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# Chemical relaxation time of polypropylene glycol and polypropylene glycol dimethylether in terms of temperature and pressure dependent hole fraction

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**Abstract :** We present a model explaining relaxation time of PPG (Polypropylene glycol) and PPGM (Polypropylene glycol dimethylether) with different molecular weights, PPG2 ( $M_w = 2 \text{ kg mol}^{-1}$ ), PPG3 ( $M_w = 3 \text{ kg mol}^{-1}$ ), PPGM1 ( $M_w = 1 \text{ kg mol}^{-1}$ ), and PPGM2 ( $M_w = 2 \text{ kg mol}^{-1}$ ), as a function of hole fraction at various fluid phase temperatures and high pressures. Proposed model based on the structural relaxation behavior of chain molecules given by “thermo-occupancy” function in terms of temperature and temperature-pressure dependent hole fraction is discussed and compared with the free volume

model. The former is the most universal behavior than the latter in terms of temperature and pressure. We discuss activation energy parameter and transmission coefficient for the species in terms of chain length and end groups such as dimethylether. Scaling relaxation time parameter in the proposed model has similar trend with relaxation time parameter of Adam-Gibbs theory. © Global Scientific Inc.

**Keywords :** Relaxation time; Free volume; Hole fraction; Fluid-phase temperature; Simha-somcynsky hole theory.

## INTRODUCTION

The relaxation behavior of polymers has been extensively studied in terms of temperature and pressure<sup>[1-7]</sup>. Similarly, the temperature dependency of dielectric relaxation of some polymers has been expressed with three parameters using Vogel-Fulcher (VF) form, viz.  $\tau = \tau_0 \exp[B/(T - T_0)]$ <sup>[8, 9]</sup>. The

pressure dependence of  $\tau$  as the phenomenological extension of the VF equation has been analyzed by a number of studies<sup>[10 11 5]</sup>.

Dynamic lattice liquid (DLL)<sup>[12]</sup> can describe the molecular rearrangements<sup>[13]</sup>. The molecular rearrangements are responsible for not only temperature but also the free volume that provides an adequate description of the isothermal and isobaric depen-

dencies of structural relaxation<sup>[13]</sup> and has an enlightening concept to explain the structural relaxation behavior of polymers<sup>[13]</sup>. Wand *et al.*<sup>[14]</sup> enhanced the Simha–Somcynsky equation of state (SS EOS) in order to represent the *PVT* behavior of polymers and gases at low pressures. Induced modification of the free volume contribution of the SS EOS along with proposed universal constants have been found guides for, among others, the actual work. On the other hand, Dlubek *et al.*<sup>[15]</sup> has applied the free volume theory of Cohen and Turnbull<sup>[16,17]</sup> to the structural relaxation processes in some liquid polymers, viz.  $\tau = C^{-1} \exp(\gamma V_f^*/V_f)$  where  $V_f$  is the mean specific free volume and  $\gamma V_f^*$  is the minimum specific free volume required for the occurrence of a structural relaxation process.

Extensive experimental efforts of explaining the relaxation phenomena have been studied thermodynamically in terms of temperature and pressure<sup>[10,14,18,19]</sup>. Alternatively, we have developed a theoretical model to interpret the relaxation time of the polymers as a transport phenomenon relating the Eyring Significant Structure (ESS) transport theory and the Simha–Somcynsky (SS) hole theory<sup>[20,21]</sup>. In our model, we employed the poly(propylene glycol) (PPG) and poly(propylene glycol dimethylether) (PPGM) compounds using the temperature and pressure dependent specific volume and dielectric relaxation measurements given by Prevosto *et al.*<sup>[22]</sup>

## THEORIES

### The SS-EOS Theory

Simha–Somcynsky (SS) developed an equation of state (EOS) based on the lattice-hole model<sup>[20]</sup> yielding the temperature and pressure dependent occupied site fraction,  $y(P, T)$ . The occupied site fraction,  $y$ , and the complementary hole fraction,  $h$ , are given by the following equation:

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

where  $s$  is the number of segments in a molecule, and  $N$  and  $N_h$  are the number of molecules and holes, respectively. The SS theory is formulated in terms

of scaled volume,  $\tilde{v}$ , scaled temperature,  $\tilde{T}$ , and scaled pressure,  $\tilde{P}$ , viz.:

$$\tilde{V} = V/V^*; \quad \tilde{T} = T/T^*; \quad \tilde{P} = P/P^* \quad (2)$$

where the scaling parameters are defined as follows:  $V^*$ ,  $T^*$  (by  $q_z \varepsilon^* / ck$ ), and  $P^*$  are defined correspondingly as molar volume  $v^*$  of the molecule, a balance between attraction and thermal energy contributed by the external degrees of freedom, and the ratio between molecular attraction energy  $q_z \varepsilon^*$  and volume. The number of interchain nearest neighbors in a lattice of the coordination number,  $z$ , is given by  $q_z = s(z-2) + 2$ .

