Viscosity as a consequence of dielectric dissipation: 2. Equation parameters from molecular interactions

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Expressions are derived for the parameters of the viscosity equations from the previous part of this work. The equation parameters of relaxation time, interaction energy per unit area and elastic modulus are shown to be a consequence of the interactions between mer units and between polymer macromolecules. The fracture energy of a polymer is discussed in terms of interaction energies as a function of molecular weight.

(Keywords: viscosity; molecular interaction; relaxation time; fracture; crazing; elastic modulus)

INTRODUCTION

In the first of two papers[1], equations were derived for the viscosity of a fluid. In particular, the viscosity of a polymer melt was expressed in terms of three major parameters: dielectric relaxation time, τ_p, interaction energy per unit area, S_p, and shear elastic modulus, G. For the viscosity equations to be valid, it was proposed that all these parameters should be a consequence of intermolecular potential energy of interaction between either polymer macromolecules or between their constituent mer units. This second paper seeks to justify that proposal by deriving expressions for the major physical properties of a polymer in terms of interaction energies, with particular emphasis upon τ_p, S_p and G, which are required for the viscosity equations.

Convention suggests that the viscosity equations of part 1 might be applied to the unit frictional drag factor of entanglement and reptation theories[2] to obtain expressions for the viscoelastic[3] and fracture[4] behaviour of a polymer. However, the polymer melt viscosity equations have no need to invoke entanglement if the interaction energy between polymer macromolecules can be shown to increase with increasing molecular weight.

A recent paper[5] explores the advantages of 'diffuse' entanglement over point entanglements or temporary network models. Perhaps the concept of 'diffuse' entanglement is the first stage of considering the interaction between whole polymer chains, without the topology of entanglement being itself the dominant factor. An ideal model might allow entanglement to explain the diffusion effects which are admirably modelled by reptation tubes[3], but not need entanglement to explain cohesive strength or viscoelastic effects. The key to such a model must lie in van der Waals intermolecular forces, which have been applied successfully to glassy materials[6] and to the surface free energy[7] and adhesion[8] of polymers. The Flory–Huggins interaction parameter[9] is a well known use of interaction potentials in polymer theory, but the interaction between polymer molecules is always via the intermediary of a solvent in this case.

Before considering interactions which are particular only to polymers, it is appropriate first to examine which of the physical properties of a polymer can already be explained and predicted by the interaction between the constituent mer-unit groups in a polymer. The implications of bonding mer units together into a chain can then be considered, to see what special physical properties the act of polymerization can bring to a material.

MOLECULAR INTERACTIONS

Figure 1 shows the geometry of an interaction between two rigid, spherical molecules[10]. Each molecule has a van der Waals radius, r_W, an actual radius, R_T, and a separation parameter distance, r_T, at a temperature T. At $T = 0$ K, the interaction is at the minimum of a potential well at r_0 with a depth $-\phi_0$. In this paper, a subscript m is used to denote monomer unit parameters, and a subscript p to denote polymer macromolecule parameters.

The balance between repulsion and attraction forces in an interaction can be expressed by a Lennard-Jones function for the interaction potential, ϕ_T, at T:

$$\phi_T = \phi_0\left[\left(\frac{r_0}{r_T}\right)^{12} - 2\left(\frac{r_0}{r_T}\right)^{6}\right] \tag{1}$$

An alternative formulation of ϕ_T in terms of the number of degrees of thermodynamic freedom per interacting pair, F, and Boltzmann's constant, k, is:

$$\phi_T = FkT/2 - \phi_0 \tag{2}$$

Equation (2) allows an estimate to be made of ϕ_0, since a molecular pair has $\phi_T = 0$ for the first time at the boiling point of the material, T_B:

$$\phi_0 = FkT_B/2 \tag{3}$$

For example, if the thermal energy from three spatial degrees of freedom per monomer molecule is available to

