

Viscous Behavior of PS, PP, and ABS in Terms of Temperature and Pressure-Dependent Hole Fraction

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ABSTRACT: We have developed a zero-shear viscous model in terms of temperature- and pressure-dependent hole fraction computed from Simha-Somcynsky Hole Theory. This model successfully interprets the viscosity data of PS, PP, and ABS as a function of hole fraction for a broad range of temperature and pressure. We have also introduced and discussed a new term: Viscoholibility; the derivative of logarithm of viscosity with respect to hole

fraction. When the hole fraction takes highest available value, the viscoholibility approaches asymptotically to a constant value by which the viscosity changes linearly with the hole fraction. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 110–113, 2010

Key words: zero-shear viscosity; free volume; hole fraction; Simha Somcynsky hole theory; equation of state

INTRODUCTION

Viscosity, η , has been studied extensively as a function of temperature- and pressure-dependent free volume or hole fraction.^{1–10} For instance, a correlation between the viscosity and the hole fraction has been recently developed for hydrocarbons,^{2,9,10} their mixtures,² and some polymers.^{1,6–8}

To explain the viscous behavior of a chain molecular system in terms of quantities in the SS theory, we made use of Eyring Significant Structure Theory (ESS)^{11–13} as nonequilibrium phenomena. The ESS and SS theories assume the liquid structure to be composed of solid–gas or occupied–free cells, respectively. In the ESS theory, solid-like and gas-like segments (molecules) are measured in terms of v_s/v and $(v - v_s)/v$, with v and v_s being the molar volumes of the liquid and the solid at the melting point, respectively. On the other hand, in the SS theory, the temperature- and pressure-dependent occupied site fraction, $y(T,P)$, is assumed to be as follows:

$$y = 1 - h = \frac{sN}{sN + N_h} \quad (1)$$

where h is the hole fraction, s is the number of segments in a molecule, N is the number of molecules, and N_h is the number of holes. The hole fraction computed from the Simha-Somcynsky (SS) theory is

a measure of randomly distributed highly mobile vacancies.^{2,10,14,15}

On the other hand, in the ESS theory to explain transportation of a molecule, one of the vibrational degrees of freedom is assumed to turn into a translational degree of freedom, and furthermore, under the influence of stress, the molecules successively jump into lattice vacancies measured as free volume elements of equilibrium thermodynamics.

Hence, we developed a model to interpret the transport properties of some polymer fluids based on the temperature- and pressure-dependent hole fraction as an equilibrium property of the SS theory. The model successfully correlates the experimental viscosity in terms of the hole fraction and applied to PP, PS, and ABS.

THEORIES

The SS-EOS theory

Four decades ago, Simha and Somcynsky (SS) developed an equation of state (EOS) based on the lattice-hole model, providing $\tilde{P} = \tilde{P}(\tilde{V}, \tilde{T}, h(\tilde{V}, \tilde{T}))$ derived from the configurational Helmholtz energy¹⁵:

$$\tilde{P}\tilde{V}/\tilde{T} = [1 - Q]^{-1} + (2y/\tilde{T})(y\tilde{V})^{-2}[1.011(y\tilde{V})^{-2} - 1.2045], \quad (2)$$

where it is formulated in terms of the scaled volume, scaled temperature, and scaled pressure, viz. $\tilde{V} = V/V^*$, $\tilde{T} = T/T^*$, and $\tilde{P} = P/P^*$. The scaling parameters are as follows: For an s -mer, V^* is defined by $N_A v^*/m_0$, where N_A is the Avogadro's

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number, m_0 is the molar mass of the segment, and characteristic molar volume v^* of a segment given by the segmental location r^* of the potential minimum. T^* equals to $q_z \varepsilon^*/ck$ as a balance between attraction and thermal energy contributed by the external degrees of freedom (3c) where attractive interaction parameter ε^* of a segment corresponds to the potential minimum. Finally P^* is defined by the ratio between chain attraction energy $q_z \varepsilon^*$ and volume sv^* , where q_z is the number of the first neighbor intermolecular pairs of the s -mer, viz., $s(z - 2) + 2$, with the coordination number z .

