The glass temperature of polymer blends

Edmund A. Di Marzio

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
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The entropy theory of glasses is used to derive the glass temperature, T_g, of a binary polymer blend in terms of the glass temperatures of the two substituents. The formula is $T_g = B_1 T_{g1} + B_2 T_{g2}$, where B_i is the fraction of flexible bonds of substituent i. A bond is flexible if rotation about it changes the shape of the molecule. Bonds in side groups as well as in the backbone are to be counted. This formula assumes that the free volume, taken here to be the volume fraction of empty lattice sites, is the same for each of the three materials. It has no parameters. The above equation expressed in weight fractions, W_i, is $(T_g - T_{g1})W_1(\gamma_1/\omega_1) + (T_g - T_{g2})W_2(\gamma_2/\omega_2) = 0$, where ω_i is the weight of a monomer unit and γ_i is the number of flexible bonds per monomer unit. A more general treatment is given. One variation of the more general treatment which expresses the properties of the blend in purely additive terms gives $T_g = B_1 T_{g1} + B_2 T_{g2} + K B_1 B_2 (T_{g1} - T_{g2})(V_{01} - V_{02})$, where V_{0i} are the free volume fractions of the homopolymers at their glass temperatures and K is a constant. The added term is usually small. The most general form of the equation requires the energy of interaction between the two unlike molecules, which can be estimated by volume measurements on the blend.

(Keywords: polymer blends; glass transition; polymer alloys; polymer glasses)

INTRODUCTION

Compatible polymer blends are simply one-phase, two-component systems, both components being polymers. Polymer blends are exceptional in that two polymers picked at random are usually not compatible. This is due to London dispersion forces between unlike molecules being the geometric mean of the forces between corresponding like pairs (see the discussion following equation (15)). Nevertheless, many blend systems have recently been discovered[1]. Aids to forming polymer blends are choosing appropriate molecular weights, covalently coupling the two polymers and, of course, picking compatible monomer species.

One of the tests of blend compatibility is that the system has one rather than two glass temperatures. So it is sensible to have estimates of glass transition temperatures. The entropy theory of glasses (also called the Gibbs–Di Marzio (GD) theory) has been successful in predicting the glass transition temperature for many physical systems[2,3]. Related to the problem at hand, the glass temperature has been predicted for copolymers[4], for plasticizers[5] and for blends of different molecular weights of the same species (polydisperse systems[2]). A comment and equation (6) have been published previously[3] but the treatment was obtuse and not picked up by the polymer community. The basic equation of the GD theory is equation (7) and it can be used to predict glass temperatures as a function of molecular weight, plasticizer content, copolymer content and relative amounts of the two components, all simultaneously! In this paper we derive a formula for the T_g of compatible blends of large molecular weights, equation (6). This formula is identical in form to the Gordon–Taylor (GT) equation[6], equation (22), except that K has a different interpretation. There are no parameters; only the chemical structures need be known.

The entropy theory of glasses is an equilibrium theory

that has been successful in predicting the location of the glass temperature, but not in predicting the all important kinetic properties. It starts with the observation that all materials, even glasses, have equilibrium properties and asks what they are. The Flory–Huggins lattice model, so successful for liquid polymers, is simply applied to low temperatures. A second-order thermodynamic transition is found to occur at low temperatures and this transition is identified with the glass transition because the observed glass transition has the same discontinuities in thermal expansion coefficient and specific heat as predicted by the theory. The cause of glass formation is attributed to the decrease in the number of configurations of the system to relatively small values. The number of configurations becomes so small that flow, which is viewed as a jumping from one allowed configuration in phase space to another, is impeded. According to the lattice model this occurs at a finite temperature which we identify with the glass transition temperature[2]. Note that relatively recent Monte Carlo simulations show that the Huggins version of the lattice model which was used in our computations is very accurate[7,8]. This means that the statement that the number of system configurations is decreasing drastically to small values at a finite temperature is valid even though the transition may not be perfectly sharp. Thus if, at a minimum, the inverse character of the relationship between viscosity and configurational entropy is accepted, the thermodynamic entropy can be used to predict the location in T, P space of the glass transition.

