Application of a Simon-type equation to the relationship between glass transition temperature and pressure for polymers

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Abstract

The application of a Simon-type equation to the relationship between glass transition temperature and pressure for polymers is described. An equation of this form can be derived if it is assumed that one of the Ehrenfest relationships is valid and that the ratio $\Delta C_p/(V_g \Delta \alpha)$ depends linearly on pressure. Data obtained by high-pressure DTA for polystyrene were analyzed and it was found that the Simon equation provided a better fit than did a quadratic equation.

INTRODUCTION

It has been known for many years that the relationship between the melting point T_m and pressure P_m along the melting curve can be empirically expressed by the Simon equation

$$(P_m - P_0)/a = (T_m/T_0)^c - 1 \tag{1}$$

in which P_0 and T_0 are the coordinates of the triple point of the given solid, and a and c are constants characteristic of the material. Because P_0 is usually much lower than P_m, the simpler equation

$$P_m/a = (T_m/T_{m,0})^c - 1 \tag{2}$$

is widely used, where $T_{m,0}$ is the melting point at atmospheric pressure. The melting curve for many materials is well fitted by this equation [1].

The Simon equation (2) has also been derived by Slater who made the assumption that the Grüneisen equation of state and the Lindemann melting equation hold along the melting curve [2]. In this analysis, the

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constant a was correlated with the internal pressure $(\partial U/\partial V)_T$ at $T_m = 0$, with the implicit assumption that the extrapolation of eqn. (2) to this limit is valid [2]. A phenomenological derivation of the Simon equation was also proposed by Voronel [3] which was based on the Clausius–Clapeyron equation and an assumption that the ratio of the heat of melting ΔH_m to the volume change ΔV_m is a linear function of pressure, i.e.

$$dP_m/d(\ln T_m) = \Delta H_m/\Delta V_m = c(P_m + a) \tag{3}$$

A physical interpretation of the constants was also given in this contribution [3].

An analogous argument may be applied to the relationship between the glass transition temperature T_g and pressure P_g. In the present paper, the validity of this application will be examined.

ASSUMPTION AND DERIVATION OF T_g–P_g RELATION

In the case of the glass transition, rather than the Clausius–Clapeyron equation, it is appropriate to start with one of the Ehrenfest equations

$$dT_g/dP_g = T_g V_g \Delta\alpha/\Delta C_p \tag{4}$$

where V_g is the volume at T_g, and $\Delta\alpha$ and ΔC_p are the magnitudes of the discontinuities in the thermal expansion coefficient and the heat capacity at constant pressure at T_g and P_g, respectively. In fact there is the conjugate equation

$$dT_g/dP_g = \Delta\kappa/\Delta\alpha \tag{5}$$

where $\Delta\kappa$ is the discontinuity in the isothermal compressibility at T_g, but only eqn. (4) has been experimentally proved to hold [4–7]. The widely discussed relationship between the Prigogine–Defay ratio and the number of the order parameters required remains a matter of controversy [8–15]. In fact, eqn. (4) can be derived from a consideration of the intersection of the entropy surfaces for the liquid and the glass as a function of T and P, whereas eqn. (5) is based on a consideration of the volume surface. From this standpoint alone, it seems somewhat inconsistent that the usual experimental verification of eqn. (4) based on the T_g–P_g relationships is determined dilatometrically. In this contribution, we will not address this issue and merely assume the validity of eqn. (4).

A further assumption is that $\Delta C_p/(V_g \Delta\alpha)$ is a linear function of pressure, i.e.

