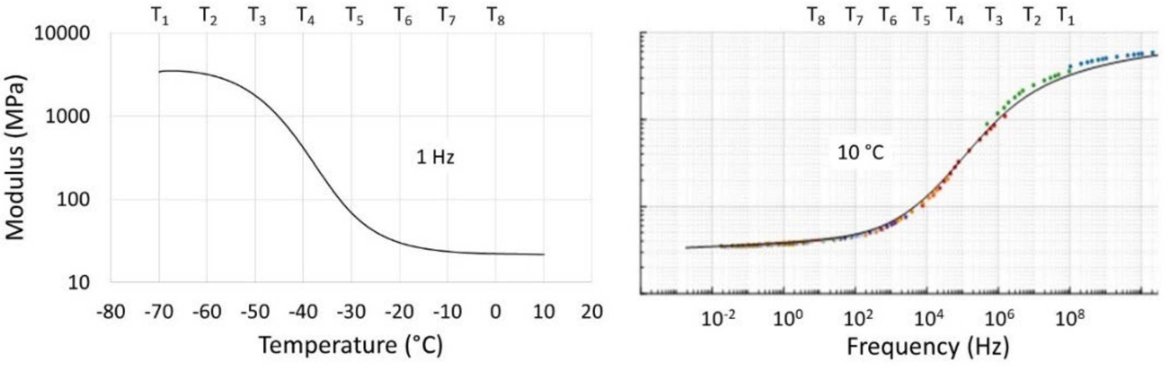


Figure 9. Time-temperature superposition.

5.0 Time-Dependent Modulus

We are interested in why the modulus of amorphous polymer changes as the frequency of test changes. In reference to Figure 6, we consider a cell during cyclic deformation with frequency increasing from the lower pair to the upper. During a single loading cycle at (τ x f) = 0.01, the cell fluctuates to the elastomer phase 100 times. The low modulus of the elastomer phase dominates the strain, so the cell responds as an elastomer. An expanded view of a similar condition is provided in Figure 10, where the value of (τ x f) = 0.03. The glass phase is strained for only 0.03 of a cycle for every emergence of the elastomer phase.

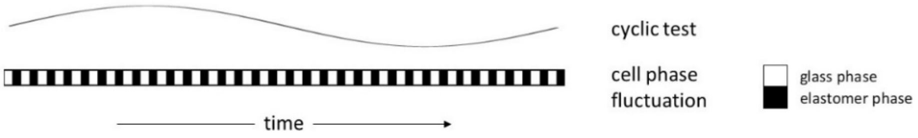


Figure 10. Typical (τ x f) condition for an elastomeric response.

As test frequency increases for this same cell, more of the strain must occur by intermolecular bond deformation while the cell is glassy. This is illustrated in Figure 11 for (τ x f) = 20. Considering a cyclic strain at the frequency shown, a cell fluctuating between glass and elastomer phases at the period indicated would respond as a glassy polymer. There are 20 glass phase cycles for every emergence of the elastomer phase. This emergence would reduce the time average modulus only slightly.

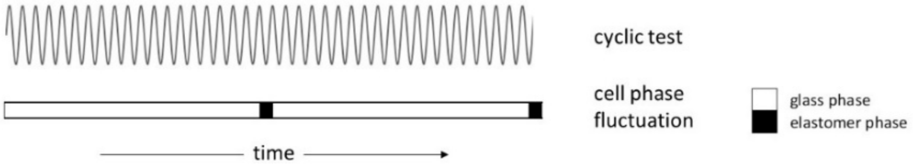


Figure 11. Typical (τ x f) condition for a glassy response.

5.1 Time-Dependent Modulus Calculation

The predicted value of Young's modulus as a function of test frequency is given in Equation 1. It is a rough estimate, offered in lieu of an expression developed by finite element analysis of a network of cells.

For our representative polyurethane, the modulus of the glass phase is 3500 MPa and that of the elastomer phase is 35 MPa. Equation 4 is the predicted value of modulus (E) of the material given these phase properties. The expression within the outer parentheses is for individual cell moduli. During the glass transition, the eight (T_1 - T_8) cell types will, in general, respond to a cyclic strain with a different modulus. The range in modulus over the eight T_j cell types is caused by the range in τ_j.

$$E = \sum_{j=1}^{8} \gamma_j \left(3500 \left(\frac{(\tau_j \text{ x f})}{(\tau_j \text{ x f}) + 100} \right) + 35 \left(\frac{100}{(\tau_j \text{ x f}) + 100} \right) \right)$$

Equation 4. Modulus (in MPa) for the representative polyurethane elastomer.

The material responds to deformation with a high, glassy modulus and low strain for (τ_j x f) cycles (or fraction of a cycle for (τ_j x f) < 1) until the cell changes phase. The stress in the cell then drops to zero, the strain energy is lost, and the cell responds with a low, elastomeric modulus and high strain. We do not have sufficient theory to estimate the duration of the individual phases, but as discussed in Section 8, propose that τ is dominated by the glass phase. Although we cannot model phase duration, we can reasonably assume that the value of (τ_j x f) determines an effective time-averaged volume fraction of the two phases. We therefore model a T_j cell, fluctuating between the glass and elastomer phases with period τ_j, to have the effective volume fractions of the two phases given in Equation 5. The temperature dependence of these fractions is caused by the temperature dependence of τ_j.

$$\left(\frac{(\tau_j \text{ x f})}{(\tau_j \text{ x f}) + 1}\right) \text{ glass phase volume fraction of } T_j \text{ cells} \qquad \left(\frac{1}{(\tau_j \text{ x f}) + 1}\right) \text{ elastomer phase volume fraction of } T_j \text{ cells}$$

Equation 5. Effective volume fractions of the two phases during a cyclic test.