The SS-EOS equation, derived configurationally from the Helmholtz energy, is given by

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{1}{1-\zeta} + \frac{2y}{\tilde{T}} Q(1.011Q - 1.2045) \quad (3)$$

where  $Q = (y\tilde{v})^{-2}$  and  $\zeta = 2^{-1/6} y (y\tilde{v})^{-1/3}$ . The minimization of the Helmholtz energy of an ensemble by  $\partial F / \partial y|_{\tilde{v}, \tilde{T}, c/s} = 0$  gives the occupied site fraction,  $y$ :

$$\frac{s}{3c} \left( \frac{s-1}{s} + \frac{\ln(1-y)}{y} \right) = \frac{\zeta^{-1/3}}{1-\zeta} + \frac{y}{6P^*} Q(2.409 - 3.303Q) \quad (4)$$

Here  $3c$  that appears explicitly in the equilibrium condition is the total degrees of freedom of the molecule. Utilizing the ideal chain flexibility employing  $3c = s + 3$  and using Eqs (3)–(4), we can compute the hole fraction,  $h = 1 - y$  as a measure of the free volume<sup>[23,24]</sup> and determine the scaling parameters,  $P^*$ ,  $V^*$ ,  $T^*$  and the structural parameter  $3c/s$  by superimposing experimental *P-V-T* data on the theoretical  $\tilde{P}, \tilde{V}, \tilde{T}$  surface.

### The Relaxation Time Theory

Debye–Stokes–Einstein equation relates the relaxation time  $\tau$  with viscosity,  $\eta$ <sup>[11]</sup>

$$\tau = \frac{4\pi\eta r^3}{3kT} \quad (5)$$

where  $k$  is the Boltzmann constant and  $r$  is the radius of a molecule. The Eyring shear viscosity can be expressed in terms of jumping frequency,  $k'$ <sup>[21,25,26]</sup> as

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

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where  $q_z h/s$  is the number of the available nearest neighboring holes,  $\nu$  is the molar volume of a segment. The Eyring jump frequency of a molecule to a hole with activation energy,  $E_a$ , can be expressed as<sup>[21, 25-28]</sup>

$$k' = \kappa \frac{kT}{h_p} \frac{Z^*}{Z} \exp \frac{-E_a}{kT} \quad (7)$$

where  $kT/h_p$  is the Eyring frequency,  $h_p$  is the Planck's constant,  $\kappa$  is the transmission coefficient, and  $Z$  and  $Z^*$  are the total partition functions for the segments in the initial and activated states, respectively, as a measure of concentration of their respective states. We assume in Eq. that the ratio of  $Z^*$  to  $Z$  is one and one of the vibrational modes in the initial state changes into translational mode in the activated state during segment transportation (relaxation). The activation energy ( $E_a$ ) in Eq., linearly proportional to the sublimation energy and inversely proportional to the number of neighboring holes (or to the hole fraction), can be stated as<sup>[21, 25, 26, 29]</sup>

$$E_a = \frac{1}{2} \frac{1-h}{h} a' q_z \Phi \quad (8)$$

where  $a'$  is the proportionality constant and  $\Phi$  is the interaction potential energy among a pair of segments assumed to be Lennard-Jones potential in the SS theory.

