Different approach for the correlation of the T_g of mixed amorphous systems

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An empirical equation relating the glass transition (measured dynamically) of mixed systems to their pure components T_gs can be fitted by the following relationship:

$$\ln T_g = m_1 \ln T_{g1} + m_2 \ln T_{g2}$$

where m is either volume or wt % of each component. The thermodynamic implications of the logarithmic relationship have been considered and it is shown that other relationships governing the T_g of mixed systems (Fox equation etc.) can be derived using certain thermodynamic constraints. A general power law dependence of log T_g on the apparent activation energy of T_g at a given frequency is also ascertained from experimental data and it is shown that this power law relationship can be obtained from the WLF approach to the glass transition. From this, a relationship concerning the apparent activation energies of T_g (at a fixed frequency) of a mixed system as a function of the pure component activation energies is derived.

INTRODUCTION

Plasticized polymers are used in a variety of industrial applications. Usually the plasticization is used to change mechanical properties from rigid, hard materials to flexible, softer materials. It is important in these systems to know the ultimate glass transition (T_g) of the mixtures.

Mixtures of amorphous organic materials can be classified into three subsections; (1) polymer–plasticizer (small molecule), (2) polymer–polymer and (3) small molecule–small molecule. Theoretical equations have been developed to describe the T_g–composition dependence of polymer–polymer and polymer–diluent systems. Unfortunately, an equation developed for one type of system is generally not applicable to the other. To place perspective on what is to follow a short review of the derived relationships is in order.

Polymer–polymer mixtures

A general expression for polymer–polymer mixtures derived by Wood[1] gives the glass transition as a weighted average of the glass transitions of the components:

$$A_iM_1M_{w_1}(T_g - T_{g_1}) + A_2M_2M_{w_2}(T_g - T_{g_2}) = 0 \qquad (1)$$

where M_1 and M_2 are the mole fractions of the components of the mixture, M_w are the 'mer' molecular weights of the polymers, T_{g_i} are the pure component glass transitions and the A_i are related to the thermal expansion coefficients of the pure components. If the A_i are the difference in thermal expansion coefficients above and below T_g, reduces to the Gordon–Taylor equation[2]:

$$(1 - m_1)(T_g - T_{g_1}) + m_2K(T_g - T_{g_2}) = 0 \qquad (2)$$

where the m_i are the component weight fractions and K is a constant, usually positive. Fox[3] derived a more simplified version of the Wood equation assuming that the quantity $A_1M_1T_{g_1}/A_2M_2T_{g_2} = 1$ producing:

$$\frac{1}{T_g} = \frac{m_1}{T_{g_1}} + \frac{m_2}{T_{g_2}} \qquad (3)$$

where the m_2 values can be the weight or volume fraction of the pure components. Equation (3) is derived assuming free volume dominance of T_g[4] and any deviations from the equation are usually interpreted in terms of changes in free volume due to mixing.

It is worth noting that random copolymers are 'mixtures' of mers with varying T_g values and, as such, the composition dependence of their T_gs have been predicted by many of the polymer-polymer equations. Gibbs and DiMarzio[5] also demonstrated that random copolymers could be considered to be mixtures of mers. They obtained a theoretical equation similar to equation (1) if the A_i represented the number of bonds of 'mers'. The Gibbs–DiMarzio theory also applies to polymer–plasticizer systems[6].

Polymer–plasticizer mixtures

The simplest experimental equation for the change in T_g of a polymeric system with the addition of a plasticizer is:

$$T_g = T_{gp} - Bm_2 \qquad (4)$$

where T_{gp} is the polymer glass transition, m_2 is the weight fraction of plasticizer and B is the constant. This form of the T_g equation has been obtained by a number of authors via a variety of approaches; isofree volume[8]; isoviscous[9] and viscous flow[10] and active groups[11]. Unfortunately, equation (4) only applies for a low percentage concentration of plasticizer[12] in a polymer.

Kelly and Bueche[13] derived an equation which covered the entire composition range by considering polymer–diluent viscosity relationships and the effect of free volume

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Table 1 Correlation coefficient and standard deviation for equations (3) and (8)

	Fox Equation				Equation (8)				
System	Weight fraction correlation coefficient	Standard deviation	Volume fraction correlation coefficient	Standard deviation	Weight fraction correlation coefficient	Standard deviation	Volume fraction correlation coefficient	Standard deviation	No. of data points
(a) Small molecule–small molecule									
1 Butanol/methanol[22]	0.974	5.7	0.974	5.8	0.998	1.8	0.998	0.56	11
2 Butanol/ethanol[22]	0.997	6.0	0.990	6.3	0.997	3.2	0.997	0.67	11
3 Propanol/methanol[22]	0.534	2.0	0.534	2.0	0.840	0.49	0.840	0.19	11
4 Ethanol/methanol[22]	0.876	4.8	0.876	4.8	0.929	1.6	0.928	0.46	11
5 Propanol/ethanol[22]	0.903	1.0	0.903	1.0	0.991	1.0	0.991	0.1	11
6 Butanol/propanol[22]	0.977	2.3	0.997	2.2	0.991	2.5	0.991	0.24	11
(b) Polymer–small molecule									
7 Polycarbonate/ bisphenol-A diphenyl carbonate[21]	0.994	11.3	0.997	6.1	0.998	2.6	0.999	0.15	11
8 Poly(methyl methacrylate)/methyl methacrylate[25]	0.994	22.3	0.995	19.4	0.992	7.0	0.974	2.1	10
9 Polystyrene/styrene[27]	0.995	29.6	0.997	24.3	0.992	6,7	0.992	3.0	8
10 Polystyrene/toluene[27]	0.998	25.0	0.998	24.0	0.995	15.2	0.987	2.5	6
11 Poly(styrene)/β-naphthyl salicylate[23]	0.967	31.0	0.974	27.5	0.979	2.6	0.984	0.8	7
12 Poly(vinyl acetate)/ toluene[29]	0.975	43.5	0.984	34.6	0.986	7.8	0.992	1.0	11
13 Polystyrene/phenyl salicylate[23]	0.976	39.0	0.970	43.7	0.982	6.0	0.986	1.3	9
(c) Polymer–polymer									
14 Poly(vinylidene fluoride)[24] poly(methyl methacrylate)	0.980	32.1	0.995	15.3	0.966	5.6	0.989	0.8	6
15 Poly(styrene)/ poly(phenylene oxide)[26]	0.983	19.0	0.986	17.1	0.988	2.0	0.989	0.37	5
16 Poly(methyl methacrylate)/[30] poly(vinyl acetate)	0.939	24.3	0.955	20.7	0.952	0.2	0.967	0.1	5