SS-EOS is defined in terms of occupied site fraction, y , to be computable by minimization of Helmholtz energy of an ensemble, $\partial F/\partial y|_{\tilde{V}, \tilde{T}, c/s} = 0$:

$$(s/3c)[(s - 1)/s + y^{-1} \ln(1 - y)] = (Q - 1/3)/(1 - Q) + (y/6\tilde{T})(y\tilde{V})^{-2} [2.406 - 3.003(y\tilde{V})^{-2}]. \quad (3)$$

where $Q = 2^{-1/6}y(y\tilde{V})^{-1/3}$. The SS-EOS has been applied to low- and high-molecular-weight systems to describe their thermodynamic properties and extended to interpret the nonequilibrium properties, viz. viscoelasticity, physical aging, etc. The hole fraction¹⁶ has been also utilized to express a variety of equilibrium and kinetic processes such as viscosity,^{1,3,5-10} ionic conductivity,¹⁷ etc.

The theory of viscosity in terms of hole fraction

The Eyring shear viscosity¹¹⁻¹³ is expressed by Yahsi et al.^{2,10} as follows:

$$\eta = \frac{6s}{q_z h} \frac{kT}{\sqrt{2}vk'} \quad (4)$$

where $q_z h/s$ is the number of the nearest available neighboring holes, v is the molar volume of a segment, and k' is jumping frequency of a segment (molecule) into a hole. The Eyring jumping frequency with activation energy, E_a , is expressed as follows¹¹⁻¹³:

$$k' = \kappa \frac{kT Z^*}{h_p Z} \exp \frac{-E_a}{kT} \quad (5)$$

where h_p is the Planck's constant, κ is the transmission coefficient, and Z and Z^* are the total partition functions for the segments in the initial and activated states, respectively. The term in eq. (5), kT/h_p , is called the Eyring frequency where k is the Boltzmann's constant and T is the temperature. In the derivation of eq. (5), it was taken that one of the vibrational modes in a normal initial state is turned

into translational one in an activated state during molecular transport. We assume that there is no more additional transformation from any initial degree of freedom to any activated one, therefore, the ratio of Z^* to Z be taken one.

To establish the activation energy in eq. (5), we need to consider contribution of well-organized molecules and holes. The total activation energy, E_a , for viscous flow is then treated as consisting of twofolds: the first is the energy required to form a hole and the second is that required for the molecule readily to jump into the hole. We naturally expect that each molecule (segment) energetically be positioned well-favored one of the positions available with the neighboring holes. The difference in energy between the best position and the average for the neighboring available positions should be proportional to the sublimation energy, E_s , and inversely proportional to the number of neighboring holes or to the hole fraction.^{2,10} The sublimation energy in equilibrium can be given by $(1 - h)q_z \Phi/2$, where Φ is the interaction potential energy among a pair of segments assumed to be Lennard-Jones as used in the SS theory. Hence, the activation energy, E_a , is then given by the following:

$$E_a = \frac{1}{2} \frac{1 - h}{h} a' q_z \Phi \quad (6)$$

where a' is the proportionality constant. Substituting eqs. (5) and (6) into eq. (4), the zero-shear viscosity can then be expressed as follows:

$$\ln \eta = \ln \eta^* + \alpha \frac{1 - h}{h} \frac{1}{T} \quad (7)$$

where the parameters η^* and α are given, respectively,

$$\eta^* = \frac{6sh_p}{\sqrt{2}q_z \kappa h v} \quad \text{and} \quad \alpha = a' \frac{q_z \Phi}{2k}. \quad (8)$$

Here, $h v$ and Φ quantities are slowly varying functions.^{2,9,10} Nonetheless, they are kept in the parameters. The derivative of eq. (7) with respect to h at constant T yields the following:

$$\left. \frac{\partial \ln \eta}{\partial h} \right|_T = - \frac{\alpha}{h^2 T} \quad (9)$$

where the negative sign means that the viscosity decreases as the hole fraction increases. The change of logarithm of viscosity with respect to h at constant T is inversely proportional to square of the hole fraction.