Combining Eqs (6) - (7) in Eq. (5), the scaled relaxation equation is given by

$$\ln(\tilde{\tau}T) = \alpha Y_h, \quad Y_h = \frac{1-h}{h} \frac{1}{\tilde{T}} \quad (9)$$

where the scaled quantity  $\tilde{\tau} = \tau/\tau^*$  with the scaling parameter

$$\tau^* = \frac{8\pi r^3 s h_p}{\sqrt{2} q_z h \nu \kappa k T^*} \quad (10)$$

and  $\alpha$  is the slope

$$\alpha = a' \frac{q_z \Phi}{2kT^*} \quad (11)$$

Here  $h\nu$  and  $\Phi$  are slowly varying functions of temperature and pressure<sup>[21, 25, 26, 29, 30]</sup>. Therefore, they are kept in the coefficients. Here the quantity,  $Y_h$ , in Eq. is a ratio of a number of occupied sites to unoccupied sites (holes) divided by the scaled temperature: the number of occupied sites for each empty

site per unit temperature. Thus,  $Y_h$  contributes to the calculation of relaxation in two-fold: First, it depends on the structural occupancy; second, it is inversely related to temperature and also correlated with vibrational energy of a relaxing molecule. Because of this significant contribution to our calculations, we would name  $Y_h$  as "thermo-occupancy function" correlating the relaxation.

The derivative of the logarithmic relaxation time with respect to  $h$  at constant temperature yields the following equation,

$$\left. \frac{\partial \ln \tilde{\tau}}{\partial h} \right|_{\tilde{T}} = -\frac{\alpha}{h^2} \frac{1}{\tilde{T}} \quad (12)$$

Here, we denote Eq. as a new thermodynamic quantity, "relaxiholibility", that is a derivative of the logarithm of relaxation time with respect to the hole fraction. Negativity in the relaxiholibility means the decrease with increasing hole fraction in the logarithmic relaxation time.

## CALCULATIONS

### The scaling parameters of the SS theory

The polymer materials studied in this work (Figure 1.a) are poly(propylene glycol) (PPG) and poly(propylene glycol dimethylether) (PPGM), with different molecular weights PPG2 ( $M_w=2$  kg mol<sup>-1</sup>), PPG3 ( $M_w=3$  kg mol<sup>-1</sup>), PPGM1 ( $M_w=1$  kg mol<sup>-1</sup>), and PPGM2 ( $M_w=2$  kg mol<sup>-1</sup>). Specific densities of these polymer melts were taken from the Tait equation<sup>[22]</sup> fitted to temperature range of 303-473 K and pressure range of 0.1-180 MPa. The SS theory includes calculated specific density data to obtain the characteristic parameters viz. the scaling pressure, scaling temperature and scaling volume, which are simultaneously fitted to the density data using the coupled Eqs - with the theory. TABLE 1 shows these computed parameters with the average and maximum relative percentage error in volume given by

$$\% \Delta V = \frac{100}{N} \sum \frac{V_{theory} - V_{exp}}{V_{exp}} \quad (13)$$

where  $V_{theory}$  is the specific density calculated from the SS theory and  $V_{exp}$  is the one calculated from the Tait equation, and  $N$  is the number of data. The theory

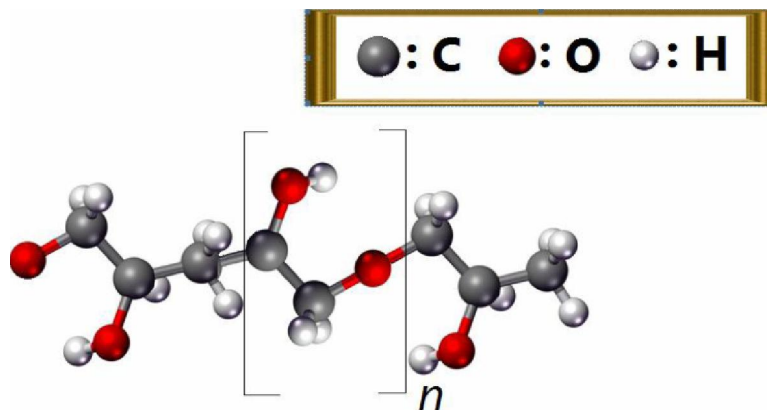


Figure 1a : The logarithm of relaxation time ( $\ln \tau$ ) versus  $1/h$  for all the species

