Viscosity as a consequence of dielectric dissipation: 3. Complex modulus through intermolecular forces

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The elastic modulus of a polymer is explained as a function of temperature and frequency in terms of intermolecular forces between adjacent mer-units and between polymer macromolecules. The dielectric dissipation model for polymer viscosity is applied to the storage modulus to obtain values for the mechanical loss modulus.

(Keywords: elastic modulus; intermolecular forces; loss modulus; viscosity; relaxation time; dielectrics)

INTRODUCTION

Part 1 of this work[1] first demonstrated that viscosity can be explained quantitatively as a consequence of dielectric energy dissipation during the relative motion of molecular dipoles in a shear field. Subsequent to the submission of Part 1, Alberdi and coworkers[2] have demonstrated experimentally that polymer melt viscosity is proportional to dielectric relaxation time, as predicted.

Part 2 then intended to show that all the parameters of the viscosity equations for a polymer melt could be derived from intermolecular force theory[3]. This ambition was not fulfilled, in so far as the elastic modulus of a rubber or polymer melt was assumed to be due to the configurational entropy of the constituent mer-units distributed within the bounds of the polymer macromolecule. This assumption follows conventional treatments of elastic modulus[4] but conflicts with the basic theme of this work: that *all* the mechanical properties of a polymer can be explained via intermolecular force theory.

This paper concludes the series of reports by extending the elastic modulus theory for a polymer glass, which is based upon intermolecular force theory, into the rubber and melt zones for a polymer. The consequences of this new model for storage modulus are then examined by applying the original concept of dielectric energy dissipation to derive expressions for the dynamic loss modulus of a polymer.

STATIC ELASTIC MODULUS

This section derives expressions for the elastic modulus of a polymer over all the temperatures at which a zero or low frequency dependence is observed.

Consider a polymer macromolecule to be a sphere of radius R_p, which is composed of N mer-units having a radius R_m and a Lennard–Jones potential energy function separation parameter r_m. Each adjacent mer-unit pair interacts with an energy ϕ_m in a potential well of depth ϕ_{0m} located at a temperature of absolute zero and a distance r_{0m}, such that:

$$\phi_m = \phi_{0m}\left[\left(\frac{r_{0m}}{r_m}\right)^{12} - 2\left(\frac{r_{0m}}{r_m}\right)^{6}\right] \tag{1}$$

Polymer macromolecules interact in the same way, but within a geometrical configuration which is dictated by the stronger mer-unit interactions. Noting that $r_p \equiv R_p = N^{1/3}R_m$ and that ϕ_{0m} for a polymer macromolecule with low polarity becomes $\phi_{0p} \simeq \phi_{0m}$

$$\phi_p = \phi_{0m}\left[\left(\frac{R_{0m}}{R_m}\right)^{12} - 2\left(\frac{R_{0m}}{R_m}\right)^{6}\right] \tag{2}$$

The bulk modulus, B, can be expressed as the interaction energy density per interacting unit. For mer-units with a volume $V_m = 4\pi R_m^3/3$ and 12 surrounding interactions per mer-unit:

$$B \simeq \frac{12\phi_{0m}}{V_m} \tag{3}$$

The linear Young's modulus, E_m, due to the interacting mer-units can be derived by considering a mer-unit pair of length $4R_m$ and cross-sectional area πR_m^2 being separated with a linear modulus of $(\partial^2\phi_m/\partial r_m^2)$. E_m is given by[3]:

$$E_m = 15.3\frac{\phi_{0m}}{R_m r_m^2}\left[13\left(\frac{r_{0m}}{r_m}\right)^{12} - 7\left(\frac{r_{0m}}{r_m}\right)^{6}\right] \tag{4}$$

T_g can now be defined by the condition for $E_m = 0$ at the point $r_m = 1.1087 r_{0m}$, which can be translated into a temperature by means of a relationship between ϕ_m and the number of degrees of thermodynamic freedom per mer-unit, A, and Boltzmann's constant, k.

$$\phi_m = AkT + \phi_{0m} \tag{5}$$

Poisson's ratio, ν, can be calculated by combining

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equations (3) and (4) and using the standard expression[5]:

$$E = 3B(1-2\nu) \tag{6}$$

For example, by using the typical value of $r_m = 1.1r_{0m}$ below T_g and letting $R_m \simeq r_m$ for volumetric purposes, then $\nu = 0.33$.