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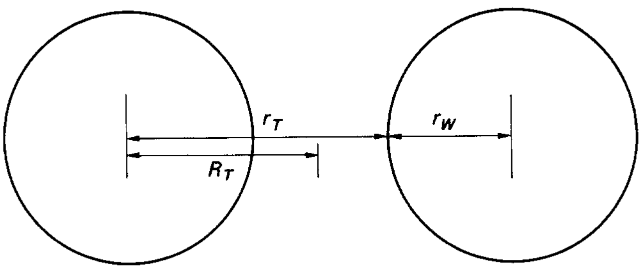

Figure 1 The geometry of an interaction between two rigid, spherical molecules

two interacting styrene molecules, then $F=6$ and $\phi_{0m}=1.75\times10^{-20}$ J since $T_{Bm}=418$ K for styrene[11]. In general, F is not a simple integer, since the thermal energy per molecule must be divided among many interactions: for example, a body-centred cubic packing of molecules gives 12 interactions per molecule. The statistical nature of F is beyond the scope of this paper, and appropriate values of F will be chosen to illustrate any effects of interaction.

The force which resists a change in the molecular separation of a molecular pair is given by $(\partial\phi_T/\partial r_T)$ and the linear elastic modulus associated with this force is given by $(\partial^2\phi_T/\partial r_T^2)$. These relations, in combination with equations (1), (2) and (3), control the physical properties of 'monomeric' materials[6] and will be shown to control the basic physical properties of a polymer through the interaction between adjacent mer units.

The interaction potential is a consequence of the interaction between induced and permanent dipoles, which are associated with the charge distribution around each molecule. The attraction potential, ϕ_A, can be expressed in terms of the polarizability, P, and the dipole moment, μ, of each molecule by the sum of the induced–induced, induced–permanent and permanent–permanent dipole interactions respectively[10]:

$$\phi_A r_T^6 = -1.2\times10^{-18}P^2 - 2\mu^2 P - \frac{2\mu^4}{3kT} \tag{4}$$

MER-UNIT INTERACTIONS

This section reviews the physical properties of a polymer which can be attributed to the first level of molecular interactions: those between adjacent, not—chemically—bonded, mer units. The example of polystyrene[11] is used throughout this paper to illustrate the use of any derived equations. Styrene is typified by a low permanent dipole, $\mu_m=4\times10^{-31}$ C m, and interactions between mer units are dominated by the polarizability, $P_m=1.4\times10^{-29}$ m^3. Other relevant data points are: $r_{Wm}=2.92\times10^{-10}$ m, $r_{0m}=3.25\times10^{-10}$ m and $R_{0m}=3.09\times10^{-10}$ m, which are calculated from a van der Waals volume of 1.04×10^{-28} m^3.

For the mer-unit pairs, let equation (2) become:

$$\phi_{Tm} = 1.5kT - \phi_{0m} \tag{5}$$

From the geometry of *Figure 1*, r_{Tm} can be expressed in terms of the average expansion coefficient, β, up to temperature T:

$$r_{Tm} = r_{0m}(1+1.9\beta T) \tag{6}$$

Expanding equation (1) as a power series up to terms in $(\beta T)^2$, and combining with equation (5):

$$\beta^2 \simeq 0.01k/\phi_{0m}T \tag{7}$$

For example, for polystyrene with $\phi_{0m}=1.75\times10^{-20}$ J, we obtain $\beta=1.65\times10^{-4}$ K^{-1} at $T=293$ K: experimentally[11] $\beta=1.71\times10^{-4}$ K^{-1}.

Consider two non-chemically-bonded mer units being separated. The linear elastic modulus of this pair, which resists separation, can be expressed as $(\partial^2\phi_{Tm}/\partial r_{Tm}^2)$ and also in terms of the macroscopic Young's modulus, E. Over the pair length of $4R_{Tm}$ and a cross-sectional area of πR_{Tm}^2:

$$\frac{\pi}{4}R_{Tm}E = \frac{\phi_{0m}}{r_{Tm}^2}\left[156\left(\frac{r_{0m}}{r_{Tm}}\right)^{12} - 84\left(\frac{r_{0m}}{r_{Tm}}\right)^6\right] \tag{8}$$

For example, for polystyrene at $T=293$ K, equation (8) predicts a value of $E=3\times10^9$ N m^{-2}, which corresponds with the experimentally observed value.

