Internal Pressures and Thermal Pressure Coefficients for Solid Polymers

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SYNOPSIS

The temperature and pressure dependence of the thermal pressure coefficient and internal pressure for eight polymer solids are calculated. The principal results are as follows: (1) The pressure dependence of the thermal pressure coefficient at constant temperature is relatively small. (2) For some solid polymers, as a function of temperature, a maximum in the thermal pressure coefficient is predicted in the solid region, and the temperatures corresponding to the maximum values are estimated. (3) For most solid polymers, the zero-pressure internal pressure increases with increasing temperature over the entire temperature range to the glass transition temperature or the melting point. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A few years ago,[1] the temperature and pressure dependence of the thermal pressure coefficient and internal pressure for poly(vinyl acetate) above and below the glass transition temperature were discussed. In this work, the results are extended to eight solid polymers. In calculation, we use the equation of state previously reported.[1] The equation of state describes the experimental pressure–volume–temperature (PVT) data above and below the glass trasition temperature well and yields reasonably accurate values for derivative quantities such as the internal pressure.

The polymers used for this study are poly-(orthomethylstyrene) (PoMS), polystyrene (PS), poly(vinyl acetate) (PVAc), polycarbonate (PC), polyarylate (PA), polysulfone (PSF), poly(vinyl fluoride) (PVF), and poly(chlorotrifluoroethylene) (PCTFE). For PVAc,[2] three thermodynamic histories were employed to form the glass, namely, (a) variable formation, (b) constant formation at atmospheric pressure, and (c) constant formation at 800 bars.

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EQUATION OF STATE

In this work, the equation of state[3] used is given by

$$V = V_0[K/(K + P)]^c \qquad (1)$$

with

$$K = k_0 \exp(-k_T) \qquad (2)$$

where V is the specific volume at pressure P and temperature T and V_0 is the value of V at $P = 1$ bar and temperature T. Units are cm^3/g, bars, and kelvin. The constant C is related to the constant k_0 by the equation[3]

$$k_0 = CB_{00} \qquad (3)$$

where B_{00} is the value of the isothermal bulk modulus, $B = -V(\partial P/\partial V)_T$, at $T = 0$ K and $P = 0$. For the solid polymer, the temperature dependence of V_0 and k_T are given by[3]

$$\ln V_0 = a_0 + a_1 T^2 \qquad (4)$$

and

$$k_T = k_1 T^2 \qquad (5)$$

where $a_0 = \ln V_{00}$, $a_1 = \frac{1}{2}A_0$, and $k_1 = \frac{1}{2}A_0\delta$. Here

V_{00} is the value of V at $T = 0$ K and $P = 0$, and A_0 is the derivative of the zero-pressure thermal expansivity, $\alpha_0 = (d \ln V_0/dT)$, with respect to temperature and is independent of temperature. The constant δ is the Anderson–Gruneisen constant.[3]

From Eq. (1) the isothermal compressibility, $\beta = 1/B$, and thermal expansivity $\alpha = (\partial \ln V/\partial T)_P$ are expressed as

$$\beta = C/(K + P) \qquad (6)$$

and

$$\alpha = \alpha_0 - \beta P(dk_T/dT) \qquad (7)$$

where, for solid polymer

$$dk_T/dT = 2k_1 T \qquad (8)$$

The parameters in Eq. (1) were determined for 11 polymers.[3]

THERMAL PRESSURE COEFFICIENT

Using Eqs. (6) and (7), the thermal pressure coefficient $\Gamma = (\partial P/\partial T)_V$ can be expressed as

$$\Gamma = \alpha/\beta \qquad (9)$$

$$= GA_0KT + (GA_0 - 2k_1)PT \qquad (10)$$

where $G = (\partial B/\partial P)_T = 1/C$. From this we have

$$(\partial \Gamma/\partial P)_T = (GA_0 - 2k_1)T \qquad (11)$$

$$= (G - \delta)\alpha_0 \qquad (12)$$

According to Eq. (10), the thermal pressure coefficient of solid polymer changes linearly with pressure at constant temperature. For most polymer solid, since $GA_0 > 2k_1$, Γ is an increasing function of pressure, while for the special case where $GA_0 < 2k_1$, such as PC and PVF, Γ is a decreasing function of pressure. If the isothermal bulk modulus is a function of volume only, then[3] $G = \delta$ and so Γ is a function only of temperature and is independent of pressure.

For solid polymers, since both GA_0 and k_1 are of the order[3] of 10^{-6}, over the short range of pressure, the variation of Γ with pressure can be ignored. For PA, for example, by fitting to the PVT data of Zoller,[4] it was found that[3]

$$a_1 = 4.03041 \times 10^{-7} \qquad C = 1.21729 \times 10^{-1}$$

$$k_0 = 6.54972 \text{ ts } 10^3 \qquad k_1 = 2.81553 \times 10^{-6}$$

In this case, Γ varies 5.3% over the pressure range from 0 to 1.8 kbars.

