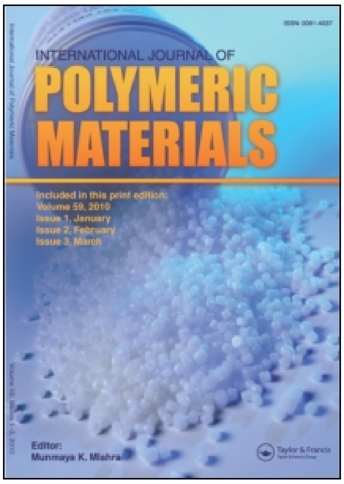

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Glass Transition of Polymers and Its Rheological Behavior

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Issues of predictability of the glass transition temperature under various environmental conditions are discussed.

KEY WORDS Glass transition, rheological behavior, environmental effects.

INTRODUCTION

Polymeric glasses may be formed as a result of gradual reduction of the rate of molecular motion by lowering temperature, increasing pressure or combining both. When the rate of cooperative rearrangement of polymer chain segments becomes of the same order of magnitude as the rate of cooling or pressuring, in other words, when the relaxation time is comparable to the time scale of observation, the glass transition of an amorphous polymer occurs. Here, polymeric materials undergo a marked change in physical, mechanical and rheological properties, associated with the virtual cessation of long segment motion of molecules which corresponds to the liquidlike motion of polymeric chains, characteristic of a rubbery state. In the glass state, atoms and small groups of atoms move against the local restraints much as atoms vibrate around their equilibrium positions in a crystal lattice, except that the glass state does not have the regularity of the crystalline state. However, after the vitrification, with temperature and pressure kept constant, some properties such as volume, enthalpy and modulus etc. will continue to relax, exhibiting an irreversibility of the glass state.

The objective of study into these irreversible processes should be the attempt to predict the reliability of a polymeric material designed for a special purpose when it is subjected to the actual critical environment. For example, the hydrostatic pressure under deep sea that a submarine has to withstand, the abrupt drastic elevation of both temperature and pressure incurred by the fuel seal of a rocket upon its launching and meanwhile the shock wave created across the launching silo by counter-impact may induce a shift of glass transition temperature, enormously affecting the material property and possibly resulting in malfunction. The disastrous accident of the U.S. Space Shuttle Challenger launching in 1985, ascribed to the malfunction of a seal and resulting leak of fuel (as a consequence of the elevation of glass transition temperature under tremendous pressure and the vehicle's highly increasing speed, i.e. large N_{De}) left the world with a bitter and horrible memory. Nevertheless, for this reason, subsequent launches of Shuttles Columbia, Atlanta and Discovery which brought the Hubble space telescope into its orbit were all delayed beyond their scheduled dates. These follow-up events are sufficient to manifest the simple fact that material performance must necessarily be predictable to ensure compliance with design specifications throughout the designated crucial circumstances.

FUNDAMENTALS

Thermodynamic Considerations

As shown in Figure 1, in the PVT space,[1] the rubber or liquid state of an amorphous polymer, usually regarded as in equilibrium, can be represented by a liquid (L) surface, whose differential equation takes the form:

$$dV_L = V_L\alpha_L(P, T)\,dT - V_L\beta_L(P, T)\,dP \tag{1}$$

On the other hand, glasses (G), in a non-equilibrium state, must be identified with another parameter ξ besides T and P, so that the variation of volume of a glass is described by:

$$dV_G = V_G\alpha_G(P, T)\,dT - V_G\beta_G(P, T)\,dP + \left(\frac{\partial V_G}{\partial \xi}\right)_{P,T} d\xi \tag{2}$$

For constant values of ξ, i.e. $d\xi = 0$, there should be a family of iso-ξ surfaces, each representing a specified glass. A glass specified by P, T and ξ will continuously reduce its volume by increasing ξ towards the equilibrium surface during relaxation at given P and T, signifying a successive variation from one specified glass to another.