The glass transition temperature, T_g, can be predicted from equation (8) by using the condition that E tends to zero at T_g, such that:

$$r_{Tm} = 1.109 r_{0m} \tag{9}$$

Free volume theories for T_g might be based upon equation (9), but the constant ratio between the volume at T_g and the van der Waals volume is only a consequence of molecular interactions. The condition of equation (9) is the same condition as for the melting point of a monomeric solid.

In terms of T_g, equation (9) becomes:

$$2\beta T_g = 2\left(\frac{0.01kT_g}{\phi_{0m}}\right)^{1/2} = 0.109 \tag{10}$$

For example, equation (10) predicts $T_g=371$ K for polystyrene, in comparison with the accepted value of $T_g=373$ K[11].

The molecular weight dependence of T_g can be demonstrated by incorporating an attraction potential energy per mer unit into equation (1) due to the dispersion forces between adjacent polymer macromolecules. By noting that $P_p=N_T P_m$ and $r_{Tp}^3 \simeq N_T R_{Tm}^3$ for each macromolecule, the additional attraction potential per mer unit becomes, where N_T is the degree of polymerization:

$$\frac{\phi_{Ap}}{N_T} \simeq \frac{2\phi_{0m}}{N_T}\left(\frac{R_{0m}}{R_{Tm}}\right)^6 \tag{11}$$

Equation (8) can now be reformulated for the T_g condition:

$$156\left(\frac{r_{0m}}{r_{Tm}}\right)^{12} - 84\left(\frac{r_{0m}}{r_{Tm}}\right)^6 - \frac{336}{N_T}\left(\frac{R_{0m}}{R_{Tm}}\right)^6 = 0 \tag{12}$$

For example, knowing that the limit for T_g at high N_T for polystyrene is 373 K, then equation (12) can be approximately reformulated as a general expression for T_g, which reduces with reducing values of N_T:

$$T_g \simeq 373 - 877/N_T \tag{13}$$

Equation (13) is in good agreement with the empirical relation for the T_g of polystyrene as a function of molecular weight, M[12]:

$$T_g \simeq 373-(10^5/M)$$

A consequence of the condition that $E=0$ at $r_{Tm}=1.109r_{0m}$ is interesting for future reference in the discussion on polymer fracture, since the separation condition for $E=0$ must also be valid for mechanically forced separation. The strain needed to reach the separation condition for $E=0$ can be expressed as a thermal expansion between T and T_g, or as a mechanical strain due to a stress, σ_g, to attain the condition at a constant temperature T. Equating the equivalent strains:

$$\sigma_g = E\beta(T_g - T) \qquad (14)$$

Equation (14) is plotted in *Figure 2* for polystyrene, using $\beta = 1.5\times10^{-4}\,\mathrm{K}^{-1}$ and $E=3\times10^9\,\mathrm{N\,m}^{-2}$. Also plotted in *Figure 2* are experimental data points for the craze initiation stress for polystyrene as a function of temperature[13] at low strain rates. The correlation between σ_g and craze initiation stress suggests that the condition of $E=0$ is a condition for the yield stress and strain of a polymer, and that crazing is due to the separation of mer units in a tension experiment.

The general conclusion of this section is that the basic physical properties of a polymer can be attributed to the interaction between mer units in a polymer. The next question to answer is: how does the act of bonding mer units into a polymer chain affect the elastic and fracture behaviour of a polymer?

CHEMICALLY BONDED MER UNITS

The act of chemically bonding two mer units forces the mer units into close proximity, such that they must interact strongly at a fixed separation parameter distance, r_α, in a potential well at a depth, $-\phi_\alpha$. In the same way that ϕ_0 was related to T_B in equation (3), ϕ_α can be related to a temperature, T_α, such that the bonded mer-unit interaction can first approach zero at T_α. Combining equations (1) and (3) gives:

$$\frac{\phi_\alpha}{\phi_0}=\frac{T_\alpha}{T_B}=\left(\frac{r_{0m}}{r_\alpha}\right)^{12}-2\left(\frac{r_{0m}}{r_\alpha}\right)^{6} \qquad (15)$$