The effective volume fractions can be used to predict the cell modulus in two basic ways. If the fluctuating cell is considered to be at the same stress before and after the transition, the elastomer phase strain is 100X that of the glass phase strain due to the ratio of their respective moduli. Applying this condition, shown at left in Equation 6, yields a prediction similar to a Maxwell model. As indicated in Equation 4, we have applied this equal stress condition for transitioning cells. (To be clear, Equation 4 models the temperature and frequency dependence of a fluctuating cell as (τ_j x f) glassy springs in series with 1 elastomeric spring.) Alternatively, one could model the two phases of a transitioning cell to have the same strain. In this condition, the predicted cell modulus would be similar to that of a Kelvin model, given at right in Equation 6. (That is, (τ_j x f) glassy springs in parallel with 1 elastomeric spring.) The Maxwell model would predict the lower bound value, and the Kelvin model the upper bound value. The calculation could be modified by replacing the "100" in the Maxwell model with a value intermediate between 1 and 100. For example, if "2" were selected, the equation would model a transitioning cell in which the elastomer phase strain was 2X that of the glass phase strain.

$$E = \left(3500\left(\frac{(\tau_j \text{ x f})}{(\tau_j \text{ x f}) + 100}\right) + 35\left(\frac{100}{(\tau_j \text{ x f}) + 100}\right)\right) \qquad E = \left(3500\left(\frac{(\tau_j \text{ x f})}{(\tau_j \text{ x f}) + 1}\right) + 35\left(\frac{1}{(\tau_j \text{ x f}) + 1}\right)\right)$$

glass and elastomer at equal stress, "Maxwell model" glass and elastomer at equal strain, "Kelvin model"

Equation 6. Phase fluctuation theory interpretation of the Maxwell and Kelvin models.

The material modulus is calculated using the rule of mixtures, which is a summation over the eight individual cell moduli. In the rule of mixtures, the contribution of each cell type (T_j) to the material modulus is a function of its volume fraction (γ_j).

Modulus is a function of temperature during the glass transition because the values of τ_j are a function of temperature. (Modulus is not a function of temperature above the transition because (τ x f) is < 1 for all cells at the test frequency, or below the transition because (τ x f) is > 1 for all cells.) Therefore, to calculate the modulus with Equation 4, one must select a reference temperature. In this example, we have selected 10 °C. The values of τ for each cell are given in Figure 8. The modulus (E_j) of each of the 8 T_j cells are first computed (in a spreadsheet) as a function of frequency using the appropriate values of τ_j at 10 °C. The sum of the 8 individual moduli is then calculated using the rule of mixtures: $E = \sum_{j=1}^{8} E_j \gamma_j$, where γ_j are the volume fractions of the 8 T_j cells. The calculated modulus as a function of frequency, at a reference temperature of 10 °C, is given in the left graph Figure 12. The predicted curve matches reasonably well with the curve generated using the DMA TTS protocol, shown as the right graph in Figure 9. The modulus as a function of frequency can be calculated at any temperature. In the right graph, Equation 4 was used to predict the modulus vs. temperature curve between -50 °C and 50 °C.

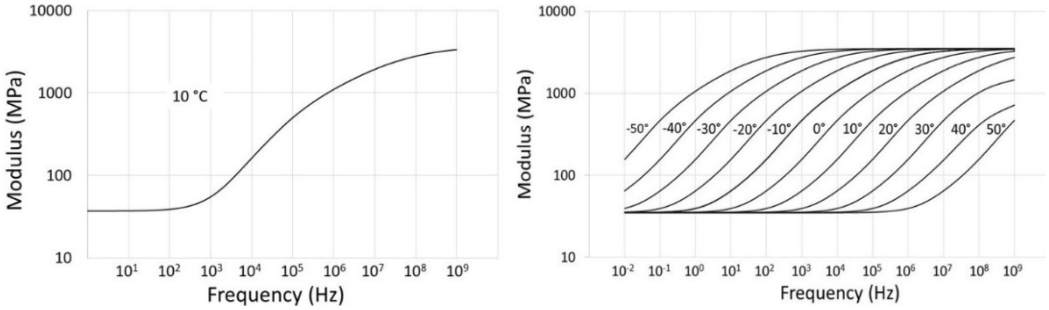


Figure 12. Calculated modulus vs. frequency of the polyurethane elastomer.

The behavior of the 8 individual cells (at 10 °C) is shown at left in Figure 13. It is clear how the material modulus increases cell-by-cell as the value of (τ x f) become equal to 1. Characterizing the material heterogeneity with only 8 homogeneous cell structures results in a smooth curve because the transition from elastomeric to glassy properties occurs over 3 orders of magnitude of frequency. At right in Figure 13, the moduli of the 8 individual cells are adjusted for volume fraction as $E_j\gamma_j$. The contribution to the modulus from cells T_1, T_2, T_7, and T_8 are relatively low because the volume fractions of these cells are low. The rule of mixtures sum of the 8 cell moduli is given as the solid line in both graphs.