THEORY

The entropy theory of glasses predicts that the transition occurs when the configurational entropy, S_c, reaches a critically small value. The Flory–Huggins version of the lattice theory actually predicts that $S_c = 0$ at a finite temperature T_2 at which a second-order transition in the

Ehrenfest sense occurs. However, we can derive the formula for the glass temperature of blends with weaker conditions.

All that is required is that there is a critical (small) value of entropy at which the glass transition occurs. Two factors contribute to the decrease in configurational entropy as we lower the temperature. The largest effect, according to our previous statistical mechanical development, is due to the many configurations of the individual molecules. If we use the isomeric state model then there are of the order of 3^x configurations (different shapes) at high temperatures for each molecule, but at low temperature the number is greatly reduced because of rotations about semi-flexible bonds to the lower energy shapes. The rate at which this decrease occurs is controlled by the stiffness energy of the molecule $\Delta\varepsilon/kT$. The formula for the fraction of bonds flexed into the $(z-2)$ higher energy positions is given by the Boltzmann expression

$$f = (z-2)\exp(-\Delta\varepsilon/kT)/[1+(z-2)\exp(-\Delta\varepsilon/kT)] \quad (1)$$

The second (and secondary) effect is due to the entropy of mixing of empty lattice sites with sites occupied by monomer units of the $x$mers. This effect is small when the van der Waals energy is sufficiently strong to squeeze out the holes. This is always true at low temperatures because the hole energy, the energy needed to break one van der Waals bond, E_h, is always coupled to temperature as E_h/kT. At high temperatures the entropy of mixing wins out over the bond energy. The formula connecting the volume fraction of holes with the hole energy is given by[2,9]

$$\ln(V_0^{\frac{1}{2}z-1}/S_0^{\frac{1}{2}z}) - z'E_h S_x^2/2kT = 0 \quad (2)$$

Here V_0 is the volume fraction of holes, z' the lattice coordination number. S_x, which is called the surface site fraction, is equal to

$$[(z'-2)x+2]n_x/\{[(z'-2)x+2]n_x+z'n_0\}$$

and $S_0 = 1 - S_x$, where n_0 is the number of holes and n_x is the number of polymer molecules. These equations describe how f and n_0 vary above the second-order transition temperature. As we cool through the glass transition, f and n_0 freeze into the values appropriate to (T_g, P_g). Below T_g, f and n_0 are constant along constant pressure lines.

To derive the formulae for the glass temperature of polymer blends with a minimum of assumptions we use the idea that glassification occurs when the configurational entropy reaches a critically small value. Thus

$$S_c(\Delta\varepsilon_1/kT_{g1}) = S_c(\Delta\varepsilon_2/kT_{g2}) = S_c(\Delta\varepsilon/kT_g) \quad (3)$$

where we are for now ignoring the contribution due to holes. Because entropy is monotonic we can immediately write

$$\Delta\varepsilon_1/kT_1 = \Delta\varepsilon_2/kT_2 = \Delta\varepsilon/kT_g \quad (4)$$

If one uses the fact that $\Delta\varepsilon$ is a weighted average of the homopolymer $\Delta\varepsilon$'s

$$\Delta\varepsilon = B_1\Delta\varepsilon_1 + B_2\Delta\varepsilon_2 \quad 5)$$

where B_i is the fraction of flexible bonds that are of type i, then substitution of equation (5) into equation (4) gives

$$T_g = B_1 T_{g1} + B_2 T_{g2} \quad (6)$$

which is our main result. The derivation of equation (6) was very simple in part because we glossed over some

details: (1) justification of equation (5); (2) proof that free volume effects are not very important; and (3) a more careful statement of the meaning of B_i. We now discuss each of these points.

