The Viscosity of Miscible Blends

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SYNOPSIS

The WLF relation connecting viscosity to temperature is used as the basis for a formal description of the compositional variation of blend viscosities. An algebraic manipulation and the use of the cognate pure-constituent Williams–Landel–Ferry (WLF) factors provide a means of introducing composition and pure-constituent viscosities explicitly. Further progress follows through the use of a predictive theory of the compositional variation of glass-transition temperatures for random, single-phase blends. Particular versions of a general relation so obtained are explicated. The theory gives as the simplest case the benchmark linear rule of mixtures, from which it is clear that both positive and negative deviations can arise. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Part of the general topic of miscible blends in relation to the behavior of their pure constituents is the viscous behavior of such materials. Relevant both to the processing and end use of polymeric materials, in the continuum approach the topic has been treated in a phenomenological manner with an emphasis on providing for the possibility of various behaviors through the use of adjustable parameters.[1,2] Conceptually, this method makes any connection to pure-constituent properties an indirect one at best. Of more use would be a method of connecting blend and pure-constituent viscosities through properties that are not adjustable or, if they are, that can be determined either from pure-constituent behavior or from data other than viscosity data.

I offer here a method of connecting blend viscosity with pure-constituent behavior for those compatible systems in which the various mer–mer interactions do not differ greatly. The simplest nontrivial relation given in terms of pure-constituent properties alone is more complex than the benchmark "logarithmic rule of mixtures" (LROM), which is shown to be a particular version of this relation.

THEORY

The purpose of this contribution is largely pragmatic; that is, to provide relations for blend viscosity η through means of known practical use. Mostly, this problem has been addressed through the use of the Doolittle equation for viscosity as a function of free volume and temperature. However, this method results in what is more or less formal guesswork regarding the additivity rules which must be adopted or imposed rather than extracted. Consequently, I do not use this method *per se*. I do, however, use the related Williams–Landel–Ferry (WLF) equation, which can be written in terms of the ratio η/η_0 of blend viscosity at temperature T to the reference value of this property at the blend moving reference temperature T_0. This then leads to a method for deriving rather than imposing blend relations.

Suppose formally, then, that for pure constituents we may take $T_0 = T_g$ and the following blend relation arises[3]:

$$\log \eta/\eta_0 = \frac{-c_1(T - T_g)}{c_2 + (T - T_g)} \qquad (1)$$

Such a supposition maintains continuity of the form of the blend WLF relation with corresponding relations for the various pure constituents. When connected to a simple model, the viscosities here are

Newtonian. When this relationship is taken as purely empirical, that is not so.

Consistent with various empirical results and for the sake of simplicity, the quantities c_1 and c_2 of eq. (1) are taken as materials-independent (i.e., "universal") constants. No doubt there are blends for which this may not be an acceptable approximation. Indeed, there likely are blends for which eq. (1) in form is not appropriate. Such systems can be considered later, however, the convenience of these two approximations providing a very simple starting point according to which the viscosity ratio η/η_0 is determined solely by the compositional variation of the blend glass-transition temperature T_g.

Regardless of the particular form of the compositional variation of T_g, it is useful to rewrite eq. (1) to include explicitly the pure-constituent viscosity ratios $\eta_i/\eta_{0,i}$. Thus, for a binary blend with a single independent composition variable x, in general

$$\log \eta/\eta_0 = x \log \eta_1/\eta_{0,1} + (1 - x)\log \eta_2/\eta_{0,2}$$

$$- \frac{1}{c_2 + (T - T_g)} \{ x \log \eta_1/\eta_{0,1}(T_{g_1} - T_g)$$

$$+ (1 - x)\log \eta_2/\eta_{0,2}(T_{g_2} - T_g)$$

$$+ c_1[xT_{g_1} + (1 - x)T_{g_2} - T_g]\} \quad (2)$$

This is a direct manipulation of eq. (1) in the manner

$$c_1(T - T_g) = xc_1(T - T_g)$$

$$+ (1 - x)c_1(T - T_g) \quad (3)$$

with

$$\frac{xc_1(T - T_g)}{c_2 + (T - T_g)} = \frac{xc_1(T - T_{g_1})}{c_2 + (T - T_{g_1})} + R_1 \quad (4a)$$

and

$$\frac{(1 - x)c_1(T - T_g)}{c_2 + (T - T_g)}$$

$$= \frac{(1 - x)c_1(T - T_{g_2})}{c_2 + (T - T_{g_2})} + R_2 \quad (4b)$$

where the remainders R_1 and R_2 are evaluated directly from eq. (4).