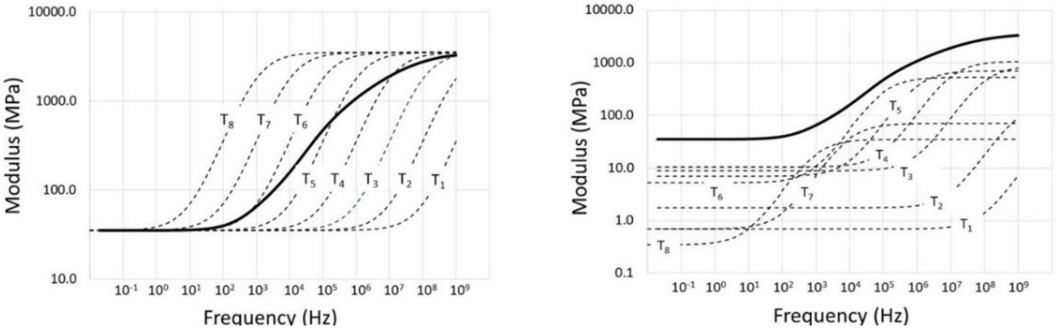


Figure 13. Calculated modulus vs. frequency of the individual cells in the polyurethane elastomer at 10 °C.

6.0 Temperature-Dependent Modulus: The Glass Transition

The modulus as a function of temperature for our model polyurethane is given in Figure 7. A polymer responds with a high modulus if, during the period of observation, all cells spend most of their time in the glass phase. With heating, a temperature is reached, cell-by-cell, at which polymer segments spend most of their time in the elastomer phase. Thus, the modulus decreases over a range of temperature as the value of the Deborah number (τ x f) approaches 1 for each cell type. The cell-by-cell glass transition for our model elastomer (measured at 1 Hz) is illustrated in Figure 14. It shows the network of cells in Figure 2 as a function of temperature. The T_1 cells are the first to respond as elastomeric, and the last are the highly ordered T_8 cells.

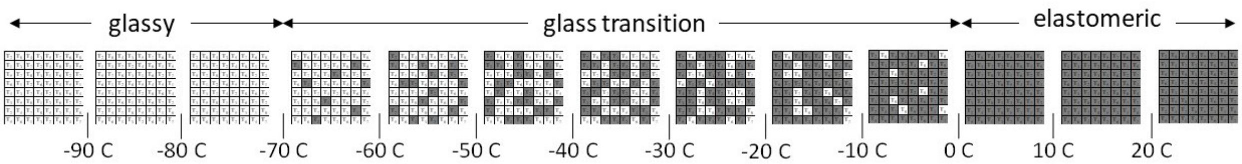


Figure 14. The phase fluctuation model of the glass transition.

It is common to represent the glass transition with a single temperature. The "glass transition temperature" (T_g) is typically measured using a period of observation of about 1 second. If we define the T_g as the temperature at maximum loss, then the T_g is the temperature at which the highest volume fraction of cells meets the condition $\tau_j = 1/f$. For our model polyurethane, the T_4 and T_5 cells have the highest volume fraction. Using the τ_j values in Figure 8 for these cells, the T_g of the model polyurethane at 1 Hz is -35 °C. Because the phase fluctuates, the transition temperature of each cell depends on the period of observation (1/f), and occurs when $1/f = \tau_j$. For example, at 10^5 Hz, using the τ_j values for the T_4 and T_5 cells, the T_g is 15 °C.

To our knowledge, depiction of the glass transition as in Figure 14 is novel, and at variance with currently held beliefs. It is outside the scope of this paper to discuss these differences in detail. However, the glass transition and viscoelastic behavior are inseparable, so it would be appropriate to provide a brief summary. The glass transition is generally explained as a gradual increase in segmental mobility with an increase in temperature [1-3,7,9,10]. Mobility is associated with the ease of viscous flow. We note in particular that homogeneity is assumed, which is a fundamental difference between the two descriptions. So, in Figure 15, we show a series of homogeneous states of intermediate mobility during the transition. The author does not wish to misrepresent the legacy theory, but this is the interpretation developed from published literature. There is no mention in the referenced works of a phase-separated structure. Therefore, we indicate chain mobility as gradually increasing with temperature as shades of gray.

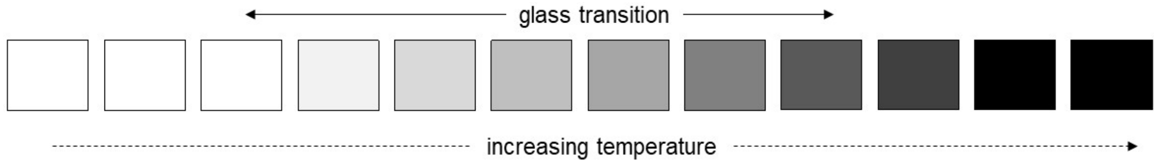


Figure 15. The legacy model of the glass transition.

Equation 4 can be used to calculate the modulus as a function of temperature, similar to the method used to calculate modulus vs. frequency. For this calculation, the value of f is set at a reference frequency. We have chosen 1 Hz. The contribution to the modulus from each cell is first calculated as a function of temperature (in a spreadsheet) using the value of τ_j for the given T_j in Figure 8. The sum of the 8 individual moduli is then calculated using the rule of mixtures: $E = \sum_{j=1}^{8} E_j \gamma_j$. This summation is plotted in the left graph of Figure 16. There is a discrepancy between predicted and measured values, as indicated. However, given the simplicity of the assumptions used throughout, the general trend is in good agreement with data. The modulus as a function of temperature can be calculated at any frequency. In the right graph, Equation 4 was used to predict the modulus vs. temperature curve at 10 Hz and 0.1 Hz for comparison with the predicted curve at 1 Hz.