on T_g. Their equation is:

$$T_g = \frac{\alpha_S \bar{V}_S T_g + \alpha_p(1 - \bar{V}_S)T_{g(P)}}{\alpha_S \bar{V}_S + \alpha_p(1 - \bar{V}_S)} \qquad (5)$$

where $\bar{V}_S$ is the volume fraction solvent and α_S and α_p are the thermal coefficients of expansion of solvents and polymers, respectively. Their equation is only considered valid if dipolar interactions between the plasticizer and polymers are neglected or considered negligible. Equation (5) can be rearranged to yield a form similar to equation (1).

Jenckel and Heusch[14] allowed for interactions between components by adding an interaction term to the weighted T_g values of the pure components:

$$T_g = m_S T_{g_S} + m_P T_{g_P} + D m_S m_P \qquad (6)$$

where D is the interaction constant. In terms of equation (1), equation (6) can be written:

$$T_g = \frac{m_S A_S T_{g_S} + m_P A_P T_{g_P}}{m_S A_S + m_P A_P} + \frac{m_S m_P D}{m_S A_S + m_P A_P} \qquad (7)$$

Kovacs and Braun[15] and Kanig[16] have derived equations of a form similar to equation (6) with the interaction parameter a function of the ratio of specific excess free volume of mixing, v^E, to the free volume v_{12}.

The difficulty in utilizing expressions such as those above lies in the inability to determine the specific constants of the equations*. Only in the case of the Fox equation, where only the mass or volume fractions and the T_gs of the individual components are needed, would a calculation of T_g as a function of composition be easy.

In our studies on mixed amorphous systems, we noted that the following correlation based on pure component T_gs and mass fractions fit the T_g composition data of many mixed amorphous systems:

$$\ln T_g = m_1 \ln T_{g_1} + m_2 \ln T_{g_2} \qquad (8)$$

We have tested a variety of systems with equation (8). The systems were chosen so that the T_g values of the pure components as well as several intermediate compositions were known. It would have been desirable to compare the correlated data of equation (8) with the general equation for polymer–plasticizer (equation 7) and polymer–polymer (equation 1) blends. These equations, however, require additional data that is often not available for the specific systems studied. The Fox equation (3), however, does not require data beyond pure component T_gs and their weight or volume

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* In all the equations cited concerning polymer–plasticizer blends, it is assumed that intimate molecular mixtures of the components are attained. If they are not, multiple glass transitions may occur for the blend, where the T_gs of the pure components, and a blend T_g are observed. An example of a supposedly intimate blend is the system poly(vinyl acetate)/benzyl benzoate[17], exhibiting uncorrelated relaxations in the glass transition region. Other examples are polystyrene/di-n-butylphthalate[18], and polycarbonate/n-butyl-4,5,7-trinitrofluoreneone-2-carboxylate[19] where specific interactions between polymer and diluent occur and the systems are not intimately blended on a microscale.

fractions. We therefore chose it as a representative equation for comparison with equation (8). This comparison is shown in *Table 1*. The systems compared consist of 6 small molecule –small molecule mixtures, 7 polymer–small molecule mixtures and 3 polymer–polymer mixtures. The data are compared using weight and volume fractions (assuming volume additivity). Correlation coefficients and standard deviations for a least squares fit of the data are also included. It is clear from the data that the correlation coefficients and standard deviations are better for equation (8) than equation (3). This is particularly evident for the small molecule–small molecule systems. An example of each class of mixed systems is shown in *Figures 1–3* with the lines representing the best fit of equations (3) and (8) and the points representing the experimental data. An illustration of the differences between equations (3) and (8) is plotted in *Figure 4* for a hypothetical mixture. It is seen that the logarithmic correlation is intermediate between the linear 'ideal curve' and the Fox equation.

Logarithmic correlations such as equation (8) have been used to predict modulus (shear or Young's)[35,36] and coefficients of expansion[37] for composite systems and the moduli of interpenetrating polymer networks[38]. In these cases moduli or coefficients of expansion take the place of the T_gs in equation (8).