A similar operation can be performed upon equation (2) to obtain a linear modulus, E_p, associated with the separation of polymer macromolecules:

$$E_p = 15.3\frac{\phi_{0m}}{NR_m^3}\left[13\left(\frac{R_{0m}}{R_m}\right)^{12} - 7\left(\frac{R_{0m}}{R_m}\right)^{6}\right] \tag{7}$$

Equation (7) defines a new transition temperature, T_p, at the point $R_m = 1.1087\,R_{0m}$. This transition may be identical to the liquid state transition T_{ll} discussed by Boyer[6], and probably defines the melting point of a polymer.

The modulus E_p is only observed in the range $T_g < T < T_p$, since $E_m \gg E_p$ for $N \gg 1$. E_p thus defines the plateau modulus of a polymer in the rubber zone.

For $T > T_g$, equation (7) is still valid, but the linear modulus $E_p \ll E_m$ predicts the macroscopic constant volume deformation condition of $\nu = 0.5$ from equation (6). The mer-units are able to redistribute themselves upon deformation above T_g to minimize the elastic energy stored in the material. This redistribution occurs around a monomeric relaxation time τ_m, which should be identical with the dielectric relaxation time derived in Paper 2. The equations of this section have no frequency dependence, since only static molecular pairs are considered in the model. The next step is to define a mechanism for a time dependent elastic modulus for $T > T_g$ where a rubber reverts to a brittle condition at high deformation rates, and above T_p where a polymer tends to a plateau value of E_p at high frequencies.

Note that the permanent dipole between mer-units along the chain backbone has not been invoked at this stage. Within the spherical collapsed coil model of this report, the effect of the dipole strength will be as a perturbation of the main dispersion force equations. However, the independence of E_p upon molecular weight for high molecular weight polymers is probably due to this dipole, as is the plateau value of fracture strength at high molecular weights[3].

DYNAMIC MODULUS

Consider the instantaneous deformation at constant volume of the two monomer pairs shown in *Figure 1*. The extension of one pair by Δr_m must result in a contraction of the orthogonal pair by $\Delta r_m/2$. The total difference in interaction energy of combinations of mer-units, $\Delta\phi_m$, can be calculated by substituting the values of $(r_m + \Delta r_m)$ and $(r_m - \Delta r_m/2)$ for r_m into equation (1) and expanding the resulting energy difference as a power series to terms in $(\Delta r_m/r_m)^2$:

$$\Delta\phi_m = 9\phi_0\left(\frac{\Delta r_m}{r_m}\right)^2\left[13\left(\frac{r_{0m}}{r_m}\right)^{12} - 7\left(\frac{r_{0m}}{r_m}\right)^{6}\right] \tag{8}$$

$\Delta\phi_m$ can be expressed as a linear modulus E_{md} under an extension Δr_m, to obtain an equation complementary to equation (4):

$$E_{md} = -11.5\frac{\phi_{0m}}{R_m r_m^2}\left[13\left(\frac{r_{0m}}{r_m}\right)^{12} - 7\left(\frac{r_{0m}}{r_m}\right)^{6}\right] \tag{9}$$

Equation (9) shows exactly the same transition condition as equation (4), but is valid only for $r_m > 1.1087r_{0m}$ in the region where $\Delta\phi_m$ is negative in equation (8). The condition of $\Delta\phi_m$ being negative indicates a small volumetric compression for a rubber undergoing a rapid linear extension, and must be observed as a rise in temperature.

Equation (9) is valid only at the instant of deformation by Δr_m, and the rearrangement of mer-units within the time scale of τ_m constitutes the time–frequency dependence of the rubber modulus. Equation (9) defines the upper modulus limit at high ($> 1/\tau_m$) frequency, and equation (7) defines the lower rubber plateau modulus at lower frequencies or longer times. Interestingly, E_m is now seen to be almost continuous through T_g at high deformation rates.

The final condition to be described is the relaxation of E_p under constant volume deformation above T_p. A procedure identical with the derivation of equation (9) yields a relation for E_{pd} when $T > T_p$:

$$E_{pd} = -11.5\frac{\phi_{0m}}{NR_m^3}\left[13\left(\frac{R_{0m}}{R_m}\right)^{12} - 7\left(\frac{R_{0m}}{R_m}\right)^{6}\right] \tag{10}$$

E_{pd} must be time–frequency dependent again as the macromolecules rearrange themselves in the time scale of a macromolecular relaxation time τ_p to eliminate the extension ΔR_p. Published data for the stress relaxation modulus of a polymer melt show that τ_m is independent of N and that τ_p is proportional to $N^{3.4}$: see Lin[7], for example.