Justification of equation (5)

The expression for the entropy derived by Gibbs and Di Marzio is easily adapted to blends. The result is

$$S_c = kxn_x\left[\frac{(z'-2)}{2}\ln\left(\frac{V_0}{S_0}\right) + \frac{n_0}{(x_1 n_1 + x_2 n_2)}\ln\frac{V_0^{\frac{1}{2}z'-1}}{S_0^{\frac{1}{2}z'}}\right.$$
$$\left. + \ln\left\{\frac{[(z'-2)x+2](z'-1)}{2}\right\}\right] + \sum_{i=1}^{2}(x_i-3)n_i$$
$$\times\{\ln[1+(z-2)\exp(-\Delta\varepsilon_i/kT)]+f_i\Delta\varepsilon_i/kT\} \quad (7)$$

In obtaining equation (7) from equation (20) of Reference 2 we assumed random mixing of the two species of molecules. V_0 and S_0 are defined as before except that xn_x is replaced by $x_1 n_1 + x_2 n_2$ and $x = (x_1 n_1 + x_2 n_2)/(n_1 + n_2)$, where x_i is the total number of flexible bonds per chain and is γ_i times the number of monomer units per chain.

Obviously equation (5) will hold if

$$\ln[1+(z-2)\exp(-\Delta\varepsilon/kT)]+f\Delta\varepsilon/kT = A+D\Delta\varepsilon/kT \quad (8)$$

where A and D are constants. A plot of the left-hand side of equation (8) is shown in *Figure 1* and it is highly linear. Therefore, equation (5) is justified and equation (6) is obtained. The effect of higher-order terms on the right-hand side of equation (8) can be estimated by assuming the extreme case of no linear term but only a quadratic term, i.e. $A+D(\Delta\varepsilon/kT)^2$. Then, analogous to equation (4), we have

$$(\Delta\varepsilon_1/kT_{g1})^2 = (\Delta\varepsilon_2/kT_{g2})^2 = (\Delta\varepsilon/kT_g)^2 \quad (9)$$

and equation (5) would be replaced by

$$(\Delta\varepsilon)^2 = B_1(\Delta\varepsilon_1)^2 + B_2(\Delta\varepsilon_2)^2 \quad (10)$$

so that

$$T_g^2 = B_1 T_{g1}^2 + B_2 T_{g2}^2 \quad (11)$$

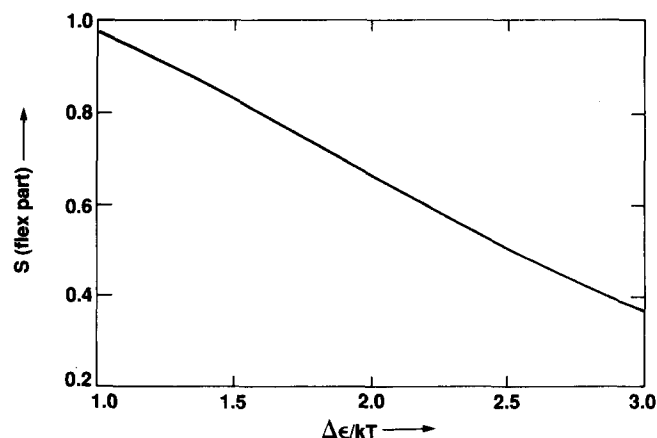Various numerical examples show that equation (11) gives blend T_gs that are only a few degrees different from

Figure 1 The contribution to the configurational entropy due to flexes *versus* $\Delta\varepsilon/kT$. For homopolymers $\Delta\varepsilon/kT \approx 2.25$. The linearity of this curve allows us to use the concept of an effective bond energy for homopolymers even though the monomer has bonds of different energies, and it allows us to define an effective bond energy for a blend of homopolymers

those obtained from equation (6). Thus, the effect of higher-order terms in equation (8) is negligible and equation (5) is justified.

Free volume effects are not important

Because equation (1) relates f to $\Delta\varepsilon/kT$ and equation (2) relates E_h to the free volume V_0 we can write the entropy as a function of the variables $(\Delta\varepsilon/kT, E_h/kT)$ or $(\Delta\varepsilon/kT, V_0)$ or (f, V_0) or $(f, E_h/kT)$. Therefore, we can write, analogous to equation (3),

$$S_c(\Delta\varepsilon_1/kT_{g1}, V_{01}) = S_c(\Delta\varepsilon_2/kT_{g2}, V_{02}) = S_c(\Delta\varepsilon/kT_g, V_0)$$
(12)

We could have made the substitutions from equations (1) and (2) directly into equation (8) but this would have limited us to a particular form for S_c. We wish to show, however, that our result is more general.