T_α becomes significant when it is used in the expression for dielectric relaxation time, τ_p, suggested by Frölich[14] in terms of an activation energy per molecule, ΔH:

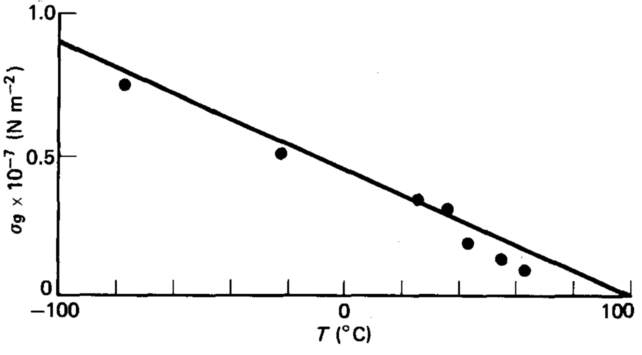

Figure 2 Stress for craze initiation, σ_g, at low strain rates as a function of temperature, T: ———, present work; ●, experimental data of Haward *et al.*[13]

$$\tau_p = \tau_0 \exp\left(\frac{\Delta H}{k(T-T_\alpha)}\right) \qquad (16)$$

Here $k(T-T_\alpha)$ is the free energy available for the permanent dipole of each mer unit to oscillate after the first point of possible neutralization of the interaction energy, $-\phi_\alpha$, has been reached at T_α: each mer unit then has two spatial degrees of freedom, with the third being blocked by the chemical bond. The activation energy, ΔH, can be equated with $\phi_0 = 3kT_B$ as the energy barrier at the depth of the potential well. Equation (16) becomes:

$$\tau_p = \tau_0 \exp\left(\frac{\phi_0}{k(T-T_\alpha)}\right) \qquad (17)$$

Polystyrene is a good example to illustrate the action of ϕ_0 as an activation energy barrier. An empirical equation was used in part 1 to predict the dielectric relaxation time[1]:

$$\tau_p = \tau_0 \exp\left(\frac{1236}{T-323}\right) \qquad (18)$$

The activation energy, $\Delta H = 1236k = 1.73\times10^{-20}\,\mathrm{J}$, corresponds to ϕ_0 for styrene, and $T_\alpha = 323$ K. Examining equations (1) and (2) it is apparent that r_α must be less than r_{0m}, such that $r_\alpha = 0.94r_{0m}$. In order for the interaction to be neutralized, for the dipoles to oscillate, the mer units must cross the minimum of the potential well at $-\phi_0$: thus, ϕ_0 becomes a barrier for the dipole freedom.

T_α becomes the brittle–ductile transition temperature of a polymer, since viscous deformation can start at this temperature[1].

The second major consequence of forcing mer units into close proximity by chemical bonding is that a permanent polarization is induced in the charge clouds between mer units. Following the suggestion of Flory[15], this permanent polarization can be represented by an effective dipole moment per mer unit, μ_0. This effective dipole moment can be calculated by using equation (4) and noting that $\phi_A = 3kT_\alpha$ and $r_T = r_\alpha$ and also that there are two polarizing bonds per mer unit. For example, polystyrene has $\phi_A = 1.4\times10^{-20}\,\mathrm{J}$ and $r_\alpha = 3.07\times10^{-10}\,\mathrm{m}$, which give $\mu_0 = 2.5\times10^{-24}\,\mathrm{C\,m}$ by using the term in μ^2P of equation (4).

The author proposes that the fracture energy and elastic modulus (and hence viscosity) effects in a polymer are a direct consequence of the effective dipole moment, μ_0, which differentiates a polymer from a monomeric solid. The aim of the next section is to explain the increase of interaction energy per unit area, S_p, with increasing N_T for $T > T_g$ by using the effective dipole μ_0.

The effective dipole has two possible levels of interaction: individual dipole with other individual dipoles, or the aggregate total dipoles, μ_T, of adjacent macromolecules can interact. These two cases are considered separately below, in order to isolate the effects which can be attributed to each.