Conventional techniques[4] can be applied to describe the stress relaxation modulus, E_t, of a polymer melt above T_p as a function of time after the application of an

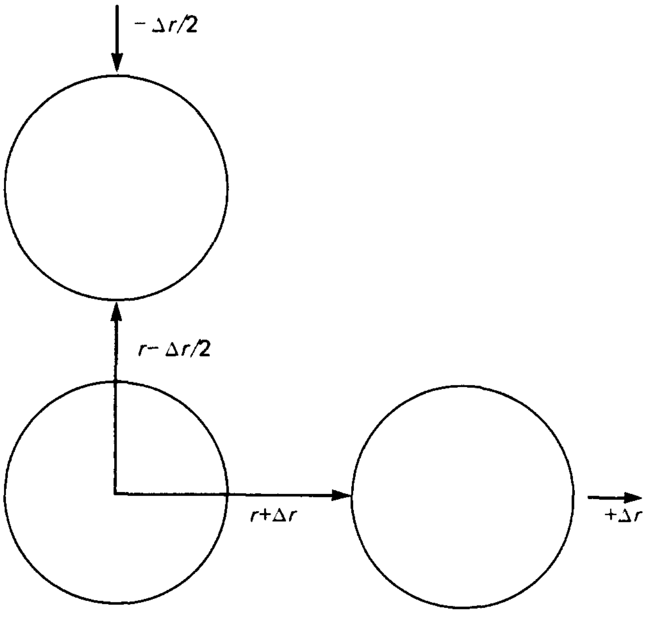

Figure 1 Deformation of orthogonal pairs of mer-units at constant volume

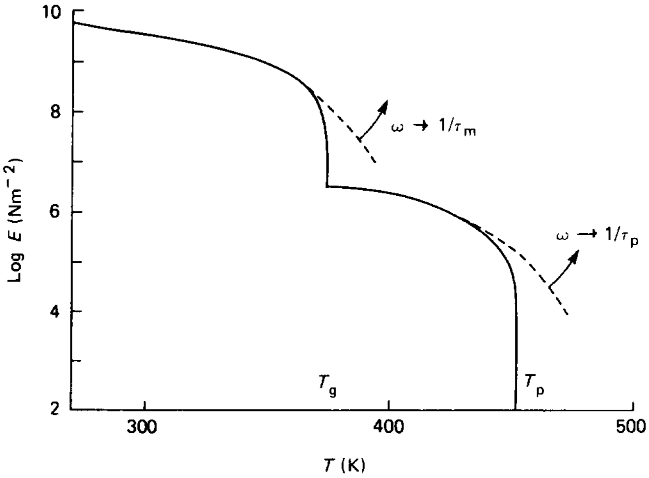

Figure 2 Elastic modulus E' of polystyrene as a function of temperature

instantaneous deformation:

$$E_t = E_{md} e^{-t/\tau_m} + E_{pd} e^{-t/\tau_p} \qquad (11)$$

or as a dynamic storage modulus, E', as a function of frequency ω:

$$E' = E_{md}\frac{\omega^2\tau_m^2}{(1+\omega^2\tau_m^2)} + E_{pd}\frac{\omega^2\tau_p^2}{(1+\omega^2\tau_p^2)} \qquad (12)$$

It is now possible to construct a full plot of elastic modulus as a function of temperature. *Figure 2* shows E as a function of T for polystyrene using equations (4) and (7), with the frequency dependency of E shown schematically as dotted lines: data points are $\phi_0 = 1.75 \times 10^{-20}$ J, $r_{0m} = 3.25 \times 10^{-10}$ m, and expansion coefficients of 1.5×10^{-4} and $5 \times 10^{-4}\,\mathrm{K^{-1}}$ above and below T_g respectively. The plot is in good agreement with standard published curves[5] and is made for a polystyrene with $N = 2000$.

LOSS MODULUS

For a polymer melt, a phenomenological approach can be taken to quantify the elastic energy lost during a stress relaxation experiment by the reduction of elastic modulus as a function of time. An equation for the loss modulus E'', corresponding to equation (12), can be written[4]:

$$E'' = E_{md}\frac{\omega\tau_m}{(1+\omega^2\tau_m^2)} + E_{pd}\frac{\omega\tau_p}{(1+\omega^2\tau_p^2)} \qquad (13)$$

The validity of equation (13) is demonstrated in *Figure 3*, where G'' is plotted as a function of frequency at $T = 433$ K for a polystyrene with $N = 2000$. The experimental data of Onogi and coworkers[8] is shown as a solid line, and the two components of equation (13) are shown as dashed lines corresponding to the data points $G_{md} = 10^5\,\mathrm{N\,m^{-2}}$, $G_{pd} = 10^9\,\mathrm{N\,m^{-2}}$, $\tau_p = 13$ s and $\tau_m = 4 \times 10^{-6}$ s. The agreement is good if allowance is made for a spread of relaxation times in τ_p, which is expected in a practical polymer sample.