Thermodynamic implications

If equation (8) is considered a valid description of T_gs of a mixed system as a function of composition, the following can be derived from thermodynamic considerations. Consider the change in T_g as a function of pressure:

$$\frac{d}{dP}(\ln T_g) = \frac{1}{T_g}\left(\frac{dT_g}{dP}\right) \qquad (9)$$

and equation (6) becomes:

$$\frac{1}{T_g}\left(\frac{dT_g}{dP}\right) = \frac{m_1}{T_{g_1}}\left(\frac{dT_{g_1}}{dP}\right) + \frac{m_2}{T_{g_2}}\left(\frac{dT_{g_2}}{dP}\right) \qquad (10)$$

N.B. the weight fraction is constant. Equation (10) can be considered in two ways:

(1) as a general equation which interrelates the T_gs and glass transition temperature dependence of mixed systems in a functional form. In this form dT_g/dP must be known or evaluated for the mixtures as well as the pure components. Although dT_g/dP is similar in many polymeric systems[39,40] we could not find any data concerning the T_g pressure dependence of mixed systems and therefore it was impossible to evaluate equation (10) as written;

(2) as a special case where $(dT_g/dP) \approx (dT_{g_1}/dP) \approx (dT_{g_2}/dP)$. In this form, the derivatives cancel from equation (9) and the Fox equation is obtained. This suggests that the Fox equation may be a special case of equation (8), and also that in cases where data correlates via the Fox equation, the pressure dependence of the T_g of the mixture as well as the individual components may be similar.

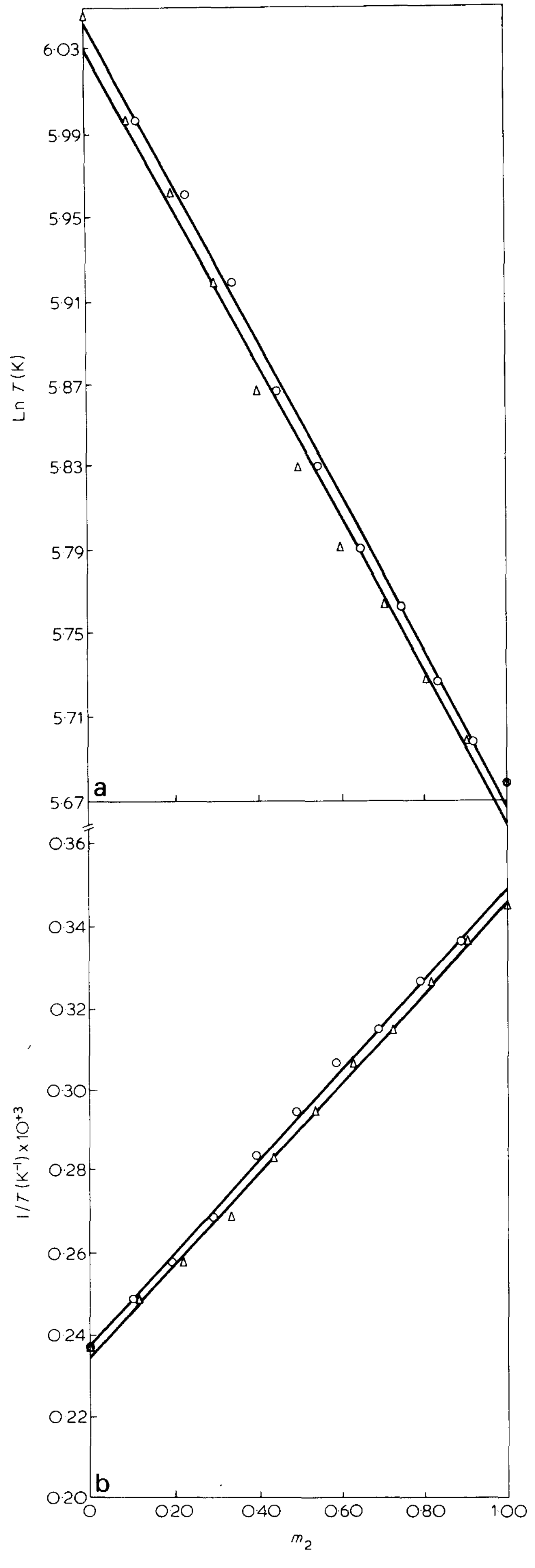

Figure 1 (a) LnT_g *versus* weight and volume fraction bisphenol-A diphenyl carbonate in bisphenol-A diphenyl carbonate–polycarbonate mixtures. Dielectric T_gs (120 Hz). OUr correlation: ○, volume fraction, *R* = 0.99737; △, weight fraction, *R* = 0.99420. (b) 1/T_g *versus* weight and volume fraction bisphenol-A diphenyl carbonate in bisphenol-A diphenyl carbonate–polycarbonate mixtures. Dielectric T_gs (120 Hz). Fox equation: △, weight fraction, *R* = 0.99846; ○, Volume fraction, *R* = 0.99901

The data in *Table 1* suggest that volume fraction as well as mass fraction provides an acceptable fit of the experimental T_g data. If equation (8) is considered in terms of volume fraction, the change of $\ln T_g$ with pressure becomes:

$$\frac{\mathrm{d}}{\mathrm{d}P}(\ln T_g) = \frac{1}{T_g}\,\frac{\mathrm{d}T_g}{\mathrm{d}P} = \Sigma_i \frac{\mathrm{d}\bar{V}_i}{\mathrm{d}P}\ln T_{g_i} + \frac{\bar{V}_i}{T_{g_i}}\,\frac{\mathrm{d}T_{g_i}}{\mathrm{d}P} \qquad (11)$$