CALCULATIONS

Scaling parameters of the SS theory

The polymer materials we have considered are PP, PS, and ABS. The scaling parameters, P^* , V^* , T^* , and the structural flexibility parameter $3c/s = 1$, of SS-EOS are given by Kadijk and Vandenbrule¹ as $V^* = 1.1860 \text{ cm}^3/\text{g}$, $T^* = 10,900 \text{ K}$, and $P^* = 478.6 \text{ MPa}$ for PP, $V^* = 0.9662 \text{ cm}^3/\text{g}$, $T^* = 12,220 \text{ K}$, and $P^* = 700.4 \text{ MPa}$ for PS, and $V^* = 0.9409 \text{ cm}^3/\text{g}$, $T^* = 11,490 \text{ K}$, and $P^* = 842.8 \text{ MPa}$ for ABS. These parameters were then used for the determination of the hole fraction by eq. (3), and later used in viscosity calculations.

Calculation of viscosity parameters

Viscosity data of these polymers¹ are given for pressures ambient to 100 MPa and various temperatures charted in Figure 1. The viscosity data with the hole fraction computed from the SS theory are fitted with eq. (7) using nonlinear regression method in Mathematica to minimize the χ^2 merit function given by the sum of squared residuals $\sum_i (\ln(\eta_{\text{eq}}/\eta_{\text{exp}}))^2$. Figure 1 shows a plot of $\ln \eta$ versus $(1-h)/hT$ for the polymers with the best fit lines through the points with the average deviations 1.73% for PP, 1.45% for PS, and 0.71% for ABS. Their RMS values are 0.028 for PP, 0.037 for PS, and 0.012 for ABS. Each slope of a plot in Figure 1 is a measure of activation energy in Kelvin unit, evident from eqs. (7) or (8), given by positive constants: 123.1, 240.7, and 306.6 in increasing order for PP, PS, and ABS, respectively. PP has slowly varying viscous behavior with respect to the function of hole fraction, so its slope is lower than ABS and PS. On the other hand, ABS and PS

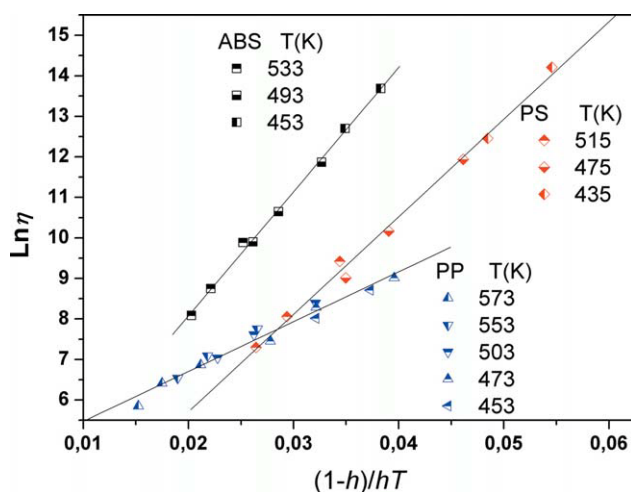


Figure 1 Logarithm of viscosity versus $(1-h)/hT$ for PP, PS, and ABS. The solid line is the best fit line through each of the data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