If we set

$$V_{01} = V_{02} = V_0$$
(13)

equation (4) follows immediately from equation (12), and equation (6) is again obtained as before. This is a happy circumstance because the free volume theory which assumes constant free volume at the glass transition[10,11] leads to equation (6) when consistently used. Note, however, that in general we cannot accept the notion that equation (13) holds, i.e. that the free volume is constant at the glass transition. Equation (2) shows that free volume is determined by the van der Waals energy, E_h, and the temperature location of the entropy catastrophe (given by $S_c \rightarrow 0$) is determined by both E_h and $\Delta\varepsilon$. Thus, in general, V_0 is not a constant at the glass transition.

To proceed further we need to calculate the free volumes via equation (2). Differentiation of equation (2) allows us to calculate $\Delta\alpha$, the break in the thermal expansion coefficient above and below the glass temperature and, therefore, to evaluate V_0 in terms of the measurable quantity $\Delta\alpha$. This is straightforward for the two homopolymers but for the compatible blend we need to estimate the effective value of E_h. Assuming random mixing we obtain

$$E_h = V_1^2 E_{h1} + 2V_1 V_2 E_{12} + V_2^2 E_{h2}$$
(14)

where V_1 and V_2 are the volume fractions of polymer of type 1 and 2, and E_{12} is the energy of a 1–2 bond. In general E_{12} bears no unique relationship to the homopolymer energies, so that we cannot express the free volume of the blend in terms of the free volumes of the homopolymers. However, if we assume that the forces are purely dispersive then* $E_{12} = E_{h1}^{\frac{1}{2}} E_{h2}^{\frac{1}{2}}$. This gives

$$E_h = (V_1 E_{h1}^{\frac{1}{2}} + V_2 E_{h2}^{\frac{1}{2}})^2$$
(15)

One can now in equation (15) substitute for each of the energies from equation (2) and obtain the free volume of the blend in terms of that of the two homopolymers.

This prescription for calculating the glass temperature of the blend uses only homopolymer properties. It is not exact because of the irreducibility of E_{12}. Further, it requires the use of equation (7) in equations (12) so that its results depend on the specific form of the entropy. We will not proceed further with this development because

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* In London theory the dispersion energy is proportional to the product of the polarizabilities; see, for example, Reference 12

miscible polymer blends violate equation (15). In fact, to the extent that equation (15) holds, the two-component system is phase separated. We emphasize, however, that if E_{12} is known the above equations can be used to predict blend transition temperatures.

A simpler treatment is to approximate the configurational entropy by

$$S_c = A + D\Delta\varepsilon/kT + CV_0$$
(16)

and to use a composition rule for the free volume. We choose

$$V_0 = B_1 V_{01} + B_2 V_{02}$$
(17)

It is easy to show that these equations lead to

$$T_g \approx B_1 T_{g1} + B_2 T_{g2} + KB_1 B_2 (T_{g1} - T_{g2})(V_{01} - V_{02})$$
(18)

with K a material constant.

A more precise definition of the bond fraction

The theory we have used is a lattice model theory and it requires that each configuration of each polymer fits onto the lattice. If we use a diamond lattice then we can picture that a bond can rotate about its neighbouring bond to any one of three isomeric states. These states can be given different energies. Our simple choice is that the energy of a chain is given by $(x-3)f\Delta\varepsilon$. The 3 occurs because the first two bonds serve to establish the orientation of the molecule in space; only the third and subsequent bonds label different internal configurations. This nearest neighbour model can be replaced by a more accurate counting procedure. These bonds need not be in the backbone; they can also be in side groups. The only requirement is that on rotation about the bond a new shape is obtained. Thus vinyl polymers have two flexible bonds per monomer due to the backbone and whatever additional flexible bonds occur in the side group. Thus poly(vinyl methyl ether) would have a total of three flexible bonds per monomer unit while poly(methyl methacrylate) would have four. Polystyrene, however, would have only two, the argument being that rotation of the benzene ring about the bond that connects it to the backbone does not result in a distinguishable shape. Proceeding in this way one can build up a table of numbers of flexible bonds per monomer. For large molecular weights we have

$$B_1 = x_1 n_1 \gamma_1 / (x_1 n_1 \gamma_1 + x_2 n_2 \gamma_2), \qquad B_1 + B_2 = 1$$
(19)

where x_i is the number of monomer units per molecule of species i and n_i is the number of molecules.