The volume change $(\partial V_G/\partial\xi)_{P,T}\,d\xi$, responsible for the relaxation, can, upon introduction of the concepts of fictive temperature, T_f, and fictive pressure, P_f, referring to PVT space (Figure 1), be shown to be equal to:

$$\left(\frac{\partial V_G}{\partial \xi}\right) d\xi = V\Delta\alpha\, dT_f = -V\Delta\beta\, dP_f \tag{3}$$

Along the glass transition line with ξ = const, we have

$$dV_G(T, P, \xi) = dV_L(P, T) = dV \tag{4}$$

and the differential equation of the transition line becomes

$$\frac{dP}{\Delta\alpha} = \frac{dT}{\Delta\beta} = \frac{dV}{(\beta_L\alpha_G - \beta_G\alpha_L)V} \tag{5}$$

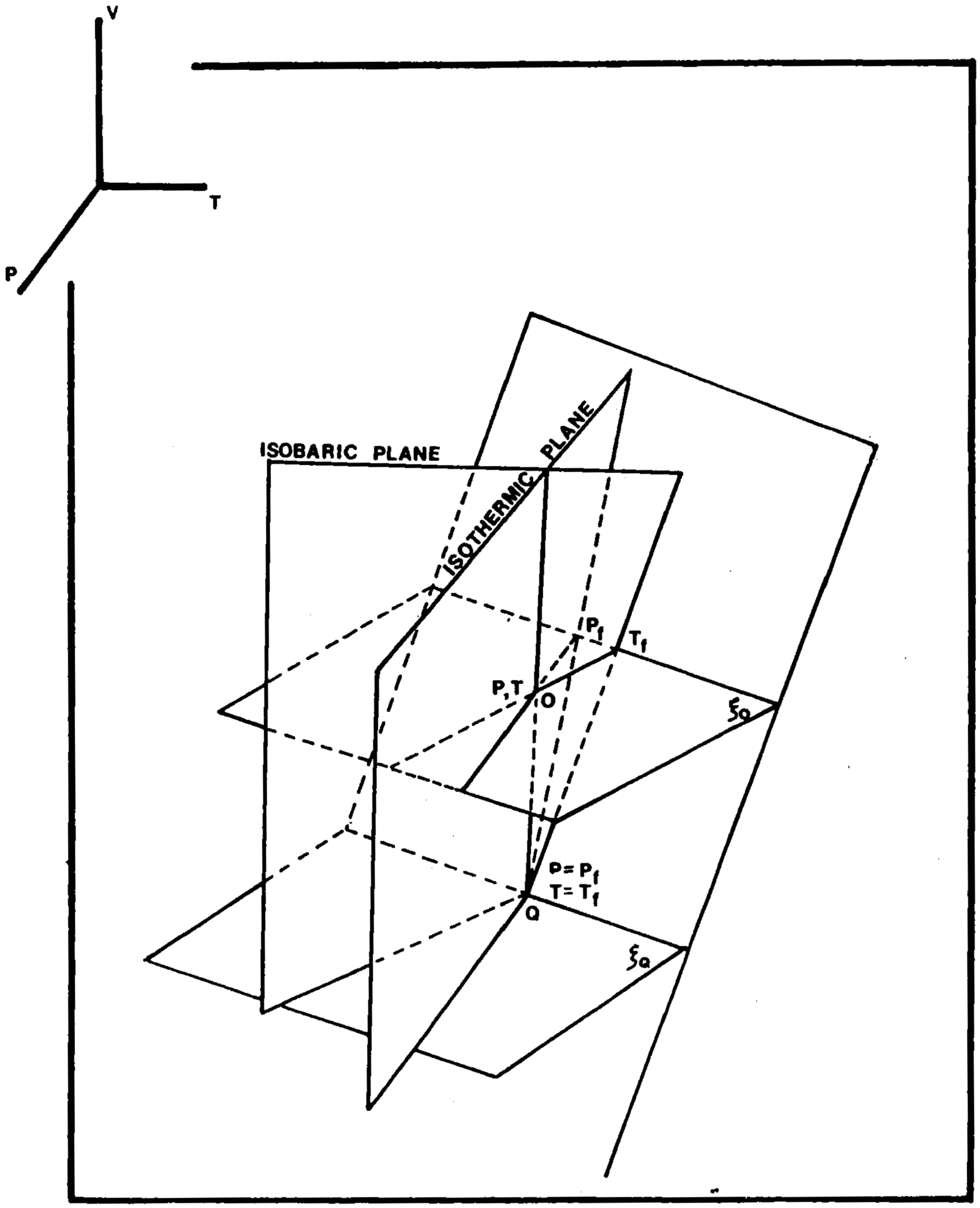

FIGURE 1 Interrelation between P_f, T_f, T and P on schematic of P-V-T space.