If $(\mathrm{d}T_g/\mathrm{d}P) \cong (\mathrm{d}T_{g_1}/\mathrm{d}P) \cong (\mathrm{d}T_{g_2}/\mathrm{d}P)$, equation (11) becomes:

$$\frac{1}{T_g} = \Sigma_i \left(\frac{\mathrm{d}V_i}{\mathrm{d}P}\right) \Big/ \left(\frac{\mathrm{d}T_g}{\mathrm{d}P}\right) \ln T_{g_i} + \frac{V_i}{T_{g_i}} \qquad (12)$$

and a relationship is obtained between the T_g of the mixed system and each component's volume fraction, glass transition pressure dependence and pressure dependence of the volume fraction. Equation (12) is not as simple as equation (10), but does provide a relationship between volume functionalities (volume fraction, density) and the glass transition.

The above relations, as well as our initial postulate were obtained from observations of the behaviour of two component systems. This relationship can be extended to multicomponent systems where equation (8) would become:

$$\ln T_g = \Sigma_i m_1 \ln T_{g_i} \qquad (13)$$

and any derivations would involve the sum of the individual components.

DISCUSSION

The question arises as to the origin of equation (8). The equation implies that the logarithm of T_g is proportional to another variable: i.e. $T_g \approx e^{\Phi}$. Since the process being considered (the glass transition) requires large scale molecular reorientations, it might be expected that this variable would be associated with the diffusion coefficient for segmental motion. $D = D_0\exp(-E_a/RT)$ suggests that at the glass transition the controlling variable might be the apparent activation energy. It is well known that the glass transition for polymers is not a single Arrhenius activated process, but exhibits temperature dependent activation energies which are well documented on a frequency–temperature transition map. This process has been described by the WLF formalism[40] as illustrated in *Figure 5*. It should be noted that a temperature–frequency response ($\log \nu_{\max}$ vs. $1/T$) of the same form is obtained for glass forming molecules[30] as for glassy polymers. This suggests that the observed curvature at high frequencies may be a fundamental phenomenon not unique to a polymer packing characteristic parameter.

The apparent activation energy at the *dynamically* measured T_g (1 Hz data) relates all types of glass forming systems. This is seen in *Figure 5* where a general correlation of log T_g with the activation energy (E_a) (interpreted from a transitional map at 1 Hz) is observed. A regression analysis of the data indicates that a power function of the type:

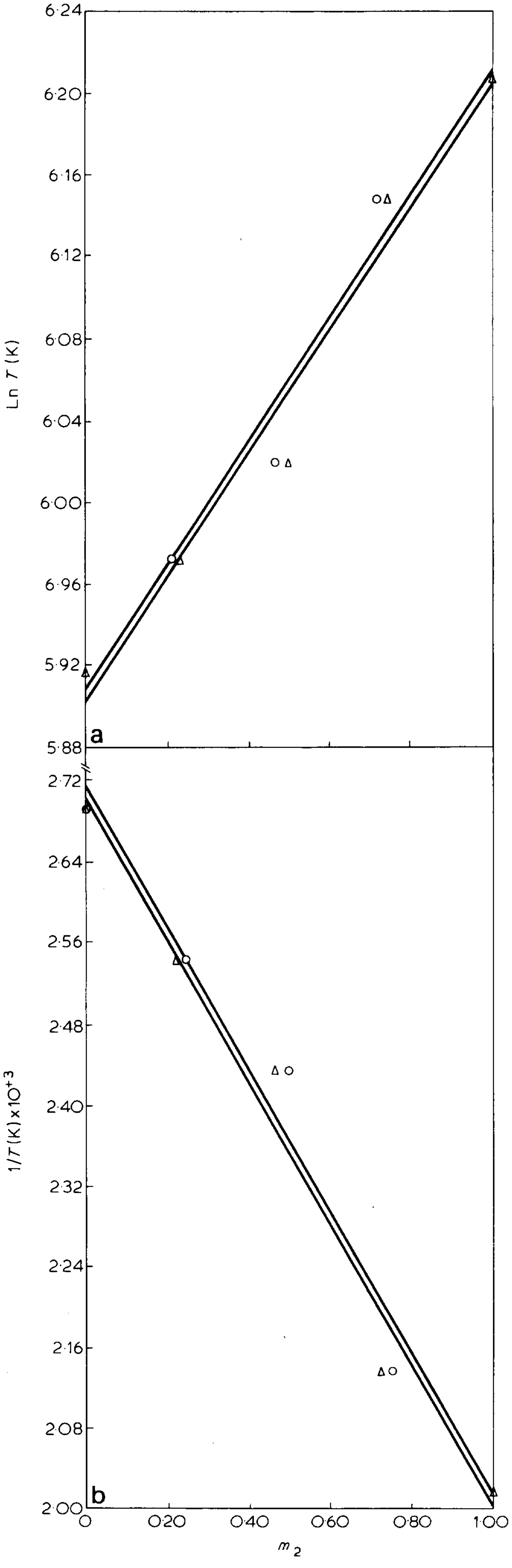

Figure 2 (a) $\ln T_g$ *versus* weight and volume fraction poly(2,6-dimethyl phenylene oxide) in poly(2,6-dimethyl phenylene oxide)–polystyrene blends. Our correlation: ○, volume fraction, R = 0.98610; △, weight fraction, R = 0.98323. (b) $1/T_g$ *versus* weight and volume fraction poly(2,6-dimethyl phenylene oxide) in poly(2,3-dimethyl phenylene oxide)–polystyrene blends. Fox equation: ○, weight fraction, R = 0.98761; △, volume fraction, R = 0.98906