For blends that are largely random and for which specific interactions are absent, a theory for the compositional variation of T_g gives this in terms of pure-constituent glass-transition temperatures T_{g_i}

and their corresponding increments of heat capacity Δc_{p_i} as[4]

$$T_g = \frac{x\Delta c_{p_1}T_{g_1} + (1 - x)\Delta c_{p_2}T_{g_2}}{x\Delta c_{p_1} + (1 - x)\Delta c_{p_2}} \quad (5)$$

The refinement that the Δc_{p_i} may be temperature-dependent is not considered here. Equation (5) used in eq. (2) provides for explicit evaluation of the terms involving T_g to give:

$$\log \eta/\eta_0 = x \log \eta_1/\eta_{0,1} + (1 - x)\log \eta_2/\eta_{0,2}$$

$$- \frac{x(1 - x)(T_{g_1} - T_{g_2})}{[c_2 + (T - T_g)][x\Delta c_{p_1} + (1 - x)\Delta c_{p_2}]}$$

$$\times [\Delta c_{p_2}\log \eta_1/\eta_{0,1} - \Delta c_{p_1}\log \eta_2/\eta_{0,2}$$

$$- c_1(\Delta c_{p_1} - \Delta c_{p_2})] \quad (6)$$

Equation (6) is not completely explicit because

$$c_2 + (T - T_g) = c_2$$

$$+ \frac{x\Delta c_{p_1}(T - T_{g_1}) + (1 - x)\Delta c_{p_2}(T - T_{g_2})}{x\Delta c_{p_1} + (1 - x)\Delta c_{p_2}} \quad (7)$$

The full version of eq. (6) includes the use of eq. (7).

As they stand, eqs. (6) and (7) represent a general relation obtained from eqs. (1), (2), and (5). However, the number of pure constituent properties required for eq. (6) to be used, eight, is too many to allow general statements about the qualitative and quantitative nature. Particular versions of eq. (6) are more suited for practical use. To this end, consider first the imposition of the condition

$$\eta_0 = \eta_{0,1} = \eta_{0,2} \quad (8)$$

This has some empirical basis and also a heuristic convenience, and reduces eq. (6) to

$$\log \eta = x \log \eta_1 + (1 - x)\log \eta_2$$

$$- \frac{\begin{array}{c}x(1 - x)(T_{g_1} - T_{g_2})[\Delta c_{p_2}\log \eta_1 \\ - \Delta c_{p_1}\log \eta_2 - (\Delta c_{p_1} - \Delta c_{p_2}) \\ \times [c_1 - \log \eta_0]]\end{array}}{\begin{array}{c}[c_2 + (T - T_g)] \\ \times [x\Delta c_{p_1} + (1 - x)\Delta c_{p_2}]\end{array}} \quad (9)$$

There are several interesting reductions of eq. (9). First, if the term in $c_1 - \log \eta_0$ is comparatively small,

$$\log \eta = x \log \eta_1 + (1 - x)\log \eta_2$$

$$- \frac{\begin{array}{c} x(1 - x)(T_{g_1} - T_{g_2}) \\ \times (\Delta c_{p_2}\log \eta_1 - \Delta c_{p_1}\log \eta_2) \end{array}}{\begin{array}{c} x\Delta c_{p_1}[c_2 + (T - T_{g_1})] \\ + (1 - x)\Delta c_{p_2}[c_2 + (T - T_{g_2})] \end{array}} \quad (10)$$

Taking c_2 as a "universal" constant, there are no adjustable parameters in eq. (10) or its subsequent versions. Equation (10) includes all composition dependences explicitly. This simplifies further if

$$\Delta c_{p_1} = \Delta c_{p_2} \quad (11)$$

to

$$\log \eta = x \log \eta_1 + (1 - x)\log \eta_2$$

$$- \frac{x(1 - x)(T_{g_1} - T_{g_2})\log \eta_1/\eta_2}{\begin{array}{c} x[c_2 + (T - T_{g_1})] \\ + (1 - x)[c_2 + (T - T_{g_2})] \end{array}} \quad (12)$$

Equation (12) is appropriate only for those blends for which T_g is a strictly linear function of composition. Note also that this relation is from eq. (9) a direct consequence of eq. (11), regardless of the value of $(c_1 - \log \eta_0)$.

A second special case of eq. (9) is obtained if

$$\Delta c_{p_2}\log \eta_1 = \Delta c_{p_1}\log \eta_2 \quad (13)$$

and is

$$\log \eta = x \log \eta_1 + (1 - x)\log \eta_2$$

$$- \frac{\begin{array}{c} x(1 - x)(T_{g_1} - T_{g_2}) \\ \times (\Delta c_{p_1} - \Delta c_{p_2})(\log \eta_0 - c_1) \end{array}}{\begin{array}{c} x\Delta c_{p_1}[c_2 + (T - T_{g_1})] \\ + (1 - x)\Delta c_{p_2}[c_2 + (T - T_{g_2})] \end{array}} \quad (14)$$

Here, both c_1 and c_2 are known. Although there is data from which the value of η_0 might be inferred, perhaps it is most prudent to take this as an unknown constant.