DISCUSSION

Relation to previous results

Couchman and Karaz[13], and Couchman[14–17] have developed an entropy theory of the glass temperature of polymer blends. Their theory is a phenomenological theory and requires knowledge of the specific heats at the glass temperature of the two homopolymers. Our theory is a microscopic theory and requires knowledge of molecular quantities. The simplest version of the theory (equation (6)) requires only a knowledge of chemical structure.

The Gordon–Taylor equation is based on the premise that the free volume at the glass temperature is a constant. There seems to be no basis for this assumption in fact.

First, the original basis for making the assumption[10,11] was that the slope of the volume at T_g *versus* T_g for various molecular weights of polystyrene was the same as the slope of the volume *versus* T_g curves below T_g. Subsequent measurements by Ueberreiter and Kanig[18] showed this assumption to be incorrect; see Reference 2 for more discussion of this point. Second, according to the lattice model, there is a unique monotonic relationship between the free volume defined as V_0 and the break in the thermal expansion coefficient, $\Delta\alpha$, above and below the glass transition. It is an experimental fact that $\Delta\alpha$ is not a constant.

Copolymers and blends are closely related. Copolymers can be viewed as chemical blends. The additivity rules used for copolymers can then be applied to compatible blends. In fact the additivity rules for blends are expected to be more accurate since no chemical bonds are involved. It is not surprising then that the formulae for copolymers have their counterparts in blends. Our formula is identical, with a slight reinterpretation of the meaning of bond fraction, from that given previously. In Reference 4 we showed that the GD theory was superior to GT theory for copolymers. Claims for blends must await the verdict of experiments.

Generalizations and limitations

The lattice model allows for the flex energy about different chemical bonds to have different values[19]. Thus we can in principle treat more complicated molecular systems. However, if we were to do this we would need to know more than one stiffness energy per molecule and knowledge of the homopolymer glass temperature would not be enough to determine all the $\Delta\varepsilon$s. We would need spectroscopic information, which we do not have. However, the approximate validity of equation (8) allows us to use an average energy for each homopolymer molecule provided that the energies are not too disparate.

Another aspect of the problem is that the theory requires that both kinds of molecules fit nicely onto the same lattice. This rarely happens with real molecules. The molecules may be incommensurate with each other, and therefore cannot fit onto the same lattice. Another possibility is that unlike molecules may fit together in a way that like molecules cannot. For example, antigens and antibodies fit together as hand and glove, but pure antigens (or pure antibodies) do not fit together well. An alternative approach to that used in this paper is to choose the degree of polymerization x to be proportional to the volume of the molecule, while the total number of flexible bonds per molecule is equal to γ times the number of monomer units per molecule. There is no ambiguity or added parameters with this procedure because specific volumes are well known. This idea has been used previously to predict successfully the specific heat discontinuity at the glass transition[20]. The effect is to adjust the relative contributions of holes and flexes to the entropy. We do not pursue this argument in this paper.

If we now relate the bond fraction to the weight fraction via

$$W_1 = \omega_1 B_1 \gamma_2/(\omega_1 B_1 \gamma_2 + \omega_2 B_2 \gamma_1), \qquad W_1 + W_2 = 1, \quad (20)$$

then equation (6) can be written as

$$(T_g - T_{g1})W_1(\gamma_1/\omega_1) + (T_g - T_{g2})W_2(\gamma_2/\omega_2) = 0 \quad (21)$$

This equation is identical to that for the glass transition of copolymers; see equation (4a) of Reference 4. The reason for this is that the additivity assumption on the flex energy was the same in both cases (i.e. equation (8)). For random copolymers, along the chain there are 1–2 flex energies as well as 1–1 and 2–2 flex energies. The 1–2 energies need not be related to the 1–1 and 2–2 energies. So for vinyl copolymers the assumption is an approximation. As pointed out in the previous paper, condensation copolymers are free of this difficulty. Blends also have no 1–2 bond energies.