In the same manner, we can construct the iso-ξ planes in the SPT (entropy-pressure-temperature) space, where the equation of the iso-ξ transition line is given by:

$$\frac{dP}{\Delta C_P} = \frac{dT}{VT\Delta\alpha} = \frac{dS}{(\alpha_L C_{PG} - \alpha_G C_{PL})} \tag{6}$$

Statistical Mechanics Considerations

The effect of tensile stress on the glass transition behavior of glass-forming polymers and its related properties are investigated on the basis of Gibbs-Dimarzio theory, which is itself based on statistical mechanics.$^{1-5}$ The *G-D* theory takes into account specific configurations of polymers, making it possible to express the thermodynamic quantities as a function of molecular parameters, such as flex energy ε, hole energy E, coordination number z, degree of polymerization x, etc. Also included in the function is an intensive parameter of the system, temperature. The extension of the theory to incorporate the effect of pressure P was accomplished by use of an "isothermal-isobaric" partition function of the system. The Gibb's free energy can then be obtained in terms of intensive parameters T and P, and two parameters, f and n_0, where f is the fraction of flexed bonds and n_0 the number of unoccupied sites. According to the theory, the second order transition temperature T_2 corresponding to zero configurational entropy increases with increasing pressure but approaches a finite asymptotic value at very high pressure.

From thermodynamic considerations, it has been shown that for the iso-ξ plane the transition line in STP space is given by Equation (6). In *G-D* theory, both n_0 and f are assumed constant when cooled down along an isobar in the glass state, therefore $\alpha_G = 0$, $C_{PG} = 0$ and we have

$$\frac{dT}{dP} = \frac{VT\Delta\alpha}{\Delta C_P} \tag{7}$$

only when $dS = 0$. Owing to the argument that Equation (7) holds for an iso-ξ transition, this result indicates that the iso-ξ transition stems from a constant entropy process, as shown by Figure 2. The effect of tensile stress combined with hydrostatic pressure on the glass transition temperature will be determined by further modifying the Gibb-Dimarzio theory.

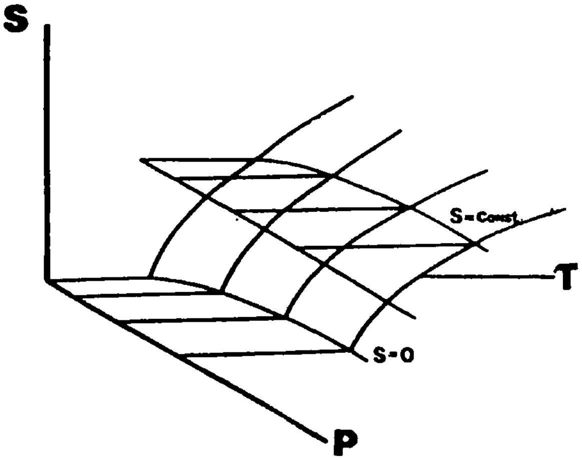

FIGURE 2 Schematic of *S-P-T* space based on *G-D* theory.

The Euler's relation for a continuous medium is given by[6]

$$U = TS + \mu N + V\tau_{ij}\varepsilon_{ij} \tag{8}$$

in which τ_{ij} and ε_{ij} represent respectively the Cauch stress tensor and Eulerian strain tensor.

The strain energy term in Equation (8) represents the energy produced by all possible combinations of stresses.

When only a tensile stress σ superimposed on hydrostatic pressure is applied to the system, the stress tensor can be written as

$$\tau_{11} = -P, \quad \tau_{22} = -P, \quad \tau_{33} = -P + \sigma, \quad \tau_{ij} = 0\ (i \neq j) \tag{9}$$

Equation (8) thus reduces to

$$U = TS - PV + \sigma V\varepsilon + \mu N \tag{10}$$

The introduction of the effect of tensile stress into the *G-D* theory can be achieved by means of a "isothermal-isobaric-isotensile" partition function of the form

$$\gamma = \sum_{f,n_0} W(f, n_0)\exp[-\beta\{PV + U(f, n_0) - \sigma V\varepsilon\}] \tag{11}$$

where $W(f, n_0)$ is the number of configurations of the system. Through Legendre's transformation,[6] we obtain the Gibb's Free energy associated with γ by

$$\begin{aligned} G(T, P, \sigma) &= U[T, P, \sigma] = \mu N \\ &= U + PV - \sigma V\varepsilon - TS = -kT \ln \gamma \end{aligned} \tag{12}$$