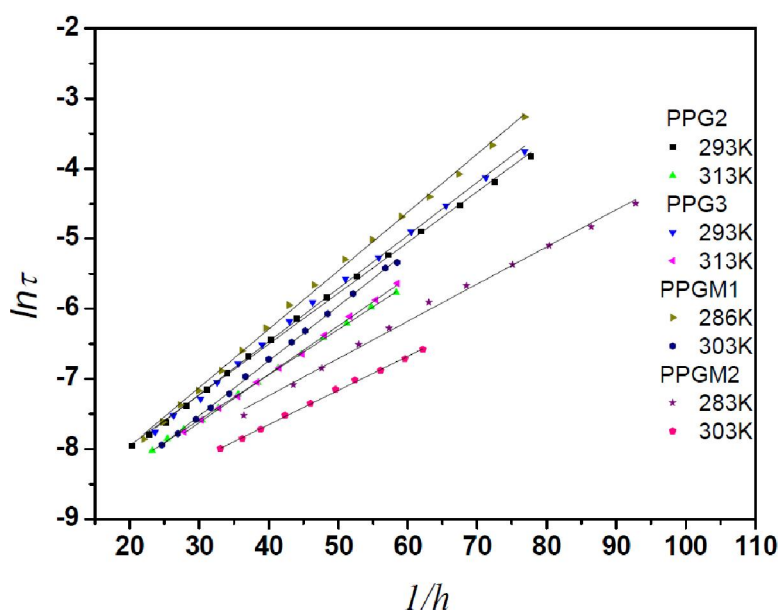


Figure 1b : The logarithm of relaxation time ( $\ln \tau$ ) versus  $1/h$  for all the species

with these parameters presented in TABLE 1 is well described with the average percentage error in specific volume 0.049% or less, and maximum percentage error in specific volume 0.37% or less for these species. Besides in the TABLE 1 we tabulated  $\langle h\tilde{V} \rangle$  and average interaction energy per segment  $\langle \Phi(K) \rangle$  where K (Kelvin) unit is used for energy scale. PPG2 has higher interaction energy with 461.4 K than PPG3 with 455.0 K. However, PPGM1 and PPGM2 have comparable interaction energy per segments with 458 K and 459.2 K, respectively. This can be due to the end-effect of which PPGM has dimethylether attachments compared to PPG. That is, PPGM has bulkier ends than PPG and almost slightly higher contribution to the average interac-

tion energy. Similar behavior can be also seen on the average interaction energy parameter  $\langle \varepsilon^* \rangle$  given in TABLE 1. PPGM1 and PPGM2 have a similar order for the interaction energy parameters: 320.1 K and 320.8 K, respectively. PPGM2 has a slightly higher interaction energy parameter than PPGM1 that is again attributed to the end groups of dimethylether. However, the average interaction energy parameter, 322.4 K, for PPG2 is higher than that of 317.9 K for PPG3. This can be due to the chain-end effect: the longer the chain, the lesser chain-end effect contribution. Hence, the interaction energy parameter decreases from PPG2 to PPG3. In terms of the average volumetric interaction parameters per segment  $\langle \nu^* \rangle$ , PPG2 with 34.56 cc/mol is slightly higher than PPG3 with 34.48 cc/mol. We see also the end effect here

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TABLE 1 : Computed characteristic parameters for SS-EOS

	PPG2	PPG3	PPGM1	PPGM2
$s$	56.10	84.42	27.63	55.47
$10^3 V^*(\text{m}^3/\text{kg})$	0.9692	0.9702	0.9928	0.9816
$T^*(\text{K})$	9213.3	9232.7	8723.9	9163.9
$P^*(\text{MPa})$	778.4	768.5	745.9	756.4
$\langle \varepsilon^*(\text{K}) \rangle$	322.4	317.9	320.1	320.8
$10^6 \langle v^*(\text{cc/mol}) \rangle$	34.56	34.48	35.93	35.39
$-\langle \Phi(\text{K}) \rangle$	461.4±0.1	455.0±0.1	458.0±0.1	459.2±0.1
$\langle h\tilde{V} \rangle$	0.02509	0.02268	0.02363	0.01757
$\% \Delta V$	0.033	0.040	0.049	0.033
$\% \Delta V_{\text{max}}$	0.15	0.16	0.37	0.18

TABLE 2 : Values of the Fitting Parameters in Eq. (9) and Some Fitting Errors as given in Eqs. (14) and (15).