INDIVIDUAL DIPOLE INTERACTIONS

The discussion on the interaction of non-chemically-bonded mer units in a previous section indicates that the individual dipoles, μ_0, have no significant interaction in the body of each macromolecule, since the basic physical properties of a polymer can be explained without any interaction other than the induced–induced dipole interactions of mer units. At the macromolecule periphery, however, the dipoles are orientated parallel where the macromolecules are in contact. In this case, the dipoles can interact with an energy, ϕ_μ, given by equation (4):

$$\phi_\mu = -\frac{2\mu_0^4}{3kTr_{\mathrm{Tm}}^6} \tag{19}$$

This interaction acts over an area πR_{Tm}^2, such that the fracture energy per unit peripheral area of macromolecule becomes:

$$\frac{2\mu_0^4}{3kTr_{\mathrm{Tm}}^6}\,\frac{1}{\pi R_{\mathrm{Tm}}^2} \tag{20}$$

In the creation of a macroscopic fracture surface in a polymer, the actual molecular peripheral area which is created is at least a factor 4 greater, for the simplest case of spherical macromolecules. The fracture energy per unit area becomes then:

$$S_{\mathrm{p}} \geqslant \frac{8}{3}\,\frac{\mu_0^4}{kTr_{\mathrm{Tm}}^6}\,\frac{1}{\pi R_{\mathrm{Tm}}^2} \tag{21}$$

For example, for polystyrene $\mu_0 = 2.5 \times 10^{-24}$ C m and let $r_{\mathrm{Tm}} = R_{\mathrm{Tm}} = R_{\mathrm{Wm}}$ for the simplified case of strong interactions causing intimate contact of the peripheral mer units. Equation (21) predicts a value of $S_{\mathrm{p}} \geqslant 180\,\mathrm{J\,m^{-2}}$.

Figure 3 shows a simplified plot of S_{p} against N_T which was used in part 1 to predict the viscosity of a polystyrene melt[16]. The value of $S_{\mathrm{p}} \geqslant 180\,\mathrm{J\,m^{-2}}$ corresponds to the upper plateau value of brittle fracture energy at high N_T.

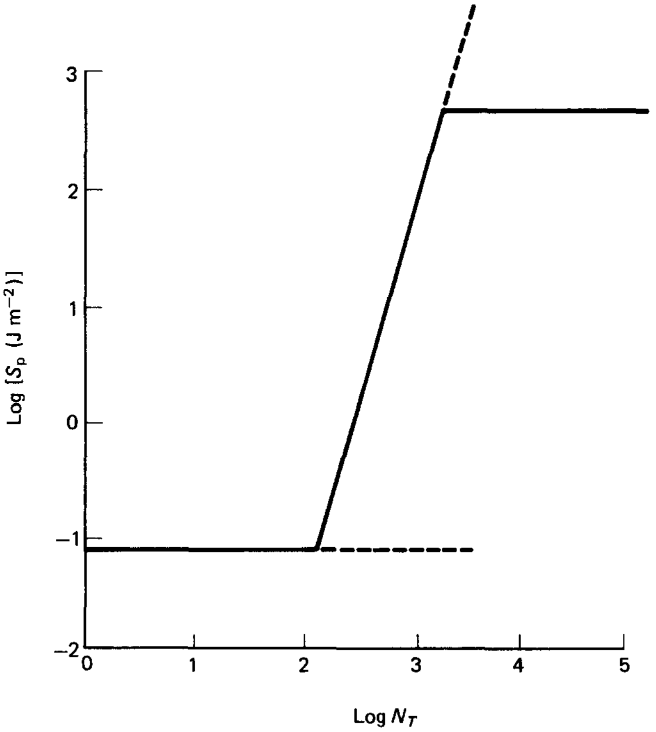

Figure 3 Simplified plot of fracture energy per unit area used to predict S_{p} as a function of N_T in part 1

The lower plateau corresponds to the surface free energy of the monomeric species. The line of gradient 3.3 which links the two plateau regions must now be explained: this intermediate region is the most important, since it dictates the molecular weight dependence of zero shear viscosity. The author proposes that this intermediate region is a consequence of macromolecular dipole interactions, as explained below.