At any particular temperature, eqs. (9), (10), (12), and (14) are all of the form

$$\log \eta = x \log \eta_1 + (1 - x)\log \eta_2$$

$$- \frac{x(1 - x)(T_{g_1} - T_{g_2})A_1}{xA_2 + (1 - x)A_3} \quad (15)$$

where A_1, A_2, and A_3 are fixed by comparing the particular equation with eq. (15). The simplest approximation to the various relations above is made

when the third terms are negligible and gives the final nontrivial viscosity mixing relation as

$$\log \eta = x \log \eta_1 + (1 - x)\log \eta_2 \quad (16)$$

This is the LROM. As the various antecedents of this expression show, both positive and negative deviations from this are possible, with corresponding negative and positive curvature of $\log \eta$ with respect to x.

In both eqs. (12) and (14) the numerators are generally the stronger functions of composition and these differ most from eq. (16) at $x \cong \frac{1}{2}$. For eqs. (12) at this composition the form at $x = \frac{1}{2}$ is

$$\log \eta_{1/2} = \log(\eta_1\eta_2)^{1/2}$$

$$- \frac{1}{4} \left\{ \frac{(T_{g_1} - T_{g_2})(\Delta c_{p_1} - \Delta c_{p_2})}{c_2 + \left[T - \frac{(T_{g_1} + T_{g_2})}{2}\right]} \right\} \psi \log \eta_1/\eta_2 \quad (17)$$

TESTS OF REPRESENTATIVE RELATIONS

These tests are of two types, quantitative and qualitative. One important issue is whether both positive and negative deviations from linearity can occur. As the form of eqs. (12) and (14) indicate, such is the case. However, stringent quantitative tests of the formal relations given here require several pure-constituent data, the fewest of which is four [see eq. (12)], as well as blend data.

For blends of polystyrene (PS) with tetramethyl polycarbonate (MPC), T_g is a linear function of composition, T_{g_1} and T_{g_2} are known, and the zero-shear values of η_1, η_2, and η have been measured at 230°C.[5] For these blends, then, a critical comparison of theory and experiment is possible because all pertinent pure-constituent properties are known, as is η. The reported values of the pure-constituent properties then show that at this temperature, eq. (12) for PS/MPC blends is:

$$\log \eta = x(16 \times 74) + (1 - x)(10 \times 12)$$

$$- \frac{x(1 - x)622 \times 28}{x(81) + (1 - x)(175)} \quad (18)$$

Here c_2 is taken as 51.6°C.[3] The reported and calculated values of $\log \eta$ versus x are given in Figure 1.

For no other miscible blend could I find sufficient pure-constituent and other data for an additional critical comparison between observed and predicted blend viscosity. For PS blends with poly(2,6-dimethyl-1,4 phenylene oxide), Prest and Porter[6] reported a viscosity enhancement due to blending, but their results are generally WLF relation-shifted measurements and cannot be compared usefully with formal relations themselves derived from the WLF equation.

It would seem that additional experimental data are needed to provide further tests of the theory
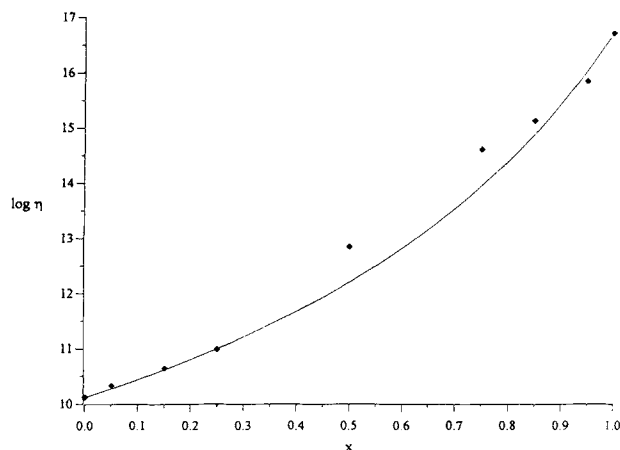
Figure 1 Experimental and calculated variation of log η at 230°C with amount x of MPC for blends of MPC with PS. The curve is calculated from eq. (18) of this paper from pure-constituent data given by Wisniewsky and colleagues.[5] The diamond shapes are the data of Wisniewsky and coworkers. Blends were made by freeze-drying in benzene at 50°C.[4]

given here. The general reason for this is that the conjunction of necessary pure-constituent data and blend data currently seems rare.

CONCLUSIONS

None of the blend relations given here require specific interactions for the non-linear variation of log η with composition, and thus all of these are limiting cases. Both positive and negative curvatures are provided for, and under certain circumstances an absolute comparison between theory and experiment is possible.

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