From Eq. (10) we have

$$(\partial \Gamma/\partial T)_P = GA_0K(1 - 2k_1T^2)$$
$$+ (GA_0 - 2k_1)P \qquad (13)$$

At $P = 0$, Eq. (13) becomes

$$d\Gamma_0/dT = GA_0K(1 - 2k_1T^2) \qquad (14)$$

$$= \frac{\Gamma_0}{T}(1 - 2k_1T^2) \qquad (15)$$

where Γ_0 is the value of Γ at $P = 0$. Equation (15) shows that if the temperature is low, $d\Gamma_0/dT$ will be positive. As the temperature is high enough, $d\Gamma_0/dT$ becomes negative. At some intermediate temperature T_Γ, $d\Gamma_0/dT = 0$. This means that if $T_\Gamma < T_g$ or T_m, where T_g is the glass transition temperature and T_m is the melting point, the maximum Γ_0 is real in the solid region. In this case, Γ_0 increases with increasing T below T_Γ and decreases with increasing T above T_Γ. From Eq. (15) it follows that

$$T_\Gamma = \left(\frac{1}{2k_1}\right)^{1/2} \qquad (16)$$

This can be used to estimate the values of T_Γ. For PVF, for example, by fitting to the PVT data of Weir,[5] it was found that[3] $k_1 = 6.24802 \times 10^{-6}$. The maximum Γ_0 is then predicted to occur at $T_\Gamma = 282.89$ K for $P = 0$. Since the melting point[3] of PVF is 490.15 K, the maximum Γ_0 is real in the solid region.

If $T_\Gamma > T_g$ or T_m, then Γ_0 increases as temperature increases over the entire temperature range to T_g or T_m. For many polymers, since the value of Γ_0/T for solids is generally of the order of 10^{-2} bars deg^{-2}, Γ_0 is a weak fumction of temperature. For PVAc-glass b, for example, Γ_0 varies by 10.5% over the temperature range from 243 to 283 K. For PVAc-glass c, the variation is less than 8%. The values of T_Γ for eight solid polymers are given in Table I. In calculation, k_1 data were taken from Ref. 3.

Table I   Values of T_Γ and T_P for Polymer Solids at $P = 0$

Polymer	$k_1 \times 10^6$	T_Γ (K)	T_P (K)	T_g or T_m (K)
PoMS	5.15054	311.57	440.63	404.2
PS	3.2789	390.5	552.25	365.2
PVAc-glass a	2.23950	472.51	668.23	304.65
PVAc-glass b	2.49513	447.65	633.07	303.83
PVAc-glass c	3.58439	373.49	528.19	287.9
PC	3.55133	375.23	530.64	423.55
PA	2.81553	421.41	595.96	449.95
PSF	2.14109	483.25	683.41	458.95
PVF	6.24802	282.89	400.06	490.15
PCTFE	3.66947	369.13	522.03	491.15

INTERNAL PRESSURE

Using Eq. (10), the internal pressure, $P_i = (\partial U/\partial V)_T$, where U is the internal energy, can be expressed as

$$P_i = \Gamma T - P \tag{17}$$

$$= GA_0 K T^2 + [(GA_0 - 2k_1)T^2 - 1]P \tag{18}$$

From this it follows that

$$(\partial P_i/\partial P)_T = (GA_0 - 2k_1)T^2 - 1 \tag{19}$$

This shows that P_i is a linear function of pressure and since, for most solid polymers $(GA_0 - 2k_1)T^2 < 1$, $(\partial P_i/\partial P)_T < 0$, and so P_i is a decreasing function of pressure in the solid region.

Using Eq. (18) we have

$$(\partial P_i/\partial T)_P = 2T[GA_0 K(1 - k_1 T^2)$$

$$+ (GA_0 - 2k_1)P] \tag{20}$$

As mentioned above, since both GA_0 and k_1 are small, unless the pressure is enormous, the second term in the brackets on the right of Eq. (20) is negligibly small. Thus, let $P = 0$, Eq. (20) becomes

$$dP_i^0/dT = 2GA_0 KT(1 - k_1 T^2) \tag{21}$$

$$= \frac{2P_i^0}{T}(1 - k_1 T^2) \tag{22}$$

where P_i^0 is the value of P_i at $P = 0$. Equation

(21) shows that at some intermediate temperature T_P, $dP_i^0/dT = 0$. Thus, it follows from Eq. (21) that

$$T_P = (1/k_1)^{1/2} \tag{23}$$

Combining this with Eq. (16) yields

$$T_P = 2^{1/2} T_\Gamma \tag{24}$$

which is the relation between T_P and T_Γ; knowing one, we can calculate the other.

The values of T_P for eight solid polymers calculated from Eq. (23) are given in Table I. According to the result, with the exception of PVF, for all the polymers studied $T_P > T_g$ or T_m. Thus, for most polymers, P_i^0 is an increasing function of temperature in solid region. For PVAc-glass b, for example, by fitting to the PVT data of McKinney and Goldstein,[2] it was found that[3] $k_1 = 2.49513 \times 10^{-6}$. The maximum P_i^0 is then predicted to occur at $T_P = 633.07$ K, which is much higher than $T_g = 303.83$ K. In this case, the maximum P_i^0 does not occur in the solid region, and so P_i^0 increases with increasing temperature over the entire temperature range to T_g. Such behavior has been observed experimentally for the solid PVAc.[6]

CONCLUSIONS

The results presented in this study lead to the following conclusions:

1. The pressure dependence of the thermal

pressure coefficient at constant temperature is relatively small.

2. For some solid polymers, as a function of temperature, a maximum in thermal pressure coefficient is predicted, and the temperatures corresponding to the maximum values are estimated.

3. For many solid polymers, the internal pressure is an increasing function of temperature and is a decreasing function of pressure.

4. For most solid polymers, the internal pressure at zero pressure increases with increasing temperature over the entire temperature range to T_g or T_m.

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