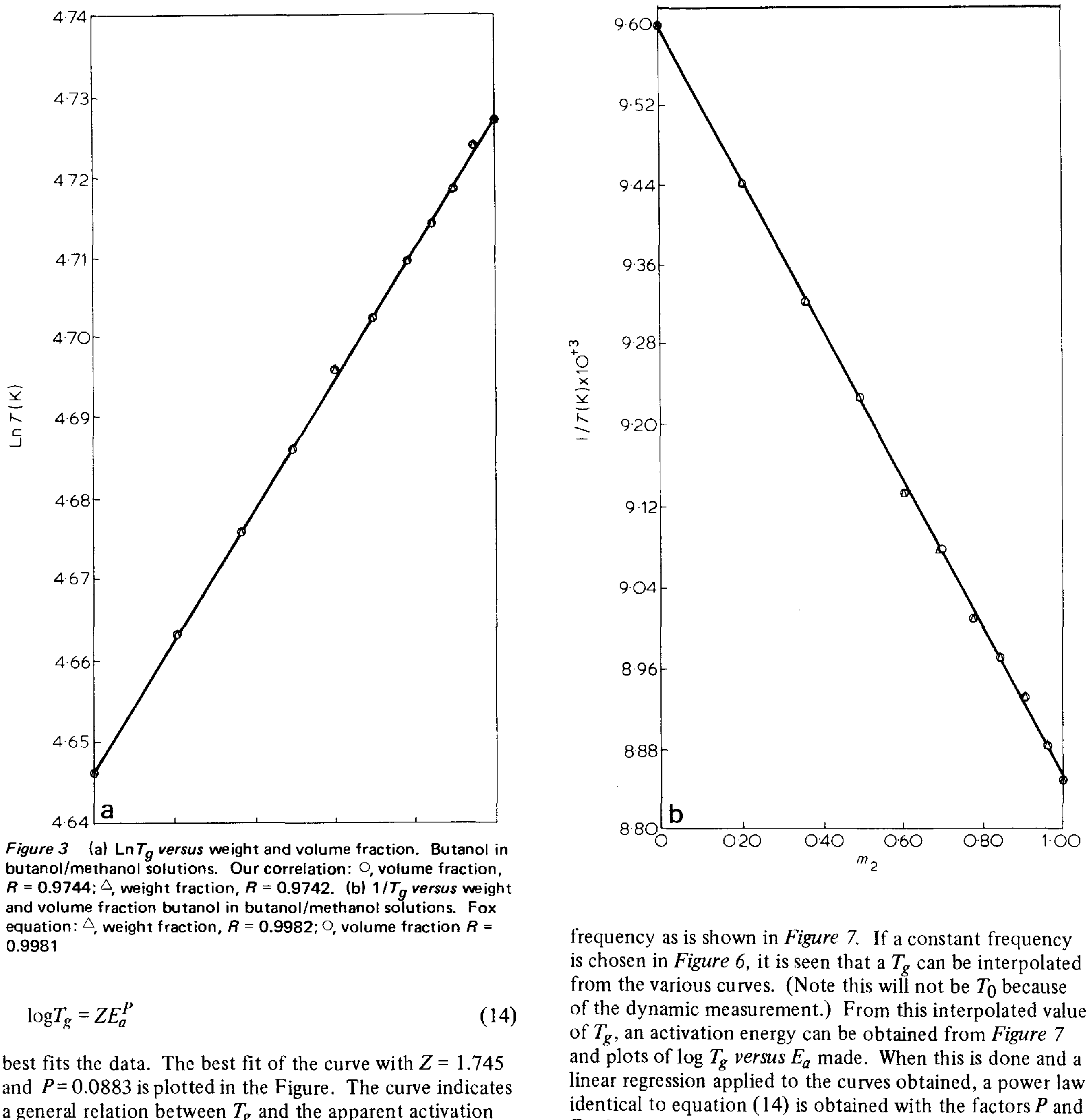

Figure 3 (a) LnT_g *versus* weight and volume fraction. Butanol in butanol/methanol solutions. Our correlation: ○, volume fraction, R = 0.9744; △, weight fraction, R = 0.9742. (b) $1/T_g$ *versus* weight and volume fraction butanol in butanol/methanol solutions. Fox equation: △, weight fraction, R = 0.9982; ○, volume fraction R = 0.9981

$$\log T_g = Z E_a^P \qquad (14)$$

best fits the data. The best fit of the curve with Z = 1.745 and P = 0.0883 is plotted in the Figure. The curve indicates a general relation between T_g and the apparent activation energy at a given frequency for the small molecules and polymers plotted in *Figure 5*. The power dependence of 0.0883 is unusual but can be explained.