Although we have not stressed the point, equation (7) allows glass temperatures to be estimated for systems that are blends, copolymers, plasticized systems and systems of different molecular weight, all simultaneously! Equation (6) (or equation (21)), however, is valid for large molecular weights only and for unplasticized systems.

One can go even further and develop general formulae that avoid the random mixing approximation. The formulae needed can be found in References 21 and 22.

Although an extensive comparison of theory and experiment is not attempted here we display data[23] for the system consisting of a blend of polystyrene and polyvinylmethylether (PS/PVME) as well as predictions from equation (21). Using molecular weights of 100 for PS and 58 for PVME monomer units and two flexible bonds per monomer for PS and three for PVME we obtain the results displayed in *Figure 2*. Equation (21) can be written as

$$T_g = (T_{g1} + RT_{g2})/(1 + R), \qquad R = W_2\gamma_2\omega_1/W_1\gamma_1\omega_2 \quad (22)$$
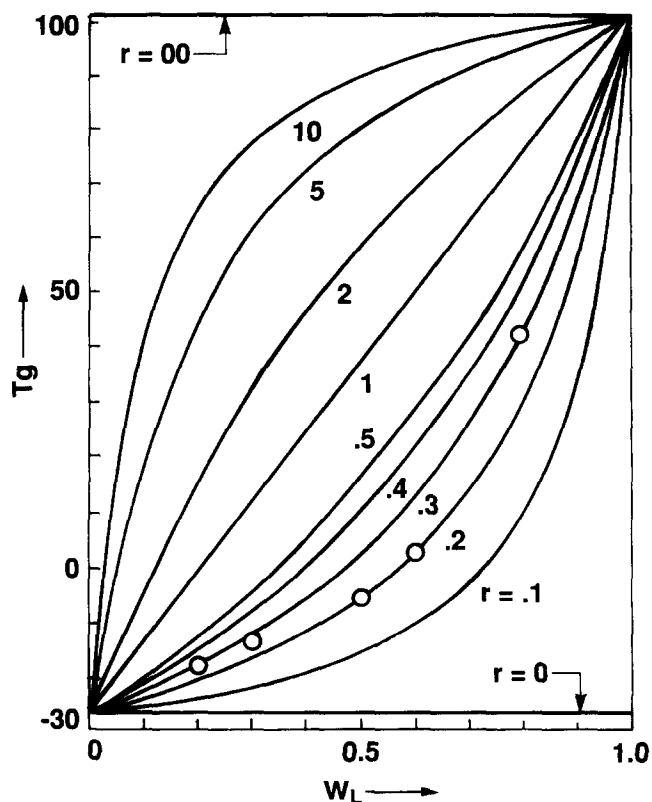

Figure 2 Glass temperature *versus* weight fraction for various values of $r = \gamma_2\omega_1/\gamma_1\omega_2$ for PS/PVME. Our best estimate of r is 0.387 but the data is best fitted by an r value between 0.2 and 0.3. The Gordon–Taylor equation gives the same curves, but r has the interpretation $\rho_1\Delta\alpha_2/\rho_2\Delta\alpha_1$. Our present best estimate of this value places it between the bounds 0.65 and 1.2

Thus the amount of bowing in the curves of *Figure 2* is determined by the ratio $r = \gamma_2 \omega_1 / \gamma_1 \omega_2$. For $r = 1$ we have a straight line. Our best estimate of the value of r for PP/PVME is 0.387, while the value which best fits the data is more nearly equal to 0.29. The predicted curves are labelled by their values of r. Data that have the shapes of the curves displayed in *Figure 2* are explainable in terms of the simple theory presented here.

The Gordon–Taylor equation is identical in form to equation (22) but the quantity corresponding to r is $K = \rho_1 \Delta \alpha_2 / \rho_2 \Delta \alpha_1$. In general the GT equation does not fit with experiment unless K is treated as an arbitrary parameter. The fit of equation (6) or, equivalently, equation (22) to experiment will be attempted at a later date.

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