The summation over f and n in Equation (11) can be replaced by their maximum

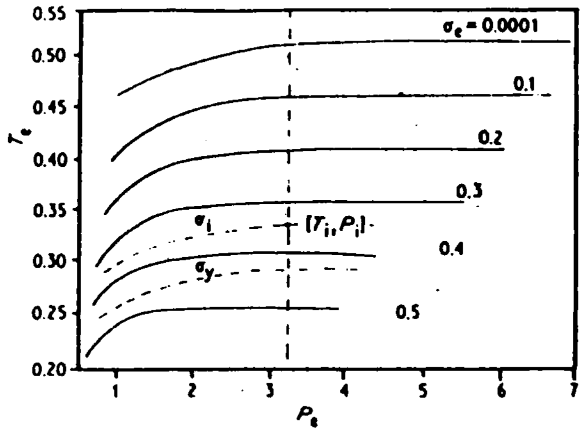

FIGURE 3 Theoretical curves of T_e against P_e with $S = 0$ and $\sigma_e = 0.0001, 0.1, 0.2, 0.3, 0.4, 0.5$.

values[7] and $S = k \ln W$. Statistical mechanics calculations furnished a host of curves[5] of T_e against P_e with $S = 0$ for various σ_e values (Figure 3).

GLASS YIELDING AND FLOW

It is well known that the glass transition temperature is reduced under a tensile stress. Experimentally, the deformation of a glass formed without a tensile stress at a temperature below T_g will be elastic at small strain, followed at higher strain by a yield point and plastic deformation, similar to the deformation in a rubber state. Yield point under tension is essentially a strain or stress-induced glass transition. Yielding under compressive or shear tresses are naturally predicted by the modified *G-D* theory: whatever the stress state—tension, compression or shear, when the strain energy increases, the glass transition temperature decreases.

In Figure 3, where T_e against P_e is plotted for various σ_e values, we consider schematically a polymer at certain temperature T_i and P_i in the glass state with the reference line (transition line) $\sigma = 0$. This point represents the state of glass which was formed at P_i without applied stress and is further cooled to T_i in the glass state. When a tensile, compressive or shear stress is applied to the glass, the reference line or the transition line (T_e against P_e with $\sigma_e \neq 0$ itself) will shift downward. If the stress is increased at an infinitely slow rate (a quasistatic loading),

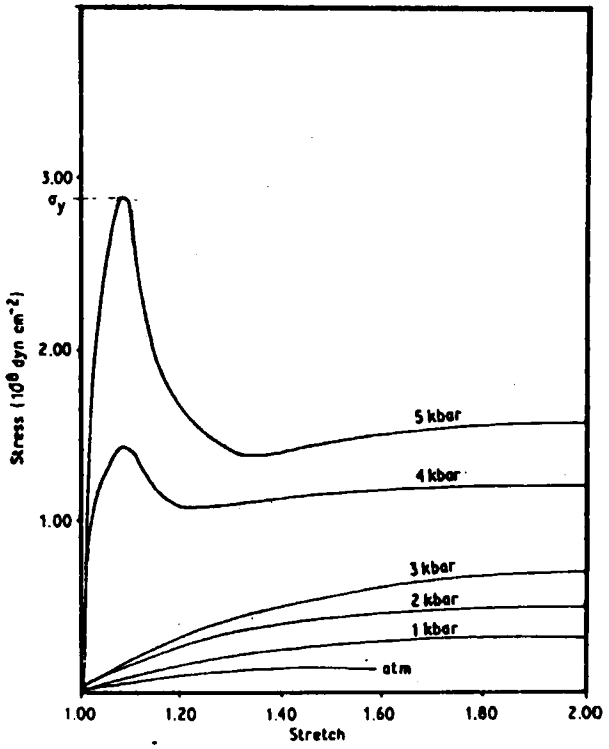

FIGURE 4 Tensile stress plotted against stretch for Solithane 113 at various pressures.