The significance of parameter τ_p in equation (13) becomes clear when polymer melt viscosity is considered. In the terminal zone, the monomeric relaxation time can be ignored. At low frequencies and shear rates, equation (13) becomes an expression for zero shear viscosity, η_0 (Ref. 9):

$$\eta_0 \simeq G_{pd}\tau_p \qquad (14)$$

For example, a study of various stress relaxation modulus experiments for polystyrene[7–9] indicates an expression for τ_p, with the same temperature dependence as τ_m, of the form:

$$\tau_p = 10^{-15} N^{3.4} e^{1236/(T-323)} \qquad (15)$$

Combining equations (14) and (15), with a value of $G_{pd} = 10^5\,\mathrm{N\,m^{-2}}$, gives[9]:

$$\eta_0 = 10^{-10} N^{3.4} e^{1236/(T-323)} \qquad (16)$$

Equation (16) can be compared with the expression from Paper 1 for η_0, which was derived by extending the theory of monomeric fluid viscosity to the case of polymer melts in terms of the static and high frequency values of dielectric constant, ε_s and ε_i respectively:

$$\eta_0 = \pi\frac{S_p}{R_m}\cdot\frac{(\varepsilon_s - \varepsilon_i)}{\varepsilon_s}\cdot\tau_m \qquad (17)$$

The parameter S_p in equation (17) is the interaction energy per unit area between sheared planes of polymer macromolecules, which is equivalent to a fracture energy per unit area. Combining equations (16) and (17) produces an expression for S_p:

$$S_p \equiv G_{pd}\frac{\tau_p}{\tau_m}.\frac{R_m}{\pi}.\frac{\varepsilon_s}{(\varepsilon_s - \varepsilon_i)} \qquad (18)$$

Using previously quoted data points, a value of $S_p \simeq 2 \times 10^{-8} \cdot N^{3.4}$ is obtained, which agrees very well with the experimental data of Kusy and Turner[10] used in Paper 1. Thus, it would appear that a combination of intermolecular forces and damping by dielectric dissipation is responsible for the fracture strength of a polymer. This agrees with the experimental conclusions of Willett and coworkers[11] that the fracture energy of a polymer is orders of magnitude greater than the energy needed to produce the observed number of broken chemical bonds.

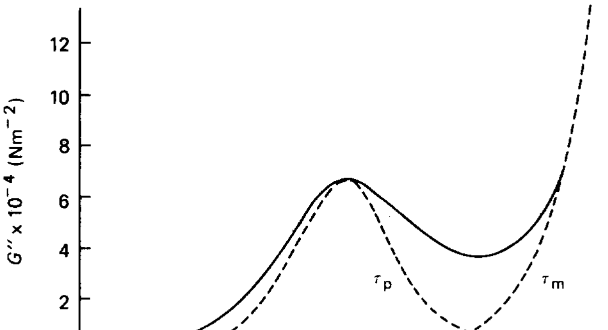

Figure 3 Loss modulus G'' as a function of frequency ω at $T = 433$ K for polystyrene with $N = 2000$ (see text)

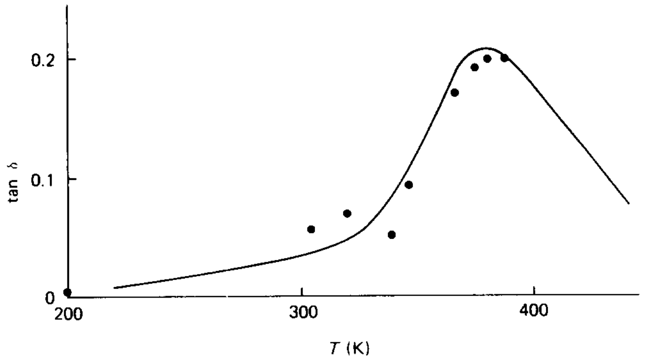

Figure 4 Comparison of the mechanical (———) and dielectric (●) values of tan δ for polyacronitrile (see text)

No mechanism for the dissipation of stored energy is proposed in equation (13) for a polymer melt. For $T < T_p$, however, equation (13) is not valid and a mechanism is needed which would allow the prediction of the loss modulus in a region where E' is time and frequency independent. The mechanism proposed is again that of dielectric dissipation. E'' can be predicted from E' by equating the loss tangent, $\tan\delta$, of mechanical and dielectric experiments:

$$\tan\delta = \frac{E''}{E'} = \frac{\varepsilon''}{\varepsilon'} \qquad (19)$$

where ε'' and ε' are the loss and storage dielectric constants respectively.