$$\Delta C_p/(V_g \Delta\alpha) = c(P_g + a) \tag{6}$$

Because this equals $dP_g/d(\ln T_g)$, integration results in

$$[(P_g + a)/(P_{g,0} + a)] = (T_g/T_{g,0})^c \tag{7}$$

where the integration constants are taken as the glass transition temperature $T_{g,0}$ at atmospheric pressure $P_{g,0}$. Because a is of the order of several hundreds of MPa, as will be shown later, the simplified equation of the Simon form for the glass transition temperature is obtained

$$P_g/a + 1 = (T_g/T_{g,0})^c \tag{8}$$

or

$$T_g = T_{g,0}(P_g/a + 1)^{1/c} \tag{8a}$$

Using an argument similar to that of Slater leads to

$$P_g = -a \tag{9}$$

At $T_g = 0$ (assuming again that the extrapolation is valid). From the thermodynamic relation for internal pressure

$$(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P \tag{10}$$

we have, at $T_g = 0$

$$(\partial U/\partial V)_{T_g=0} = -P_g \tag{11}$$

and the relation

$$a = (\partial U/\partial V)_{T_g=0} \tag{12}$$

The constant a may thus be correlated with an internal pressure. Also, we find that

$$ac = [\Delta C_p/(V_g \Delta \alpha)]_0 \tag{13}$$

where the suffix 0 refers to atmospheric pressure.

EXPERIMENTAL DATA FOR MONODISPERSE POLYSTYRENE

The glass transition temperature for an anionic polystyrene sample has been determined by high-pressure DTA. The details of the apparatus have been described in a previous paper [16], and the measurement of T_g is described in ref. 17. The specification of the sample (Toso Corporation F-2) was $M_w = 1.96 \times 10^4$ and $M_w/M_n \approx 1.01$. The sample weight for the DTA measurements was about 5–6 mg. The sample was vitrified under selected pressure at a cooling rate of 20 K min^{-1}. Successive heating runs at the same rate were started from temperatures 60–70 K below the estimated T_g. The pressure during a DTA run was held constant by a manostat [16]. The glass transition temperature was defined as that corresponding to the intersection of the glass and liquid enthalpy curves integrated from the DTA data.

The data obtained are listed in Table 1. The T_g–P_g relation was fitted to a Simon equation, eqn. (8), and to the usual quadratic equation

TABLE 1

Experimental data for P_g and T_g for polystyrene and most probable values of T_g^{cal} calculated from the Simon and quadratic equations [a]

P_g/MPa	T_g/K	$T_g^{cal}(S)$/K	$T_g^{cal}(Q)$/K
25	378.0	379.5	382.0
60	392.5	391.9	392.7
80	402.0	398.5	398.7
100	405.3	404.8	404.5
130	414.1	413.8	413.1
150	420.1	419.5	418.6
200	431.8	432.9	431.9
260	447.5	447.6	447.0
300	455.3	456.7	456.4
350	465.0	467.4	467.5
400	476.0	477.5	477.9
450	490.0	487.0	487.5
500	495.8	496.0	496.4
550	505.4	504.6	504.6
	$(T_g - T_g^{cal})^2$	310	440

The third and fourth columns contain values calculated using the Simon and quadratic equations, respectively.

$$T_g = T_{g,0} + a_2 P_g + b_2 P_g^2 \qquad (14)$$

The best fit was obtained by the least-squares method. The most probable values of the three constants in the Simon equation were calculated by using the linearized equation. Details of the calculation are given elsewhere [18].

The most probable values for the Simon equation are $T_{g,0} = 369.9$ K, $a = 246.1$ MPa, and $c = 3.78$; for eqn. (14) the best-fit parameters are: $T_{g,0} = 374.1$ K, $a_2 = 0.319$, and $b_2 = -1.49 \times 10^{-4}$ (P_g in MPa). The sum of the residual squares are given in the last column in Table 1. As can be seen, the Simon equation provides the better fit, particularly in the low pressure region. Separate measurements by DSC and by dilatometry at atmospheric pressure gave $T_{g,0} = 368.8–369.3$ K for a polystyrene cooled at the rate of 20 K min^{-1} [17]. This result is in good agreement with the extrapolated value using the Simon equation. The present analysis leads to a relatively large difference in the initial pressure coefficient of T_g. The Simon equation gives $(dT_g/dP_g)_0 = T_{g,0}/ac = 39.8$ K per 100 MPa, whereas the value obtained from the quadratic equation analysis is 31.9 K per 100 MPa. It should be noted that the value of this coefficient depends largely on the analytical form used to correlate the data. In this connection, it can be noted that a comparison of the values between the left and right sides of eqn. (4) is not an effective means for examining the validity of the Ehrenfest equation. The high-pressure DTA technique can easily provide T_g data over

a wide range as shown in Table 1. In these circumstances, the present analysis suggests that it is desirable to represent the data using the Simon equation.