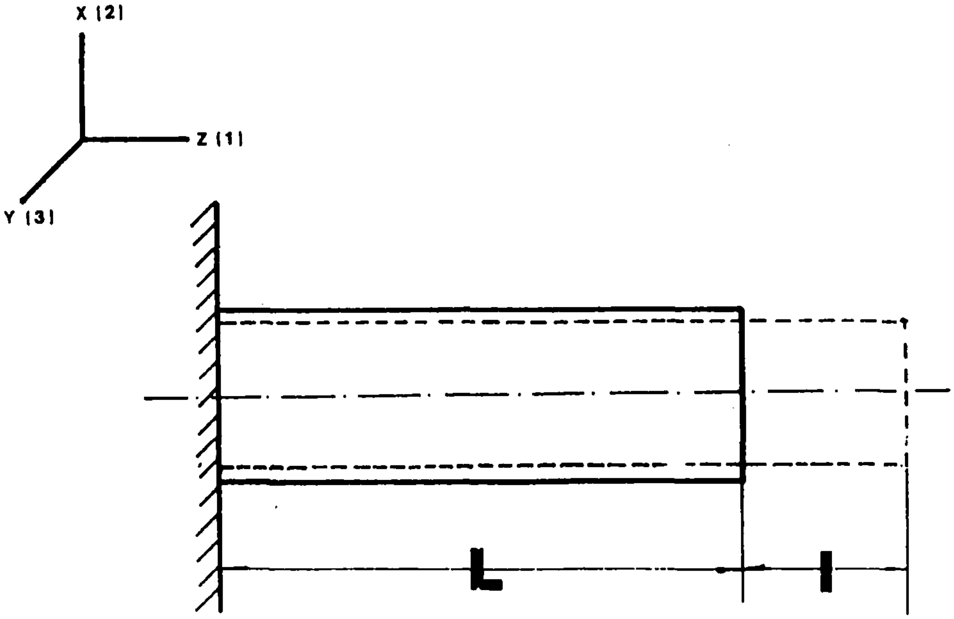

FIGURE 5 Elongational flow of a testing rod.

the glass yielding occurs at $\sigma = \sigma_i$, which corresponds to the stress-induced transition. If the stress is increased at a rate higher than an infinitely slow rate, the glass will yield at $\sigma = \sigma_y > \sigma_i$ as shown in Figure 4.

At yielding, with a corresponding extension rate S_y, the flow is supposed to be incompressible. The velocity field of an elongational flow of the sample rod under examination is (Figure 5):

$$\begin{aligned} V_1(z, t) &= \dot{\varepsilon}(t)z \\ V_2(y, t) &= -\frac{1}{2}\dot{\varepsilon}(t)y \\ V_3(x, t) &= -\frac{1}{2}\dot{\varepsilon}(t)x \end{aligned} \tag{13}$$

Let the length of the rod, when starting to flow, be L. Given the original length of the sample rod L_0, we have

$$L = L_0(1 + S_y)$$

At an extension velocity V_0 of the testing machine and stretch distance l after flow began,

$$V_1 = V_1(L + l, t) = \dot{\varepsilon}(t)(L + l) = V_0$$

Since $l = V_0t$, therefore

$$\dot{\varepsilon}(t) = V_0/(L + V_0t)$$

Then, the velocity gradient tensor $\partial V_i/\partial x_j$ and the deformation rate tensor e_{ij} are computed to obtain $I_2 = -3/4\dot{\varepsilon}(t)^2$.

If the Bingham model is adopted for the constitutive equation of the flow

$$\tau'_{ij} = \left[\mu P - \frac{\tau_0}{\pm\sqrt{-4I_2}}\right] 2e_{ij} \tag{14}$$

Incorporating the stress tensor for the elongational flow

$$\tau_{ij} = -P\delta_{ij} + \tau'_{ij} \qquad P = -\frac{\tau_{ii}}{3}$$

$$\tau_{33} = -P + \sigma \qquad \tau_{11} = \tau_{22} = -P$$

we eventually obtain:

$$\sigma = 3\mu_P \frac{V_0}{L + V_0t} + \sqrt{3}\,\tau_0 \tag{15}$$

When $V_0 \rightarrow 0$, $\sigma_i = \sqrt{3}\,\tau_0$, the yield stress at $t = 0$ for a certain extension rate is found to be

$$\sigma_y = 3\mu_P \frac{V_0}{L} + \sigma_i \tag{16}$$

Accordingly, the curves on Figure 4 make it possible to evaluate the constitutive constants μ_P and τ_0 for the tested polymeric material. Based on observation, μ_P is more dependent on pressure than τ_0.

In fact, the assumed flow transition region after yielding is quite short due to the onset of necking.

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