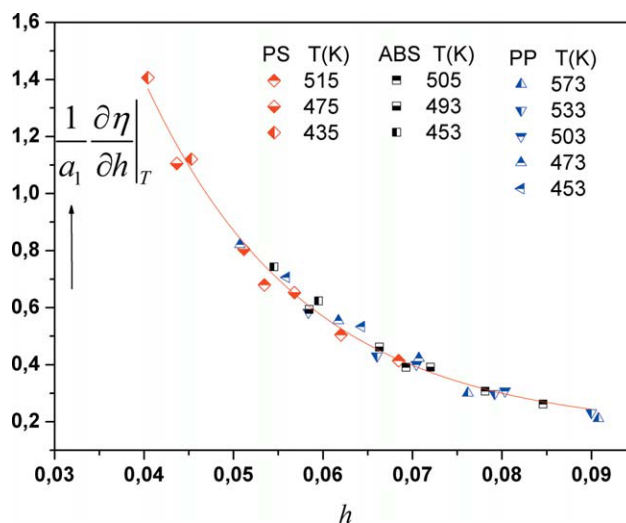


Figure 2 The derivative of logarithm of viscosity with respect to hole fraction at constant T versus h for PP, PS, and ABS. The solid curve is an exponential fit through all the data. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

have a sharper slope with respect to the function of hole fraction. The latter species require more activation energy than the former. This can be attributed to the benzene ring on the latter structures. Hence, the logarithm of the viscosity increases as the hole fraction decreases.

Furthermore, their intercepts, $\ln \eta^*$, at the viscosity axis represent the extrapolated viscosity values when the system dominates at sufficiently large hole fraction and expectedly at high temperature and low pressure. These values, $\ln \eta^*$ (Pa s), are 4.241, 0.8914, and 1.943 for PP, PS, and ABS. As explained earlier, the logarithmic viscosity of PP behaves slowly, so its lowest value, 4.241 Pa s, on extrapolating to the available highest hole fraction is quite larger than the other two species. PS and ABS change sharply with the hole fraction, so it extrapolates to the even lower values on introducing the available highest hole fraction. This can be reclaimed to the benzene rings since it produces more free volume and less viscous behavior as going to higher temperature or lower pressure. Sedlacek et al.¹⁸ have already discussed the effect of the size of the attached groups on PS and PP for the pressure and temperature sensitivity of viscosity. They have pointed out that the presence of benzene ring on PP causes significant rise of temperature and pressure sensitivity.

We name the derivative of the logarithm of viscosity with respect to h at constant T in eq. (7) as viscoholibility (viscose + hole + ability). It describes how the viscosity changes with the hole fraction. In Figure 2, the viscoholibility multiplied by the structural related parameter, α^{-1} , is plotted as a function of h for all the species, and the solid curve is the

exponential fit to the data as $\partial \ln \eta / \partial h = -\alpha[0.17 + 11.60 \exp(-h/0.018)]$. The parameter, α^{-1} , just shifts the viscoholibility in the vertical axis to overlap all the data. The change in logarithmic viscosity with respect to the hole fraction increases exponentially with the increase of hole fraction. At low hole fractions, the derivative increases rapidly with an increase of hole fraction since a small change in hole fraction causes a significant change in viscosity. On the other hand, at high hole fractions, it saturates to -0.17α from the exponential fitting. That is, the viscoholibility does not change significantly even if the amount of hole fraction is increased at about the saturated value. In another word, the logarithmic viscosity decreases linearly with the hole fraction at high hole fractions. This indicates the role of the pressure- and temperature-dependent hole fraction in viscosity mechanism.

CONCLUSIONS

In this article, we have developed a model for the viscose behavior of some polymers using the Eyring Transport Theory in terms of the temperature and pressure depended hole fraction of SS-EOS as an equilibrium theory. As can be seen from the analysis, the hole fraction as a measure of free volume dominantly plays a primary role for the interpretation of the viscosity. The logarithmic viscosity data in a broad temperature and pressure range has been attained with a compatible error. Using this formulation, it is possible to predict viscosity data for ABS,

PS, PP polymers by using the hole fraction. The hole fraction can be computed from PVT based SS-EOS and can be as well determined from other techniques such as positron lifetime spectroscopy technique (PALS).

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