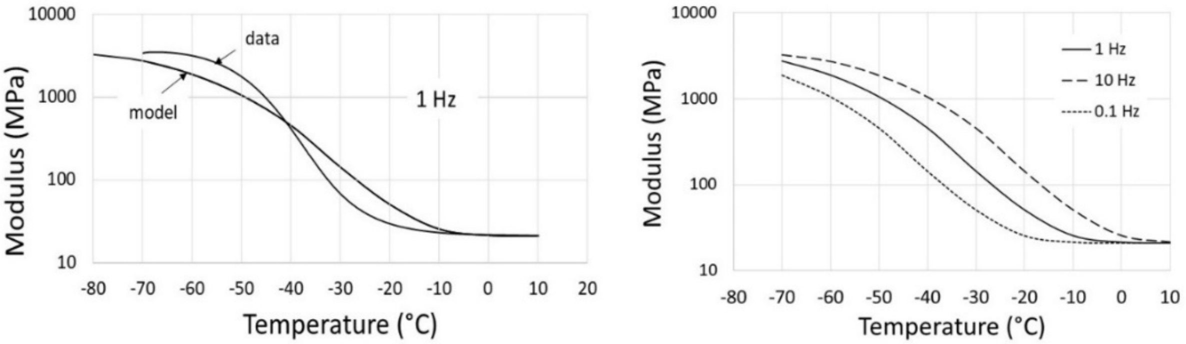


Figure 16. Calculated vs. measured modulus vs. temperature (left). Calculated effect of frequency on modulus (right).

7.0 Viscoelastic Loss

Individual cells of amorphous polymer can only respond to an imposed deformation by intermolecular bond strain in the glass phase, or by covalent bond rotation in the elastomer phase. Therefore, the response of a cell must fall on one of the two curves given in Figure 17. (The measured stress/strain curve is an average over all the cells.) Viscoelastic deformation occurs when a glassy cell under strain fluctuates to the elastomer phase, shown as the dotted line. The stress in the cell drops to zero after the phase change, and the strain energy in intermolecular bonds is lost.

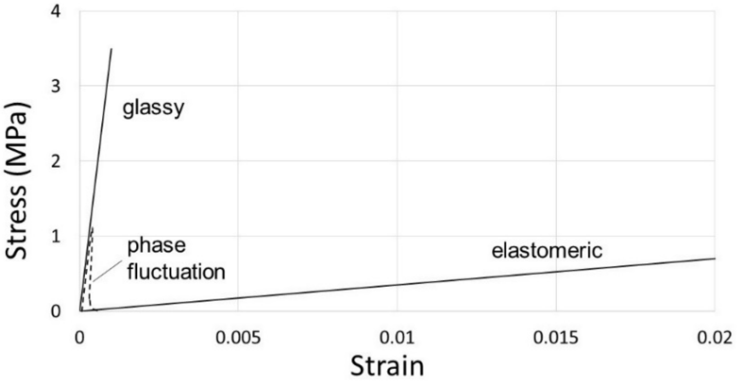


Figure 17. An illustration of the three possible responses of a cell to an imposed deformation.

7.1 The Mechanism of Energy Loss

We are interested in how energy is lost during deformation of an amorphous polymer. In the phase fluctuation theory, if a glassy cell under strain fluctuates to the elastomer, this work is lost. If the reservoir adds work to a glassy cell that does not phase fluctuate, the cell returns the work to the reservoir. However, if the cell fluctuates to the elastomer during the deformation, its strain energy cannot be returned as work. Instead, the energy must be returned as heat (of fusion) when the cell fluctuates back to glass phase.

7.2 Strain Rate Dependence of Energy Loss

Energy loss is only significant when the frequency of cyclic strain is comparable to the frequency of phase fluctuation, that is, when $D_e = (\tau \text{ x } f) = 0.1\text{-}10$. Below 0.1, there is very little energy stored in the glassy cells when they phase fluctuate, and above $(\tau \text{ x } f) = 10$, most of the glassy cell strain cycles do not experience a phase fluctuation.

The effect of strain rate on energy loss is illustrated in Figure 18 for $(\tau \text{ x } f) = 0.1$. In the figure, a cyclic strain is imposed on a fluctuating cell. Initially, energy is stored in the intermolecular bonds that form the glass phase. The glassy cell under strain then fluctuates to the elastomer phase, indicated by the asterisk, and the strain energy is lost. After the phase change, the stress in the transitioning cell drops to zero (as shown in Figure 17). When the cell returns to the glass phase and resumes loading, it is at zero strain, irrespective of the strain in the reservoir cells. As indicated in Figure 18, each transitioning cell changes phase multiple $(1/(\tau \text{ x } f))$ times during the strain cycle, and repeatedly lose energy. However, each phase transition does not dissipate the same amount of energy. For the transitioning cell, after each transition, the loading curve is the dashed line in Figure 18. Therefore, the level of stress in transitioning cells is proportional to $\Delta\sin \omega t/\Delta\omega t$. As a result, the amount of energy lost after the phase fluctuation is a function of the imposed strain rate, $\cos \omega t$. Energy is not dissipated continuously; it is dissipated in discrete events every τ seconds. With respect to an imposed cyclic deformation, $\omega t = \omega\tau = 2\pi (\tau \text{ x } f)$.

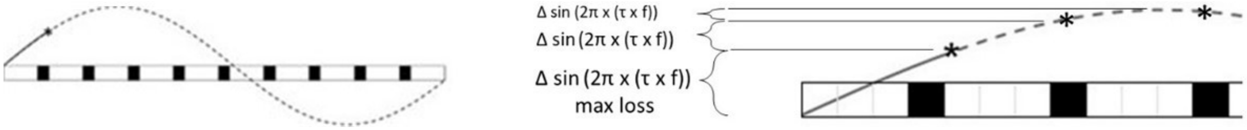


Figure 18. Schematic of the mechanism of loss vs. strain rate in viscoelastic polymers.