The validity of equation (19) is demonstrated in *Figure 4*, where the mechanical and dielectric values to $\tan\delta$ for poly(acrylonitrile) have been calculated from the data of Ishida and coworkers[12] and plotted as a function of temperature at a frequency of $100\,\mathrm{s}^{-1}$.

The significance of equation (19) lies in the well established relationships between ε'' and ε' and fundamental molecular parameters, such as dipole moment. The predictive power of equation (19) can be demonstrated very crudely by considering the example of low polarity polystyrene at a room temperature of 293 K, where the mer-units are immobile except for an oscillation around their mean position in space. In this low loss example, the thermal energy and the vibrational kinetic energy of each mer-unit of mass m can be considered equivalent:

$$\frac{m}{\tau_m^2} = kT \qquad (20)$$

The value of τ_m from equation (20) can now be used in the simplified expression for $\tan\delta^4$:

$$\tan\delta = \frac{(\varepsilon_s - \varepsilon_i)}{\varepsilon_s} \cdot \frac{\omega\tau_m}{(1 + \omega^2\tau_m^2)} \qquad (21)$$

The term $(\varepsilon_s - \varepsilon_i)/\varepsilon_s$ can be calculated from Onsager's equation[1,4], and has the relevant value at room temperature for polystyrene of 0.025, such that the loss modulus, E'', for a typical test frequency of $10\,\mathrm{s}^{-1}$ takes a value of approximately $10^7\,\mathrm{N\,m}^{-2}$.

DISCUSSION

From the preceding arguments, it is evident that the expressions for the dynamic moduli of a polymer are dominated by the relaxation times τ_m and τ_p. The relaxation time nearest the condition $\tau = 1/\omega$ in the environment of an experiment will dictate the measured values of E' and E''.

The proposal that energy dissipation in a mechanical experiment is dielectric in origin allows a fundamental molecular approach to be taken in predicting relaxation times. Many attempts have been made to solve the equations of motion for the sum of the mer-units in a polymer macromolecule[4] in order to predict τ, but most attempts fail to identify the physical nature of the equation parameters. For example, a typical form of the equation of motion of mer-unit j in the x direction would contain a unit frictional drag parameter f and a linear Hookean modulus E:

$$m\ddot{x} + f\dot{x} + E\Delta x = F_j e^{i\omega t} \qquad (22)$$

The damping term, f, should have a dependence upon ω^3 and dipole moment squared[11]. The temperature dependence of τ probably comes from the dipole moment, since the polarizability of the mer-units around the chain backbone bonding should follow the same temperature dependence as τ_m discussed in Paper 2:

$$\tau_m \propto e^{1236/(T - T\propto)} \qquad (23)$$

The elastic term, E, should have a form dictated by intermolecular potential energy of interaction, of the kind derived in equations (4) and (9).

The resulting set of N equations for each macromolecule must be quite complex, but their solution would be very useful for further progress in this subject. Of particular interest would be to see if low frequency/high temperature peaks are predicted in the dielectric parameters: many examples of such peaks have been recorded[4,12] without a satisfactory explanation.

Perhaps the most elegant way to approach the polymer relaxation time, τ_p, is to repeat the electrical tuned circuit analogy, which was used in Part 1 to predict the relaxation time of styrene monomer as a function of temperature. If C is the energy coupling via mutual inductance between two tuned circuits with a base relaxation time τ_0

$$\tau = \tau_0(1 + C^2)^{1/2} \qquad (24)$$

The interaction energy per unit area between polymer macromolecules was shown in Part 2 to be dependent upon $N^{3.3}$, such that for a unit area of polymer, where $C \gg 1$ and $C \propto S_p$

$$\tau_p \propto S_p \propto N^{3.3} \qquad (25)$$

This simplified argument has the advantage of linking the two alternative versions of the polymer viscosity equation, from Part 1 and equation (14) of this paper.

CONCLUSIONS

The three reports of this work have managed to link all the mechanical and dielectric properties of a linear amorphous polymer within the geometric model of a spherical collapsed-coil macromolecule.

The concept of viscosity as a consequence of dielectric dissipation has been extended, from the simple monomeric fluid viscosity model of Part 1, into general expressions for the loss modulus of a polymer. However, much work needs to be done to understand the nature of the relaxation times which dominate the equations for the dynamic moduli.

This final report has shown that the elastic modulus of a polymer can be explained by extending intermolecular force theory above T_g. The concept of configurational entropy of the mer-units has not been needed.

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