MACROMOLECULAR DIPOLES

Statistical considerations show that an undeformed polymer macromolecule has an end-to-end separation distance, L, which can be expressed in terms of the length, l, of each component unit in the chain backbone[12]:

$$L^2 = N_T l^2 \tag{22}$$

The vector L is the net length of the polymer chain such that the total macromolecular dipole, μ_T, is given in terms of the effective dipole, μ_0, and the length, d, of an effective dipole by:

$$\mu_T = \mu_0 (L/d) \tag{23}$$

Let each polymer macromolecule be a prolate ellipse whose long axis is identical with the vector L, and whose short axes have a length $2D$. For oriented ellipses in a shear field, the long axis lies in the direction of polymer flow and the macromolecules are separated by a distance $2D$ into sheared planes[1]. The interaction potential, ϕ_μ, between the dipoles μ_T is given from equations (4) and (23) by:

$$\phi_\mu = -\frac{2}{3}\,\frac{\mu_0^4}{kT}\,\frac{L^4}{d^4 D^6} \tag{24}$$

For the system to be in equilibrium, a force balance must exist on each macromolecule to stop it collapsing. For each mer unit, a repulsion potential provides the balance through the overlap of charge clouds, but for a macromolecule the balancing force must come from the entropic spring constant of the molecule. The energy, ϕ_{E}, associated with an extension, ΔL, of the end-to-end vector can be expressed in the simplest form, for $T > T_{\mathrm{g}}$, by[12]:

$$\phi_{\mathrm{E}} = \frac{3kT}{2N_T l^2} (\Delta L)^2 \tag{25}$$

The equilibrium condition between ϕ_μ and ϕ_{E} is complex, since ϕ_μ increases negatively with increasing N_T, but ϕ_{E} reduces. At low values of N_T this is no problem, since the dipole attraction is not sufficiently large to extend L significantly. At high values of N_T, the author has not found an exact solution for the equilibrium length, L_μ, of the macromolecule due to the force balance.

The simplest approximate solution to the equilibrium length is the condition that $D = D_0 = \text{constant}$ and $L_\mu = L_0 N_T$, so that, once a thickness D_0 has been reached, then the macromolecules grow only in the length of their L vector axis. A constant volume condition for a polymer melt or rubber provides a geometric relation between L_0, D_0 and R_{Tm}:

$$(L_0/2) D_0^2 = R_{\mathrm{Tm}}^3 \tag{26}$$

At equilibrium, equation (24) takes the form:

$$\phi_\mu = -\frac{2}{3}\frac{\mu_0^4}{kTd^4}\frac{L_0^4}{D_0^6}N_T^4 \qquad (27)$$

and the interaction energy per unit area, over an interaction area of $\pi D_0 L_\mu/2$ for a prolate ellipse, is:

$$S_p = \frac{4}{3\pi}\frac{\mu_0^4}{kTd^4}\frac{L_0^3}{D_0^7}N_T^3 \qquad (28)$$

The experimental data of *Figure 3* indicate that the exponent of N_T should be 3.3 in equation (28), but this error will be attributed to a non-exact solution for L_μ at this stage. Equation (28) describes the linking line between the two plateau values of brittle fracture energy and, more importantly, it gives the general expression for S_p which is required for the viscosity equations for a polymer melt at high values of N_T.

The force balance between dipole interaction and entropic elasticity clearly links the brittle fracture (or S_p) and the rubber elastic modulus in a polymer. Equation (28) defines the geometry of a macromolecule at equilibrium if S_p is known. A new apparent linear elastic modulus can be defined by equating the extensional energy, ϕ_E, of equation (25) with the same energy for a new molecular spring constant of length $L_0 N_T$ and a cross-sectional area πD_0^2, such that the macroscopic Young's modulus becomes:

$$E = \frac{3kTL_0}{l^2 \pi D_0^2} \qquad (29)$$

The elastic modulus at high molecular weight is now independent of molecular weight: even if the exponent of N_T in equation (28) is adjusted to 3.3, then equation (29) still retains a very weak dependence upon molecular weight.