The internal pressure for polystyrene at 293 K has been reported to be 460 MPa, and this slightly decreases with temperature [19]. The constant a is expected to correlate with the internal pressure, as shown in eqn. (12), and its value is of the same order. It will, however, be necessary to analyze the experimental data for other polymers to discuss this issue in more detail.

EXAMINATION OF THE ASSUMPTIONS

The validity of the present derivation depends on the assumption contained in eqn. (6). The pressure dependence of the denominator $V_g \Delta \alpha$ can, in principle, be obtained directly from available $P-V-T$ data, whereas the experimental determination of ΔC_p under high pressure has not been reported except for some studies of poly(vinyl acetate) using a transient hot-wire probe technique [20].

The value of C_p at a pressure P can be calculated by using the thermodynamic relation from the value $C_{p,0}$ at atmospheric pressure

$$C_p(P) = C_{p,0} + (\partial C_p / \partial P)_T \, \mathrm{d}P \tag{15}$$

where the pressure coefficient of C_p is obtained from the $P-V-T$ relation by

$$(\partial C_p / \partial P)_T = -T(\partial^2 V / \partial T^2)_P = -TV[\alpha^2 + (\partial \alpha / \partial T)_P] \tag{16}$$

It would be appropriate to calculate $C_p(P)$ for the liquid by this procedure. Moreover, it seems that the pressure effect on the specific heat is relatively small. For glasses, however, we have to assume that any value for the temperature dependence of $C_{p,0}$ is valid beyond $T_{g,0}$.

The heat capacity, $C_{p,0}^l$ and $C_{p,0}^g$, for polystyrene liquid and glass at atmospheric pressure over a wide range of temperature has been measured using a precise adiabatic calorimetric [21]. The relevant relations may be represented by

$$C_{p,0}^l = 0.613 + 3.27 \times 10^{-3}T$$

$$C_{p,0}^g = -0.031 + 4.22 \times 10^{-3}T$$

$$\Delta C_{p,0} = 0.643 - 0.95 \times 10^{-3}T$$

where C_p is in $J\,K^{-1}\,g^{-1}$ and T is in K. From this we can approximately estimate the dependence of ΔC_p on pressure, because the second-order pressure correction can be neglected. ΔC_p becomes smaller as T_g increases with increasing P. The ratio of ΔC_p at 400 MPa to that at 0.1 MPa is 0.65. Abu-Isa and Dole also reported a $\Delta C_{p,0}-T$ relation for polystyrene [22]. Their data result in a somewhat larger decrease in ΔC_p with P and the

above ratio becomes 0.38. Such a large decrease seems to be inconsistent with our DTA results, though an exact quantitative relationship of the present pressure DTA is not yet established.

The value of $(\partial C_p/\partial P)_T$ under pressure can also be calculated from the Tait equation

$$V(P, T) = V_0(T)[1 - C \ln(1 - P/B(T))] \tag{17}$$

where V_0 is the volume at atmospheric pressure, and $C = 0.0894$. $B(T)$ is a function of temperature only

$$B(T) = a' \exp(-b'T) \tag{18}$$

in which a' and b' are constants. The respective values for polystyrene have been reported by Quach and Simha [23], although the upper pressure limit of their compression experiment was 200 MPa. It should be noted that their glass data was for "low-pressure" glasses formed by cooling at atmospheric pressure. The value of $(\partial^2 V/\partial T^2)_P$ is of the order of 10^{-7} cm^3 g^{-1} K^{-2} with a sign reversal at pressures below 100 MPa. On this point, Bridgman stated that such a reversal occurred at 300–400 MPa for ordinary liquids [24]. Using these data, the necessary correction was very small; for example, ΔC_p at 200 MPa was larger by only 0.004 J K^{-1} g^{-1} than the uncorrected value of 0.234 J K^{-1} g^{-1}.