If the WLF formalism is examined, an equation relating the frequency position of T_g with temperature can be obtained[4]:

$$\log \frac{(\tau)}{(\tau_0)} = \frac{-A(T - T_0)}{+B(T - T_0)} \qquad (15)$$

where T_0 is a reference temperature, usually the glass transition temperature, $\nu(1/\tau)$ is the frequency of a dynamic measurement used in determining T_g and A and B are constants, (once thought to have a value of 17 and 51, respectively, for most polymers.) A plot of equation (15) (with A = 17 and B = 51) with various values of T_0 is shown in *Figure 6*. The slope of each of the curves at any given frequency is the apparent activation energy for T_g at that frequency as is shown in *Figure 7*. If a constant frequency is chosen in *Figure 6*, it is seen that a T_g can be interpolated from the various curves. (Note this will not be T_0 because of the dynamic measurement.) From this interpolated value of T_g, an activation energy can be obtained from *Figure 7* and plots of log T_g *versus* E_a made. When this is done and a linear regression applied to the curves obtained, a power law identical to equation (14) is obtained with the factors P and Z a function of the frequency. These results are shown in *Figure 8* along with the fit of *Figure 5*. The functional dependence of P and Z on frequency is shown in *Figure 9*. The experimental and theoretical data of *Figure 8* are similar. However, *Figure 9* indicates that the WLF formalism predicts a value of P = 0.0945 in equation (14) at 1 Hz measuring frequency. This value does not coincide with the value of 0.0883 obtained for the experimental data of *Figure 5*. Experimentally, it must be remembered:

(1) all polymers do not exhibit T_g transition maps with the values of A = 17 and B = 51 in equation (14) (for example, see values listed in *Figure 8*). Thus the data in *Figure 5* are an average log T_g vs. E_a over a variety of descriptive WLF equations:

(2) the error in interpreting the glass transition at a given frequency from a transition map for systems having activation energies greater than 100 kcal mol^{-1} can be high (±20 kcal mol^{-1}) and this error is also introduced in the correlation of *Figure 5*.

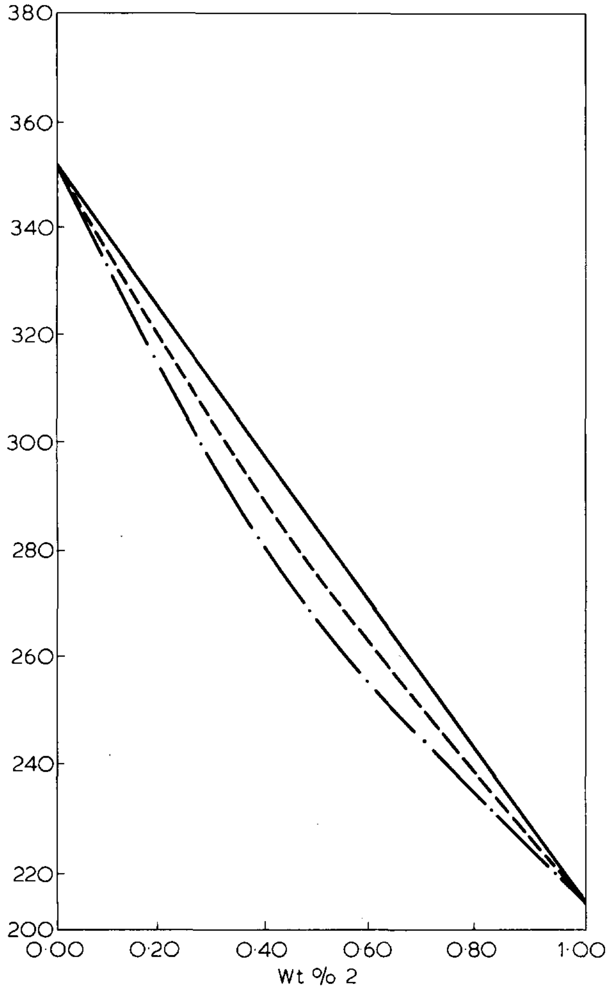

Figure 4 T_g as a function of composition for mixtures of materials with T_gs of 353K[1] and 216K[2], respectively. ———, linear correlation; — — —, our results; — · — · —, Fox results

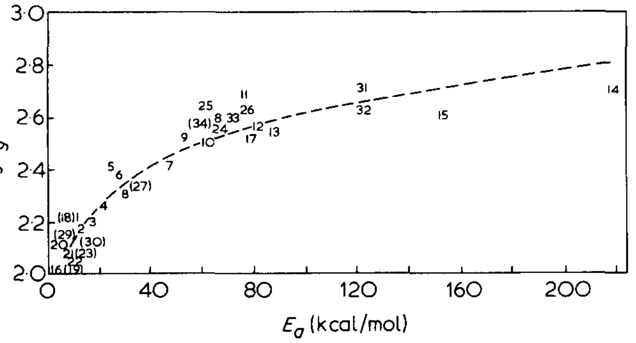

Figure 5 Log T_g (1 Hz) *versus* the apparent activation energy of T_g at 1 Hz. — — — —, best fit of data, numbers equal experimental data points (*Table 2*); — — —, log T_g = 1.743 $E_a^{0.0883}$

In comparing the experimental value of P with those obtained from the WLF equation using the values of A = 17 and B = 51 (see *Figure 8*), a value of 0.0883 is of the right order of magnitude.

The above discussion dealt with the interrelationship between dynamically measured glass transitions and their apparent activation energies at a given measurement frequency. It was shown that there is a relationship between these values and the WLF formalism. The power function $\log T_g \approx AE_a^P$, where Z and P are functions of measurement frequency, was obtained. The WLF equation provides[40]:

$$E_a = R\frac{\mathrm{d}\ln(a_t)}{\mathrm{d}(1/T)} = \frac{2.303RABT^2}{(B+T-T_0)^2} \qquad (16)$$

This quantity increases rapidly with decreasing temperature and at $T = T_0$ becomes:

$$E_a = \frac{2.303RA}{B}T_0^2 \qquad (17)$$

and indicates $\log T_g \approx E_a^{1/2}$ when T_0 is chosen as T_g.