	$10^6 \tau^*(s)$	$10^3 a$	$10^3 a'$	$10^6 \kappa$	%RMS	% $\Delta f$	CC
PPG2	2.59	2.31	0.164	0.0212	0.0045	0.73	0.9939
PPG3	2.27	2.42	0.116	0.0268	0.0058	0.85	0.9918
PPGM1	1.98	2.79	0.382	0.0309	0.0072	1.04	0.9924
PPGM2	2.10	1.75	0.125	0.0375	0.0065	0.88	0.9897

but slight decrease in the parameter. The volumetric interaction parameter for PPGM1 with 35.93 cc/mol is higher than that of PPGM2 with 35.39 cc/mol. We can state that the bulky ends in PPGMs cause the parameters to decrease from PPGM1 to PPGM2. Yet, the bulky ends in PPGM have a large contribution comparing with PPG.

### The parameters of relaxation model

For the PPG and PPGM compounds, the values of dielectric relaxation extracted from Prevosto, et al.,<sup>[22]</sup> were measured at temperatures of 293, 303 and 313 K for PPG2, of 286 K for PPG3, 303 K for PPGM2 and of 283 K and 303K for PPGM1 at pressures from 100 to 700 MPa. These data fitted to Eq. for each species are presented in TABLE 2 with the Root Mean Square (RMS) in relaxation times

$$\% \text{RMS} = \frac{100}{N} \sqrt{\sum (\tau_{\text{fit}} - \tau_{\text{exp}})^2} \quad (14)$$

where  $\tau_{\text{fit}}$  is the relaxation time calculated from the Eq. and  $\tau_{\text{exp}}$  is the experimental value. CC is the correlation coefficient of the Eq. and % $\Delta f$  is the average percentage deviation from linearity of Eq. as given by

$$\% \Delta f = \frac{100}{N} \sum \frac{f_{\text{fit}} - f_{\text{exp}}}{f_{\text{exp}}} \quad (15)$$

where  $f$  stands for  $\ln(\tau T)$ .

In Figure 1.b, we have plotted as a function of  $1/h$  for two different temperatures of all the species. The best fit line is drawn through the data for a given isotherm of each species. We can at first glance see a good linearity of the data for each isotherm and immediately state that for each isotherm the logarithm of relaxation time is inversely related to the hole fraction. As the hole fraction increases, the logarithm of relaxation decreases and all the curves almost tend to merge or saturate at a constant value at large hole fractions well above 0.05. This can be due the fact that the large hole fraction is sufficient to relax a molecule independent of their structural pattern either bulky or slimy. Besides, the relaxation curves shift to decrease when the temperature increases for each species. For instance, the curve for PPGM2 at 303 K is lower than the one at 283 K. The temperature has an obvious effect on the mobility of the relaxing molecule, hence, it is clear that the hole fraction has a strong correlation on the relaxation of a molecule. The model proposed and discussed in this article has an intention to bring up this

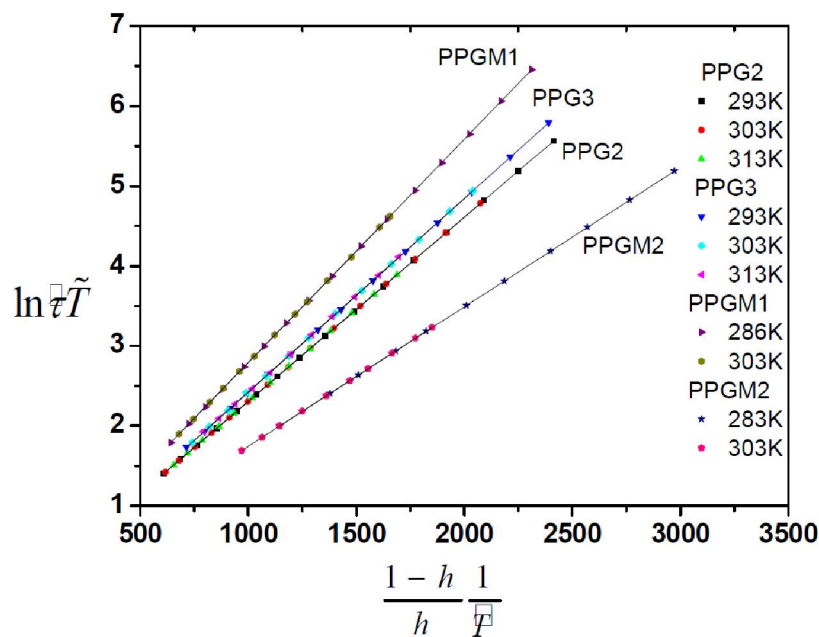


Figure 2 : versus thermo-occupancy function, , for the species with the best fit lines through the data

correlation.