Since the level of stress in transitioning cells is a function of strain rate, and the level of stress in reservoir cells is a function of strain, the measured stress is out of phase with the strain. This well-known non-Hookean behavior, shown in Figure 19, is generally modeled with an arrangement of springs and dashpots. That a dashpot accurately models time-dependent behavior for both viscous loss and viscoelastic loss does not support the proposal that viscoelasticity involves a viscous flow. The common use of a dashpot only indicates that these two phenomena have the same mechanism of energy dissipation. Specifically, glassy cells form and disperse continually in elastomers, whether the elastomer is a cross-linked viscoelastic rubber or an uncross-linked viscous liquid. Considering the introduction of energy to a viscous liquid, such as a pressure that causes it to flow, transient glassy cells would be strained. If any fluctuate to the elastomer phase during the induced flow, the energy stored in the bonds would be lost irreversibly as heat (when the bonds re-form). Stated another way, the strain rate dependency of stress in a viscous liquid is shown in Figure 18. Energy is not lost by friction between molecules during the flow, it is lost by phase fluctuation just prior to the flow.

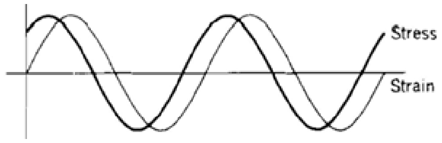


Figure 19. Phase lag between stress and strain during cyclic testing of viscoelastic polymers.

The expression for energy loss (in Joules/unit volume) for any cell is given in Equation 7. The glassy phase modulus of 3500 MPa is specific to our material. Note that $\Delta\varepsilon$ refers to the strain imposed on the glassy cell between phase fluctuations. Only glassy cells lose energy.

$$\text{Cell Energy Loss} = \tfrac{1}{2} E_g (\Delta\varepsilon)^2 = \tfrac{1}{2} (3500 \text{ MPa}) (\Delta\varepsilon)^2 = 1750 \text{ x } \Delta \sin^2(2\pi (\tau_j \text{ x } f))$$

Equation 7. The expression for energy loss in viscoelastic polymers.

Calculated energy loss (using Equation 7 in a spreadsheet) during a cycle at (τ_j x f) = 0.01 is provided in the left graph in Figure 20, together with the imposed strain. For the material in Figure 8, tested (for example) at 20 °C and 100 Hz, this would be the loss response of the T_6 cells, since $\tau_6 = 10^{-4}$ seconds. Each dot in the loss curve is the amount of energy lost in one of the 100 phase fluctuations that occur during the 10^{-2} second period of the cycle. As indicated in Figure 18, the amount of energy lost is determined by the strain rate between consecutive fluctuations. At (τ x f) = 0.01, very little energy is lost per cycle (a maximum value of 6) because the cell fluctuates to the elastomer phase before much strain energy can be stored in the glass phase. However, there is some glassy cell loading, so elastomers are slightly lossy in (τ x f) << 1 conditions.

Energy lost during a cycle in any cell for which (τ x f) = 0.1 is plotted in the right graph of Figure 20. For these cells, there are 10 phase fluctuations every cycle, thus there are 10 loss events per cycle. The maximum value of loss is significantly higher than cells with (τ x f) = 0.1. Energy stored in glassy elastic cells is also plotted in the figure. The level of energy stored elastically is normalized to $\varepsilon = 1$, so the maximum value is ½ E_g, or 1750. (Only relative values of energy stored and lost are relevant, so no units are given.) The maximum amount of energy lost, which occurs at the highest strain rate, has a value of about 600 (1750 sin^2 (2π x 0.1)).

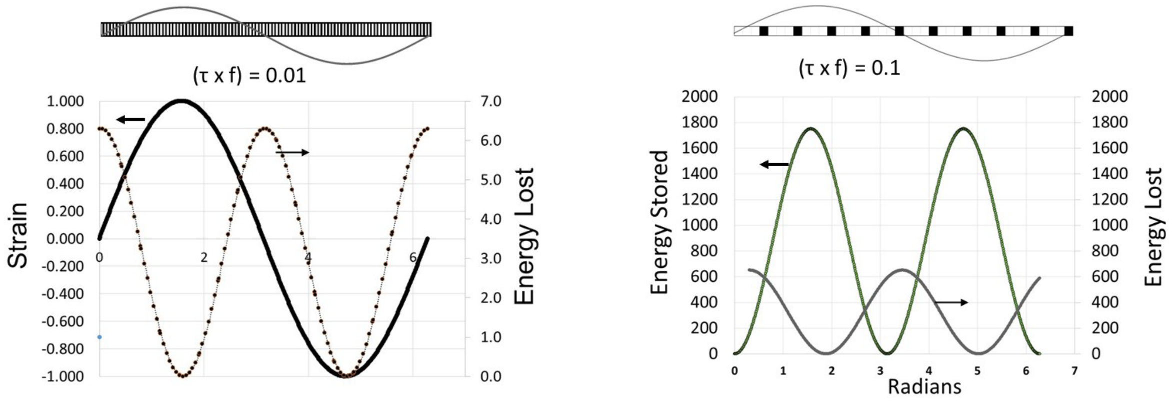


Figure 20. Energy lost vs. radians for (τ x f) = 0.01 (left) and 0.1 (right).

Calculated energy loss curves are plotted at various values of (τ x f) in Figure 21 to show how loss increases with the Deborah number, (τ x f).

