NOTE

Correlation of Blend and Pure Component Viscosities

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ABSTRACT: An equation for the viscosity of single-phase blends is derived by considering the fractions of the various kinds of bonds. For binary blends a quadratic term in viscosity is associated with unlike interactions in the melt. Both negative and positive deviations from the logarithmic rule of mixtures are possible. These deviations need not be connected to specific interactions. An extremum can occur and conditions for this are examined. In principle either an absolute maximum or an absolute minimum can occur. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 455–456, 2002

Key words: single-phase blends; viscosity; logarithmic rule of mixtures; extremum

INTRODUCTION

The viscosity of melt blends is of first-order interest in connection with their handing properties and processing conditions. In this context it would be helpful to provide rational descriptions of their behavior, in particular a means to correlate blend and constituent viscosities.

Previously I approached this problem indirectly by way of the Williams–Landel–Ferry (WLF)[1] equation and after some manipulation was able to derive a near-quadratic final expression. There, the composition dependence of blend viscosity η was driven by the composition-dependent glass transition. Here I consider the problem in a way far more direct, and I think more easily understood, physically.

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THEORY

For single-phase blends a measure of the melt viscosity, $\ln \eta$, is taken as the linear sum of the same function of viscosities associated with the various kinds of interactions. These are weighted according to the fraction f_{ik}, in which ik bonds occur. This heuristic supposition gives that for binary blends

$$\ln \eta = f_{ii}\ln \eta_{ii} + f_{22}\ln \eta_{22} + f_{12}\ln \eta_{12} \qquad (1)$$

Here the f_{ik} are bond fractions and the η_{ik} are viscosities. To consider a particular case of eq. (1), suppose for simplicity that the melt is a random mixture. If F_1 is the amount of component 1 in the blend,

$$f_{11} = F_1^2 \qquad (2a)$$

$$f_{22} = F_2^2 \qquad (2b)$$

$$f_{12} = 2F_1F_2 \qquad (2c)$$

The weighting factors f_{ik} are bond probabilities (e.g., f_{12} is the probability that moieties of kinds 1 and 2 are adjacent). From eq. (2), the determining equation for the viscosity, eq. (1), is now

$$\ln \eta = F_1^2 \ln \eta_{11} + F_2^2 \ln \eta_{22} + 2F_1F_2 \ln \eta_{12} \quad (3)$$

To put this in a form that is contiguous with the logarithmic rule of mixtures (LROM)[2] eq. (3) is rearranged, using $F_1 + F_2 = 1$, as

$$\ln \eta = F_1 \ln \eta_{11} + F_2 \ln \eta_{22} + 2F_1F_2 \ln \eta_{12}$$
$$- \frac{1}{2}[(\ln \eta_{11} + \ln \eta_{22})] \quad (4)$$

This is a generalization of the LROM, which is the first two terms of eq. (4). Note that departure from the LROM does not necessitate specific interactions, but rather follows from the fact that in binary blends there are both like and unlike interactions.

Note that with the definition

$$\ln \eta^{\text{excess}} = \ln \eta_{12} - \frac{1}{2}[(\ln \eta_{11} + \ln \eta_{22})] \quad (5a)$$

$$\ln \eta^{\text{excess}} = \ln \frac{\eta_{12}}{\sqrt{(\eta_{11}\eta_{22})}} \quad (5b)$$

eq. (4) becomes

$$\ln \eta = F_1 \ln \eta_{11} + F_2 \ln \eta_{22} + 2F_1F_2 \ln \eta^{\text{excess}} \quad (6)$$

From eq. (4) and evident in eq. (5) is that any departure of η_{12} from the geometric mean causes a deviation from the LROM. Because there is no evident basis to suppose that the geometric mean rule is general, the blend viscosity should usually be a quadratic function of composition. If $\ln \eta^{\text{excess}}$ is positive, $\ln \eta$ lies above the LROM and, if negative, below the LROM.

Consider the first composition derivative of eq. (6):

$$\frac{d \ln \eta}{dF_1} = \ln \eta \frac{\eta_{11}}{\eta_{22}} + 2(1 - 2F_1)\ln \eta^{\text{excess}} \quad (7)$$

When this vanishes there is an absolute extremum in $\ln \eta$ (and η). From eq. (7) the corresponding composition is

$$F_1^* = \frac{1}{2}\left[1 + \frac{1}{2}\frac{ln\ (\eta_{11}\eta_{22})}{ln\ \eta^{ex}}\right] \quad (8)$$

where physically $0 < F_1^* < 1$. The nature of the extremum of eq. (7) is given by the sign of

$$\frac{d^2 \ln \eta}{dF_1^2} = -2 \ln \eta^{\text{excess}} \quad (9)$$

If eq. (8) gives a physically acceptable solution, the extremum is a maximum for $\ln \eta^{ex} > 0$ [see eqs. (5a) and (5b)] and conversely a minimum for $\ln \eta^{ex} < 0$. For $\eta_{12} = \eta_{11}\eta_{22}$ but only for this is the LROM recovered. If $\eta_{11} = \eta_{22}$ any nonzero value of η^{excess} gives rise to an extremum.

CONCLUSIONS

This theory provides a rational method to describe the composition dependence of blend viscosities. It is far simpler than the approach through the WLF equation. Part of the simplicity is that only one parameter, η_{12}, is needed to correlate blend and pure constituent properties.

REFERENCES

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