Figure 2 shows a plot of  $\ln(\tilde{\tau} T^*)$  versus thermo-occupancy function,  $(1-h)/hT^*$ , for each species with the best fit line through the data with the average %RMS values 0.0072 or less and the deviation (% $\Delta f$ ) from the linearity shown in Figure 1.b (Eq. ) 1.04 or less for all species. The line through the data for each species is the best fit line given by Eq. . The slope of the curves is given by the parameter,  $\alpha$ , in TABLE 2, a measure of total energy of the molecule and the coefficient of activation energy. First, it is better to discuss the activation energy coefficient  $a'$ . PPGM1 with  $a' = 0.382 \cdot 10^{-3}$  has a larger activation energy coefficient than PPG2 with  $a' = 0.164 \cdot 10^{-3}$  and PPG3 with  $a' = 0.116 \cdot 10^{-3}$ . This can be due to the end group dimethylether bulkier than the end group of PPG. The reduction from PPG2 to PPG3 and PPGM1 to PPGM2 can be due to the chain length increase since the end effect has a decreasing effect on the parameter. Especially the very sharp decrease in PPGM2 is clearly apparent. The decrease in the parameter,  $\alpha$ , for PPGM1 and PPGM2 is responsible for the activation energy coefficient discussed above since the total interaction energy increases with the increasing chain length. Thus, the end effect has an important contribution on relaxing of the molecule. Attaching a bulky stuff like the

dimethylether on the end has an increase on the relaxation time.

The transportation coefficient,  $\kappa$ , tabulated in TABLE 2, has an increase with increasing chain length about 26% and 21% from PPG2 to PPG3 and PPGM1 to PPGM2, respectively, and also due to the attaching a bulkier molecule on the end from PPGs to PPGMs. Attaching bulkier dimethylether to PPG causes a remarkable increase about 76% in the transmission coefficient that is from  $0.0212 \cdot 10^{-6}$  for PPG2 to  $0.0375 \cdot 10^{-6}$  for PPGM2. On the other hand, scaling relaxation time parameter,  $\tau^*$ , with a unit per second per Kelvin given in Eq. has a corresponding value when the temperature is high enough and the hole fraction is sufficiently large. Parameter  $\tau^*$  decreases about 12.4% for PPG2 and PPG3 when the chain length increases. However, this effect is reduced by the end effect for PPGMs having lower values than PPGs. The increase in  $\tau^*$  from PPGM1 to PPGM2 is about 6% caused by the inversely related quantities: the hole fraction,  $h$ , and the characteristic temperature parameter  $T^*$ . The hole fraction decreases 11% from 0.0308 to 0.0273 measured at 350 MPa and 303 K, and the characteristic temperature parameter increases about 5% from 8723.9 K to 9163.9 K. A similar observation of fitting relaxation time to Adam-Gibbs theory has been conducted by Prevosto et. al.,<sup>[22]</sup> who ended up with  $\tau_0$  relax-

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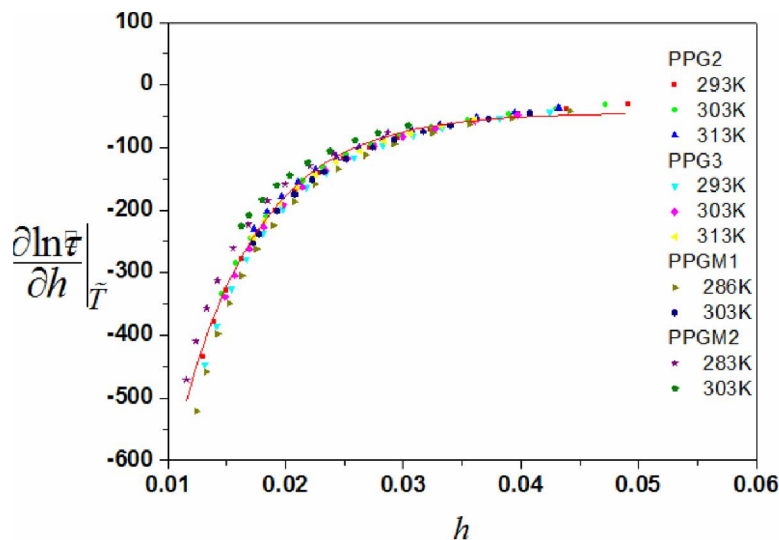