Since, in the dynamic measurements, $T > T_0$, equation (17) should not be compared with equation (14), but an analysis, as above, must be done.

Table 2 List of polymers for which activation energies available reference and the identifying numbers used — *Figure 7*

No.	Sample	Ref
1	Poly(vinylidene fluoride)	20
2	Linear poly(ethylene)	36
3	Polytetrafluoroethylene	20
4	Polyoxymethylene	20
5	Polypropylene	20
6	Poly(propyl acrylate)	20
7	Poly(ethyl acrylate)	20
8	Syndiotactic poly(methyl methacrylate)	34
9	Isotactic poly(methyl methacrylate)	34
10	Poly(vinyl acetate)	20
11	Poly(*N*-vinyl carbazole)	19
12	Polystyrene	34
13	Poly(ethylene terephthalate)	20
14	Polycarbonate	21
15	Poly(ethyl methacrylate)	20
16	Tetrahydrofuran	22
17	Bisphenol-A-diphenyl carbonate	21
18	Glycerol	30
19	Propanol	30
20	Isobutanol	30
21	Butanol	30
22	Isoamylbromide	30
23	Isobutylbromide	30
24	Phenolphthalein	30
25	Poly(2-vinyl-*N*-ethyl carbazole)	31
26	Poly(3-vinyl-*N*-ethyl carbazole)	31
27	Poly(2-methyl-2-ethylpropylene sebacate)	32
28	Poly(2,5 dimethyl butylene sebacate)	32
29	Poly(diethyl siloxane)	33
30	Poly(dimethyl siloxane)	33
31	Poly(2,6-dimethyl phenylene oxide) (PPO)	26
32	75/25 wt % PPO/polystyrene (PS) blend	26
33	50/50 wt % PPO/PS blend	26
34	25/75 wt % PPO/PS blend	26

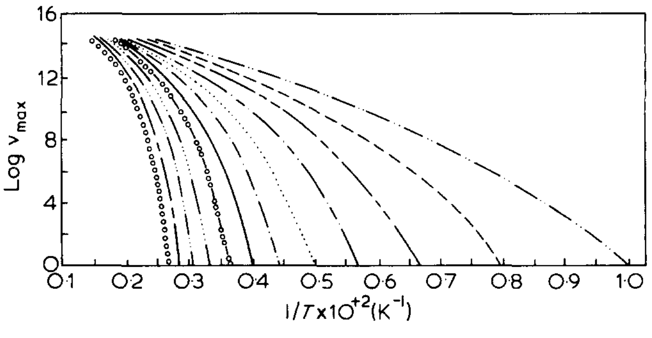

Figure 6 Log $\nu(T)$ *versus* $1/T$ (K^{-1}) for equation (21) with A = 17, B = 51, and various values of T_0 (T_g). T_g values: ·· — ·· —, 100; — — —, 125; — · · —, 150; — · — ·, 175; · · · ·, 200; — · — · —, 225; ———, 250; ooo—ooo, 275; · · · — · · ·, 300; — · · · · —, 325; — — —, 350; ooooo' 375

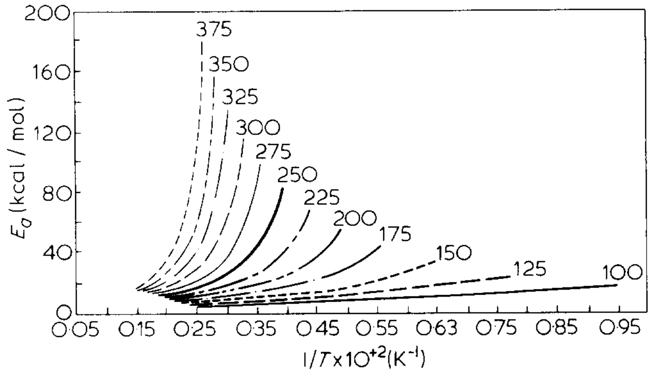

Figure 7 E_a (kcal/mol) *versus* $1/T(K^{-1})$ for the curves shown in *Figure 6* at various values of T_0 (T_g) T_g values as indicated

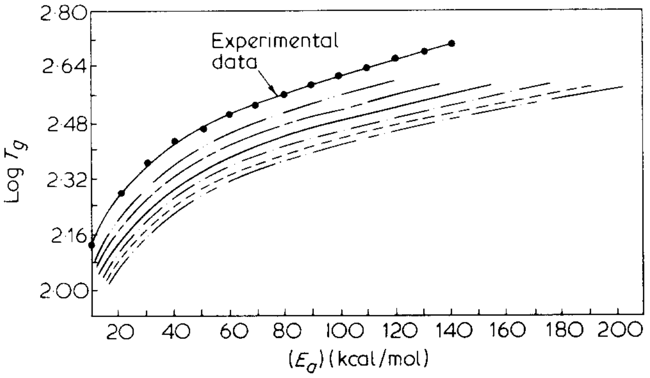

Figure 8 Log T_g *versus* apparent activation energy of T_g at 1 Hz as derived from equation (21) with A = 17 and B = 51. Best fit of *Figure 5* data also plotted

Polymer	*A*	*B*
PIB	16.5	104.0
PET (amorphous)	17.1	31.0
PET (31% crystal)	30.4	106.6