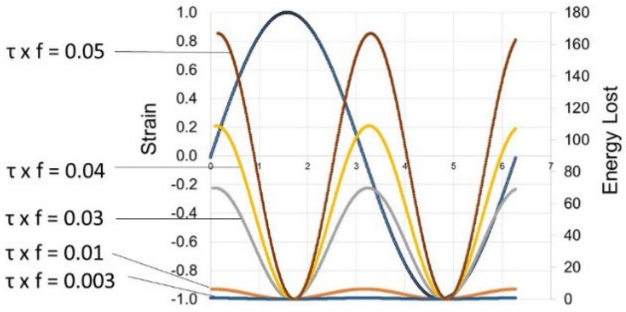


Figure 21. Imposed strain and energy lost vs. radians as a function of the Deborah number (τ x f).

From inspection of the predictions in the last two figures, it is clear that the amount of energy lost per cycle increases with (τ x f), and would be expected to reach a maximum value at (τ x f) ≈

1. However, the phase fluctuation model breaks down when (τ x f) approaches 1. When (τ x f) = 0.13, the maximum loss is 875 and it occurs 90° out of phase with the imposed strain. At (τ x f) = 0.25, the model predicts a higher maximum loss (1750), but the loss is not 90° out of phase. Instead, loss depends on the timing between the imposed strain and the phase fluctuation. At (τ x f) = 0.5, the model predicts very high values of loss (3500), that peak in phase with the strain. (3500 is the maximum possible value. It would occur if a cell transitions to the glass phase and begins loading when sin ωt = -1, and then transitions to the elastomer at sin ωt = 1, losing all the stored energy at this strain. This indicates that the maximum loss factor of a cell = 2.)

The model of phase fluctuation assumes a constant value of τ. In addition, we do not assign individual durations for each of the two phases, but instead assume that the glass phase dominates the value of τ. Thirdly, kinetics is not considered, such that phase changes are assumed to occur instantaneously. Finally, the possibility of strain-induced transitions is not considered. These shortcomings in the phase fluctuation theory significantly limit prediction of energy loss.

Using the model in its current state of development, the peak energy loss per cell is calculated on a spreadsheet as 1750 sin^2(2π x (τ x f)) up to value of 1750 at (τ x f) = 0.25. The value of loss is then set at 1750 for (τ x f) = 0.25-1. Above (τ x f) = 1, loss is again calculated, as 1750/(τ x f). The rationale for the latter relation is that 1750 is taken as the maximum loss per cycle for transitioning cells, and 1/(τ x f) is the number of times this loss occurs per cycle. The calculated rule of mixtures sum of the peak energy loss per cycle from all 8 cells is plotted at left in Figure 22, together with the calculated modulus. The energy loss is shown cell-by-cell in the right graph of Figure 22, T_8 to T_1, from left to right. The areas in which the loss plateaus correspond to the set value of 1750.

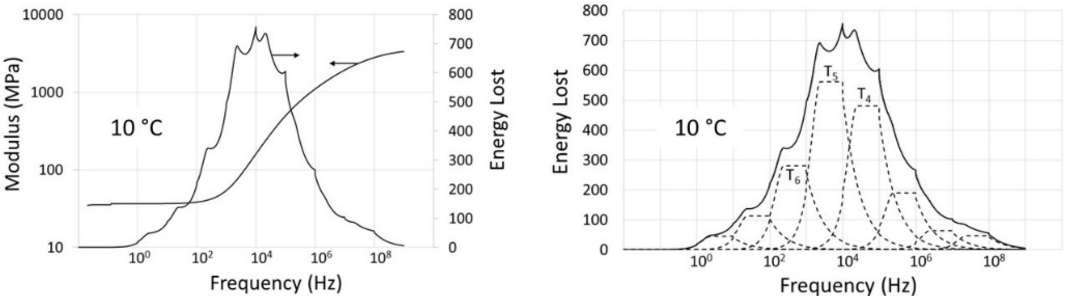


Figure 22. The modulus and loss as a function of frequency for the representative polyurethane elastomer.

7.3 The Distribution in T_j

Loss curves have the appearance of distributions. Materials with high peak loss have narrow curves, as indicated Figure 23. As can be seen from inspection of the curves (selected from the author's database), or any of the numerous tan δ plots in the literature, some loss curves are symmetric, some are skewed. In the phase fluctuation theory, the loss curve (tan δ) is taken to approximate the distribution in volume fraction of cells of common transition temperature, T_j.

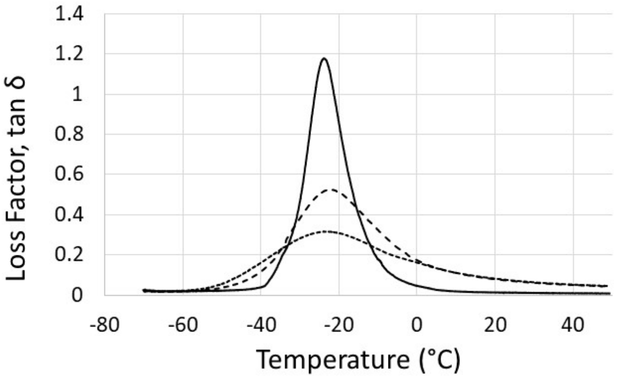


Figure 23. Representative loss curves.

The loss curve for the model polyurethane, measured at 1 Hz, is provided at left in Figure 24. The volume fraction of each of the 8 cells was determined as the value of loss at each T_j divided by the sum of all values, and re-plotted at right. These are the values of γ_j used in the modulus and loss calculations. For this material, the T_4 and T_5 cells have the highest volume fraction. The T_g is defined herein as the temperature at which (τ x f) = 1 for the highest volume fraction of cells, which for our model polymer is between T_4 and T_5. (We note that the schematic of the glass transition in Figure 14 has all eight cell types represented in equal volume fractions. The transition would be more effectively illustrated with the distribution in Figure 24.)