Equations (28) and (29) can now be tested. To do this, the data for S_p of *Figure 3* are used to calculate the parameters L_0 and D_0 from equations (28) and (26): the plateau value of E can then be calculated from these predicted values of L_0 and D_0. For example, *Figure 3* gives an empirical equation for polystyrene:

$$S_p = 7 \times 10^{-8} N_T^{3.3} \qquad (30)$$

Comparing equations (28) and (30), and using the data of $\mu_0 = 2.5 \times 10^{-24}$ C m and $d = 6.0 \times 10^{-10}$ m for polystyrene, then $D_0 = 1.4 \times 10^{-9}$ m and $L_0 = 3.9 \times 10^{-11}$ m at $T = 293$ K. Substituting these values into equation (29), and using $l = 7.1 \times 10^{-10}$ m (ref. 12), predicts a value of $E = 2.4 \times 10^5$ at $T = 450$ K. This value corresponds well to the experimental data of Plazek and O'Rourke, who found a plateau value of shear compliance[17], $J_e = 1.3 \times 10^{-5}$ m^2 N^{-1}, and also to the value of $G = 10^5$ N m^{-2}, which was used to predict the shear dependence of polymer melt viscosity in part 1.

DISCUSSION: POLYMER FRACTURE

The full brittle fracture curve of *Figure 2* can now be explained in terms of molecular interactions. At low molecular weight, the interaction between monomer units gives a fracture energy per unit area corresponding to the surface free energy of the monomer. At intermediate molecular weights, the interaction between macromolecular dipoles gives a fracture energy which increases with molecular weight to the power 3.3. At high molecular weight, $N_T > 10^3$, then the fracture between macromolecular periphery is the weak link which gives the final plateau value for fracture energy.

The author suggests that each of these mechanisms can act independently also outside the fracture envelope. Thus, crazing would be the separation of mer units within a stronger peripheral macromolecular envelope, as described by equation (14), and the interaction energy per unit area, S_p, of the viscosity equations is the intermediate fracture region which also acts at high molecular weights in a non-fracture situation.

An interesting consequence of the extended prolate ellipse geometry of the macromolecules in this model is that orientation can be treated in a straightforward way. Fracture energy must be proportional to the actual molecular peripheral area which is created in the cleavage of a macroscopic fracture plane. The fracture data of Hsiao[18] can be predicted quite well in this way. For example, the ultimate relative strength ratio of parallel to perpendicular fracture for his polystyrene sample, with $M = 68\,000$, must be given by DL/D^2. Using $D_0 = 1.4 \times 10^{-9}$ m and $L = 3.9 \times 10^{-11} N_T$ m, then the ultimate strength ratio is predicted to be 9.5, which corresponds to Hsiao's data value of about 10.

CONCLUSIONS

Predictive equations have been derived for the main parameters of the viscosity equations for a polymer melt, from part 1 of this work: equation (17) predicts τ_p, equation (28) predicts S_p and elastic modulus is given by equation (29). The basis of all these predictive equations is molecular interaction energy.

In deriving the predictive equations, a link has been established between brittle fracture and the viscoelastic properties of a polymer. The link comes from the proposal that macromolecular dipoles are created by the action of polymerizing mer units into a chain, and that the interaction between these dipoles is limited by a force balance with the elastic modulus of each macromolecule.

The geometrical model of an extended prolate ellipse for a polymer macromolecule is slightly different from the simplified ball-in-space model of part 1, but no major changes are required in the viscosity equations to accommodate the new geometry. The dimensions of an extended prolate ellipse are not dissimilar to those of a reptation tube[3], and the diffusion aspects of reptation theory can be retained in this model. However, the viscoelastic parameter predictions of reptation theory must be open to discussion, and the fracture energy predictions of entanglement network theory[4] become redundant if the model of this report is accepted. The author does not deny the concept of entanglement, but believes that too many physical parameters have been attributed to it, without considering the mechanism by which the entanglements or molecular tubes are held in place. Further consideration of intermolecular forces are required before a sound theoretical basis for polymer physics can be established.

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