Log ν: — · — · —, 0; — — — —, 1; — · —, 2; ———, 3; — - —, 4; — · · — · ·, 5

The implication of the correlation in equation (14) is that the activation energy for a mixed system can be predicted at a fixed frequency. If equation (14) is substituted into equation (13), equation (18) is obtained:

$$E_{aT}^{P} = M_1 E_{a_1}^{P} + M_2 E_{a_2}^{P} \qquad (18)$$

and a prediction of the apparent activation energy of T_g at a given frequency from the activation energy of the pure component is obtained. The WLF constants of A = 17 and B = 51 were used in deriving the expressions for the relationship of P with frequency. In many polymers,these two values do not fit the data and different values are obtained. In these cases equation (18) would be

$$Z_T E_{aT}^{P_T} = M_1 Z_1 E_{a_1}^{P_1} + M_2 Z_2 E_{a_2}^{P_2} \qquad (19)$$

where the A and P values would be dependent on the WLF parameters used in equation (15).

One might expect that for polymers the power law dependence of activation energy at T_g on the glass transition would be related to the degrees of freedom available to the polymer. It is reported elsewhere[41] that the activation energy at T_g is related to the thermodynamic measure of flex energy, ϵ, obtained from the Gibbs–DiMarzio glass transition theory by a power law expression of the form $\ln\epsilon = CE_a^D$, an expression similar to equation (14) suggesting a potential relationship between apparent chain stiffness and the activation energy at the glass transition for compatible systems.

Recently, Couchman and Karasz[42] have reported an entropic derivation of the relationship between a solid solution T_g and its component T_g values. The relationship is:

$$\ln\left(\frac{T_g}{T_{g_1}}\right) = \left(\frac{M_2\Delta C_{P_2}}{M_2\Delta C_{P_2} + M_1\Delta C_{P_1}}\right)\left[\ln\left(\frac{T_{g_2}}{T_{g_1}}\right)\right] \qquad (20)$$

where the ΔC_{P_i} are the changes in heat capacity of the pure component materials at the glass transition and M_i are their mole fractions. If we let:

$$Q = (M_2\Delta C_{P_2})/(M_2\Delta C_{P_2} + M_1\Delta C_{P_1})$$

equation (10) can be written

$$\ln T_g = Q\ln T_{g_2} + (1-Q)\ln T_{g_1} \qquad (21)$$

and is similar to equation(8) where B represents a molar average change in the heat capacity at the glass transition. In order for equations (20) and (8) to be consistent, $A = M_2$, $\Delta C_{P_2} \simeq \Delta C_{P_1}$ and $M_{W_2} \simeq M_{W_1}$. Since $M_{W_1} \neq M_{W_2}$, for many of the mixed systems used to correlate data for equation (6), it must be concluded that for equations (8) and (10) to be consistent, the change in C_P at T_g for the individual components and their molecular weights compensate one another to yield the mass fraction.

CONCLUSIONS

An empirical equation relating the glass transition (measured dynamically) of mixed systems to their pure component T_gs has been observed. The relationship is:

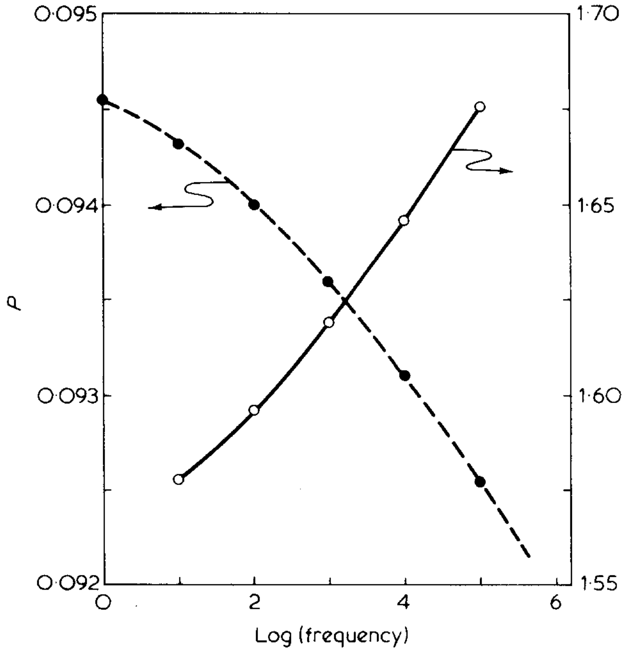

Figure 9 Z and P *versus* log (frequency) as obtained from the data in *Figures 6* and *7*. Log $T_g = ZE_a^P$ from WLF equation with $C1$ = 17 and $C2$ = 51

$$\ln T_g = m_1 \ln T_{g_1} + m_2 \ln T_{g_2}$$

where m is either volume or wt % of each component. The thermodynamic implications of the relationship have been considered and it is shown that other relationships governing the T_gs of mixed systems (Fox equation etc.) can be derived using certain thermodynamic constraints.

A general power law dependence of log T_g on the apparent activation energy of T_g at a given frequency is also ascertained from experimental data and it is shown that this power law relationship can be obtained from the WLF approach to the glass transition. From this, a relationship concerning the apparent activation energies of T_g (at a fixed frequency) of a mixed system as a function of the pure component activation energies is derived.

The simplicity and validity of the linear logarithmic relationship of a mixed amorphous system based only on its pure component T_gs has been demonstrated for three known classes of systems: (a) polymer–polymer: (b) polymer–small molecule and (c) small molecule–small molecule.

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