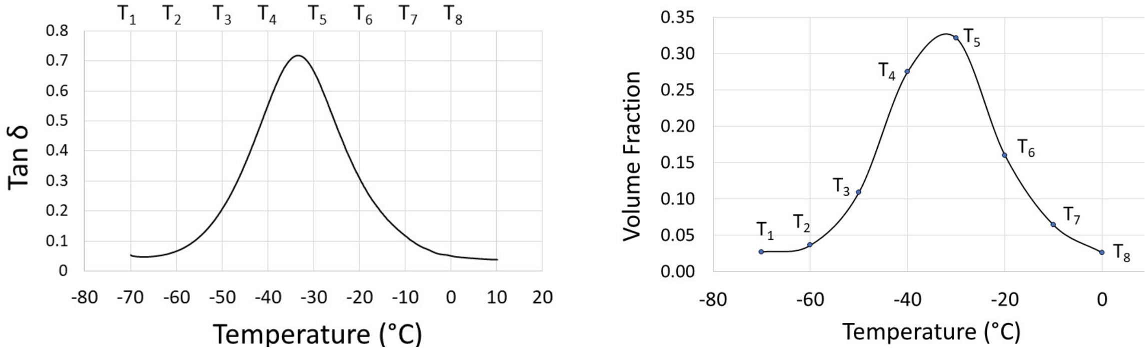


Figure 24. The loss curve, tan δ, is a measure of the distribution in T_j.

8.0 Fluctuations

We have shown that engineering predictions of modulus and loss are consistent with deformation of a network of cells whose phase fluctuates between glass and elastomer. The proposal that amorphous polymers have a time-dependent phase may be difficult to accept, however, it explains a great deal of unusual behavior. In particular, phase fluctuation explains why a rubber band is elastomeric at low deformation rates, lossy at intermediate rates, and has the properties of a glass at high rates.

Fluctuations in thermodynamic quantities are common in all substances [11-18]. They are not noticeable for large domains because the difference between mean and fluctuating values is negligibly small. However, fluctuations in thermodynamic quantities become increasingly significant as the size of the body decreases [11,14,17]. Because amorphous polymers do not crystallize, they are heterogeneous on a fine scale. (For example, for cell lengths of 1-10 nm, as shown in Figure 2, a cubic centimeter of material would contain 10^{18}-10^{21} cells. Using the smaller dimension, a 1 nm^3 cell in a hydrocarbon elastomer would contain about 40 methylene groups.) A consequence of the small cell size is that the difference between the instantaneous and mean values of energy is not negligible. As a result, (we have proposed that) energy fluctuations cause phase transitions. This proposal appears to be supported by a theoretical prediction of oscillatory phase behavior in small systems [19].

8.1 A Proposed Description of Phase Fluctuation

Regarding the nature of energy fluctuations in amorphous polymers, we note the unusual behavior of conformational changes. Conformational changes are caused by covalent bond rotation, as shown for butane in Figure 25. From left to right, the conformations are "trans", gauche$^+$, gauche$^-$, then back to trans. Butane represents a section of a hydrocarbon polymer chain, for which the pendant methyl groups would be replaced by "R". In polymers, these kinetic motions can only occur in the elastomer phase, and as mentioned, are responsible for both the high entropy and the low modulus of rubber. They are unusual kinetic motions in that bonds rotate in a stop-start manner, pausing in one of the three conformational isomers shown in the figure. (To be clear, each 120° rotation occurs in a random direction.)

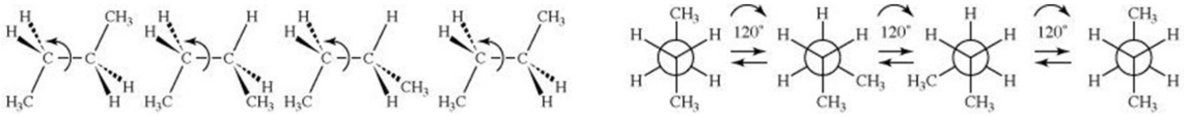


Figure 25. Rotation about carbon-to-carbon bonds distinguish the elastomer phase of polymers.

Bond rotations are not characterized by a frequency (like bond vibrations), but are instead characterized by probabilities as a function of time. Molecular dynamics models for hydrocarbons generally report the isomerization time in the range 10^{-10}-10^{-11} seconds [20]. Measured values are in the same range [21]. Covalent bond rotation is difficult to appreciate, because in spite of the fact that each bond rotates 10^{10}-10^{11} times every second, these bonds spend most of their time at rest in either a trans or gauche conformational isomer. To be specific, 1 cm^3 of elastomer would contain about 10^{22} in-chain covalent bonds, each of which rotate 10^{10} times per second. Thus, there are ~10^{32} bond rotations/second, even though each bond spends most of its time paused at equilibrium. (Due to the extended time at equilibrium, the glass phase is shown dominating τ in the illustrations of phase fluctuation in this paper.) Given the nature of bond rotation, and their importance to viscoelasticity, we should not expect a theory of time-dependent deformation to have intuitive appeal.

Molecular dynamics modeling is generally done on single, isolated small molecules in solution or the gas phase. We are focused instead on condensed, high molecular weight polymers. Specifically, we consider a covalent bond that is part of a chain segment in an elastomer phase, at equilibrium in one of the isomers while in close contact with neighboring segments. Regarding a description of phase fluctuation, we propose the following: the energy of a cell is temporarily low during the periods that covalent bond rotation is paused in an isomer. For a small cell, this is a large decrease in energy. While at equilibrium in an energy minimum, the stabilized microstate allows intermolecular bonds to form, serving to nucleate and grow a glass phase. The probability of glass phase nucleation would increase with a decrease in temperature, which supports the observed temperature dependence of τ_j. In addition, due to heterogeneity and the distribution in μ, some chain segment neighborhoods are more conducive to formation of the glass phase than others. This transition would liberate energy as the latent heat, thus transferring the fluctuation to adjacent cells. This flux of energy into glassy cells increases the probability of their transition to the elastomer phase. Phase fluctuation from elastomer to glass in one cell causes a corresponding fluctuation from glass to elastomer in another.