Figure 3 : Relaxiholibility versus hole fraction at various temperatures versus for all species. The solid curve is an exponential fit through all the data

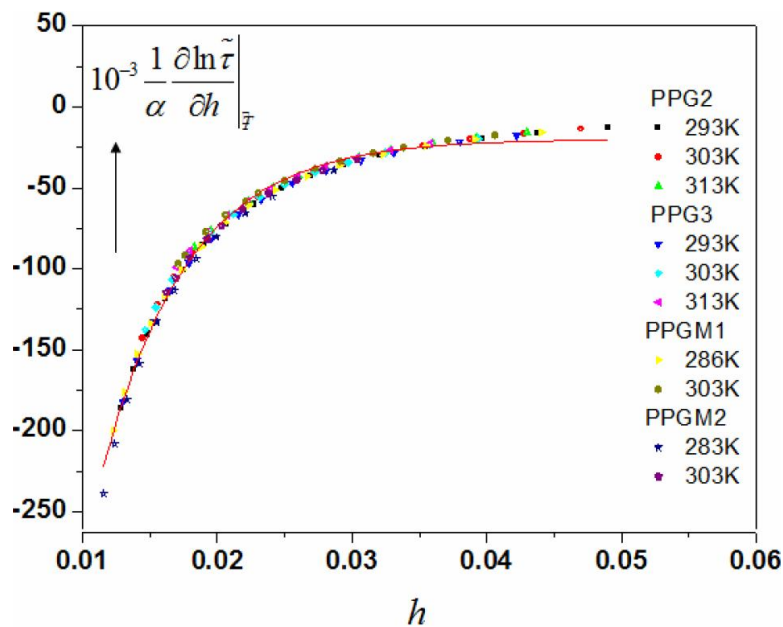


Figure 4 : Scaling relaxiholibility versus hole fraction at various temperatures for all species. The solid curve is an exponential fit through all the data

ation time parameter corresponding to high enough temperature: a sharp decrease from PPG2 to PPG3 and an increase from PPGM1 to PPGM2.

In Figure 3, the relaxiholibility defined as the derivative of logarithm of the relaxation time with respect to the hole fraction at constant temperature is plotted versus the hole fraction. When the hole fraction increases, the relaxiholibility exponentially increases and saturates to a value of -44.37. The low hole fraction strongly affects the relaxiholibility; even a small change in the hole fraction can cause a

sharp response in relaxation time. Evidently, at the low hole fraction the free volumes are very sensitive to the molecular mobility in molecular transport. However, when the hole fraction increases, the change in relaxiholibility saturates to a constant value causing that the logarithm of relaxation time linearly changes with the hole fraction. Dividing the relaxiholibility by the parameter of structure,  $\alpha$ , the Figure 3 is scaled for the all species and it is shown in Figure 4. The line is the best fit to all the data for all species with a fitting equation:

$$\frac{1}{x} \left( d \ln \tilde{\tau} / dh \right)_{\tilde{\tau}} = -20.10 \times 10^3 - 1.241 \exp(-h/0.00639) .$$

From Figure 4, it saturates to a constant value  $-20.10 \times 10^3$  when the hole fraction reaches to the highest values.

## CONCLUSION

In this paper, we have developed a model explaining the relaxation time of poly (propylene glycol) and poly (propylene glycol dimethylether) in terms of the hole fraction with the aid of the ESS transport theory and the SS-EOS hole theory. The SS-EOS hole theory based on *PVT* yielded the hole fraction but it can be determined from other techniques such as positron lifetime spectroscopy (PALS). In this work, the hole fraction dominantly played a primary role in the relaxation phenomena. In addition, the relaxation data for PPG and PPGM compounds fitted at different temperatures and high pressures were in expected trend with the molecular structures. We have also introduced a new term “relaxiholibility” to the terminology. The relaxiholibility with respect to the hole fraction increased exponentially and saturated at about 0.04 hole fraction for the polymers studied. The logarithmic relaxation time increased almost linearly with the increasing hole fraction after the saturation, however, it expectedly increased sharply with the increasing hole fraction at the low hole fractions.

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