However, Oels and Rehage reported $P-V-T$ data for a monodisperse polystyrene, with $M_w = 2.04 \times 10^4$ and $M_w/M_n \approx 1.06$, up to 400 MPa [25]. Their data were obtained from isobaric cooling of its liquid at a rate of 18 K h^{-1}. The value of α at each pressure was calculated as $(\partial \ln V/\partial T)_P$ by using V read from their figure. In the correction of eqn. (16), the term $(\partial \alpha/\partial T)_P$ is omitted; in this case the sign reversal in the second derivative of V did not occur. This correction is larger than that calculated through the Tait equation, and ΔC_p at 200 MPa is smaller by 0.010 J K^{-1} g^{-1} than the uncorrected value.

In this contribution, the ratio $\Delta C_p/(V_g\Delta\alpha)$ was finally calculated using the $P-V-T$ data of Oels and Rehage [25] and the uncorrected ΔC_p. The ratio is plotted against P in Fig. 1, and also the curve representing $c(P_g + a)$ is drawn. The ratio $\Delta C_p/(V_g\Delta\alpha)$ is approximately linear in P, despite the fact that both the numerator and the denominator are expressed quadratically. Although the results for the left- and right-hand sides of eqn. (6) coincide at atmospheric pressure, they deviate as P increases. The values of the ratio calculated from several sets of data for ΔC_p, V_g, and $\Delta\alpha$ at atmospheric pressure are in the range of 905–963 MPa. The present value of $ac = 931$ MPa is thus reasonable. It is of course possible to force the $c(P + a)$ and the $\Delta C_p/(V_g\Delta\alpha)$ lines to coincide by adjusting a and c with the condition $ac = $ constant. However, the different parameter set thus obtained could not accurately represent the T_g-P_g data.
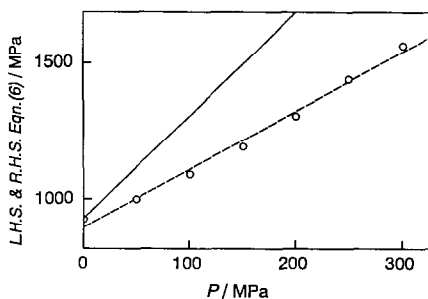
Fig. 1. Comparison of the left- and right-hand sides of eqn. (6) as a function of P: $\bigcirc$, $\Delta C_p/(V_g \Delta \alpha)$, in which ΔC_p was calculated from the relation cited in the text [21] without pressure correction and the $V_g \Delta \alpha$ term was calculated from Oels and Rehage [25]; – – –, a linear fit of the data; ——, the relation of $c(P + a)$, where $a = 246.1$ MPa and $c = 3.78$.

The discrepancy may arise from the assumption that the temperature dependence of $C_{p,0}^g$ can be extended beyond $T_{g,0}$. For poly(vinyl acetate), it is possible to compare the value of ΔC_p determined by the transient hot-wire technique [20] with that estimated from the $\Delta C_{p,0}$–T relation [26]. Because the temperature range for the latter relation is narrow, the estimated values are relatively uncertain. Despite this, there is a large difference in the ratio of $\Delta C_p(200)/\Delta C_p(0.1)$, in which the number indicates P in MPa: 0.91 by the direct measurement and 0.64 from the estimate. In this connection, the disagreement in Fig. 1 could be resolved by taking into account that the estimated pressure dependence of ΔC_p was too large.

CONCLUSION

The relationship between T_g and P_g can be expressed by a Simon-type equation in a similar manner as for the melting point. The equation can be obtained from the Ehrenfest equation by also assuming that the ratio $\Delta C_p/(V_g \Delta \alpha)$ depends linearly on P. This assumption seems reasonable, although some uncertainty in a quantitative correlation remains. The fitting of the experimental T_g–P_g data for polystyrene to a Simon equation was found to be better than to a quadratic equation. An advantage of adopting the Simon equation is that the constant a in the equation has a physical meaning in terms of an internal pressure.

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