The minimum duration of the fluctuating phase (τ) is proposed herein at about 10^{-8} seconds. This period may seem prohibitively brief, but it becomes more believable when considering molecular timescales. Conformational changes are fast when judged by macroscopic processes, but they are slow relative to other molecular activities. In addition to bond rotation, there is substantial kinetic motion in bond vibration. The frequency of vibration is ~10^{14} Hz [22]. If bond vibration were envisioned to occur at 1 Hz, elastomers would have only one conformational change every 3 hours, but otherwise be at rest. Further, there would be 12 days between phase fluctuations at the minimum value of τ.

9.0 The Legacy Theory of Time-Dependent Properties

The legacy theory of viscoelasticity characterizes amorphous polymers as viscous liquids, and proposes that deformation of a polymer during its glass transition causes an actual viscous flow [1-9]. The amount of time required for the flow to relieve the imposed stress is called the relaxation time. We note that the concept of a single relaxation time reflects the assumption of material homogeneity indicated in Figure 15. Since viscosity decreases as temperature increases, relaxation time also decreases with temperature increase. This is the accepted explanation for time-temperature superposition. Molecules are assumed to have molecular friction coefficients characteristic of a given backbone chemistry [2], which result in dissipation of energy during the flow. Thus, “molecular friction” is thought to be the mechanism of energy loss during deformation of a viscoelastic solid.

Williams, Landel, and Ferry reported the existence of a universal relation between the temperature and time of relaxation processes for glass forming liquids near their T_g [1]. The relation uses a shift factor, a_T, which is the ratio of relaxation time at temperature T to the relaxation time at T_g. The WLF equation, $\log a_T \cong -17.44\,(T-T_g) / (51.6+T-T_g)$, is widely used and reasonably accurate. It is a wholly empirical relation and not based on any mechanism of polymer viscoelasticity. Nonetheless, in the first paragraph of the WLF paper it is stated: “from the standpoint of current theories of viscoelasticity, a_T reflects primarily the temperature dependence of a segmental friction coefficient or mobility on which the rates of all configurational rearrangements depend”. In spite of the fact that no mechanism is assumed in the WLF equation, the belief that time-dependent properties involve viscous flow and frictional loss has become deeply rooted in polymer science.

Attributing time-dependent properties to viscous flow is troubling. For hydrocarbon elastomers, energy loss occurs at frequencies as high as 10^8 Hz. Thus, in the legacy theory of viscoelasticity, polymer flow velocity gradients, with a strain amplitude of 0.0001-0.001, must be established at 10^8 Hz. During the 10^{-8} second period of a cycle, the velocity gradients must reverse direction (twice) and become re-established into a new gradient.

The proposed mechanism of energy loss, molecular friction, is also a significant problem for the legacy theory. We are unaware of any description in the literature regarding the nature of molecular friction. Stating that molecular friction causes viscoelastic loss implies that the macroscopic observation of mechanical energy changing to heat must have as its origin a similar process at the molecular level, one in which molecules lose energy if they are caused to slide past one another. The phase fluctuation theory is particularly compelling for its explanation of energy loss: work is lost as heat when a glass phase under strain fluctuates to the elastomer phase.

10.0 Summary

1. Amorphous polymer is a heterogeneous network of cells. The cells have a range of structure, however ill defined, with a corresponding range of chemical potential. Thus, a “cell” is a homogeneous region of amorphous polymer that has a uniform chemical potential in both the solid (glass) phase and the liquid (elastomer) phase.
2. The cells are nanoscale, small enough that energy fluctuations cause phase fluctuations.
3. Cells in amorphous polymer fluctuate between glass and elastomer phases with a period τ. The values of τ vary widely from cell to cell, and are a strong function of temperature.
4. A cell can only respond to an imposed strain as glassy or elastomeric. The glass phase responds with a high modulus due to intermolecular bond deformation, and the elastomer phase responds with a low modulus due to covalent bond rotation. There is no phase of intermediate molecular mobility, and no viscous flow strain mechanism.
5. Whether a cell responds to a cyclic deformation as glassy or elastomeric depends on the ratio between the period of phase fluctuation (τ) and the period of observation (1/f), where f is the frequency of cyclic strain. This ratio is expressed as (τ x f).
6. If (τ x f) >>1, the cell will have a glassy modulus. If (τ x f) << 1, the cell will have an elastomeric modulus. If (τ x f) ≈ 1 the cell modulus has a time-averaged intermediate value. The modulus of the material is calculated as a rule of mixtures sum of the individual cell moduli.
7. For cells in which (τ x f) ≈ 1, the energy stored during glass phase deformation is lost when they fluctuate to the elastomer phase. The excess energy in the cell, that which was strain energy in intermolecular bonds prior to phase fluctuation, is dissipated with the latent heat of fusion when the elastomer fluctuates back to the glass phase.
8. The energy loss is a function of strain rate, because strain rate controls the level of stress in glassy cells between phase fluctuations.
9. The glass transition is a cell-by-cell property change, as the period of observation becomes equal to the period of phase fluctuation. The glass transition temperature, T_g, is the temperature at which 1/f = τ for the highest volume fraction of cells.

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