NRC Publications Archive Archives des publications du CNRC

Free volume dependence of polymer viscosity

Utracki, L. A.; Sedlacek, T.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version
acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien
DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1007/s00397-006-0133-z>

Rheologica Acta, 46, 4, pp. 479-494, 2006-10-10

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=4040c8af-b4b8-4cf4-aae2-5f0b89b2bde2>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=4040c8af-b4b8-4cf4-aae2-5f0b89b2bde2>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the
first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la
première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez
pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Free volume dependence of polymer viscosity

L. A. Utracki · T. Sedlacek

Received: 31 March 2006 / Accepted: 28 August 2006 / Published online: 10 October 2006
© Springer-Verlag 2006

Abstract The Simha–Somcynsky (S–S) equation of state (eos) was used to compute the free volume parameter, h , from the pressure–volume–temperature (PVT) dependencies of eight molten polymers. The predicted by eos variation of h with T and P was confirmed by the positron annihilation lifetime spectroscopy; good agreement was found for $h(P=\text{constant})=h(T)$ as well as for $h(T=\text{constant})=h(P)$. Capillary shear viscosity (η) data of the same polymers (measured at three temperatures and six pressures up to 700 bars), were plotted as $\log \eta$ vs $1/h$, the latter computed for T and P at which η was measured. In previous works, such a plot for solvents and silicone oils resulted in a “master curve” for the liquid, in a wide range of T and P . However, for molten polymers, no superposition of data onto a “master curve” could be found. The superposition could be obtained allowing the characteristic pressure reducing parameter, P^* , to vary. The necessity for using a “rheological” characteristic pressure reducing parameter, $P_R^*=\kappa P^*$, with $\kappa=1$ to 2.1 indicates that the free volume parameter extracted from the thermodynamic equilibrium data may not fully describe the dynamic behavior. After eliminating possibility of other sources for the deviation, the most likely culprit seems to be the presence of structures in polymer melts at temperatures above the glass transition, T_g . For example, it was observed that for amorphous polymers at $T \cong 1.52T_g$ the factor $\kappa=1$, and the deviation vanish.

L. A. Utracki (✉)
National Research Council Canada,
Industrial Materials Institute,
75 de Mortagne,
Boucherville, QC J4B 6Y4, Canada
e-mail: leszek.utracki@cnrc-nrc.gc.ca

T. Sedlacek
Polymer Center, TGM 275,
Tomas Bata University in Zlin,
Zlin, Czech Republic

Keywords PVT behavior · Equation-of-state · Free volume · Viscosity · Temperature and pressure dependence

Introduction

The concept of free volume dates back to van der Waals' (1873) thesis. Accordingly, a liquid is visualized as composed of molecules that move within cells formed by the surrounding ones (Fowler 1929; Glasstone et al. 1941). Within each of these cells, a molecule occupies an intrinsic volume (occupied volume, V_0), and an extra space needed for the thermal motion (the free volume, V_f). Thus, the total specific volume of a given liquid is: $V = V_0 + V_f$, and the free volume fraction:

$$f = V_f/V = 1 - V_0/V \quad (1)$$

Batchinski (1913) showed that zero-shear viscosity (η_0) of low molecular weight liquids at different T and P changes with the density (ρ), i.e., with f : $\eta_0 \propto \rho$. Four decades later Doolittle (1951a,b, 1952, 1954; Doolittle and Doolittle 1957) correlated viscosities with redefined free volume [$f_D \equiv V_f/V_0 = f/(1-f)$]:

$$\ln \eta_0 = a_0 - a_1/f_D = (a_0 + a_1) - a_1/f \quad (2)$$

Similarly as van der Waals or Batchinski, Doolittle expressed f_D as an empirical function of density, viz.: $f_D = (1/b\rho) - 1$, where the van der Waals adjustable parameter $b \approx V_0$.

Simha and Somcynsky (S–S) published a lattice–hole theory of liquids (Simha and Somcynsky 1969; Somcynsky and Simha 1971), deriving an equation of state (eos), which by contrast with others (e.g., see Prigogine et al. 1953a,b, 1957; Flory et al. 1964; Sanchez and Lacombe 1976, 1978; Hartmann and Haque 1985; Dee and Walsh 1988a,b;

Ougizawa et al. 1989), not only describes the pressure–volume–temperature surface (PVT), but also explicitly provides the free volume parameter as a function of T and P : $h=h(T, P)$. Several reviews reported that the S–S eos performed better than the others simpler eos (Curro 1974; Zoller 1989; Rodgers 1993; Rudolf et al. 1995).

Since the early 1970s, a number of publications examined validity of the Doolittle empirical Eq. 2 replacing the empirical f_D by the extracted from S–S eos hole fraction (Utracki 1974, 1983a–c, 1985, 1986; Utracki and Simha 1981, 1982; Utracki and Ghijssels 1987; Kadijk and van den Brule 1994; Sedlacek et al. 2004, 2005):

$$\ln \eta = a_0 + a_1 Y_s \quad (3)$$

where η is either the zero-shear viscosity ($\eta=\eta_0$), or viscosity at constant stress, $\eta=\eta(\sigma_{12}=\text{constant})$, and $Y_s \equiv 1/(h + a_2)$. It is noteworthy that Eq. 3 predicts that η is a function of T and P only through $h=h(T, P)$, what defines a “master curve” of the dependence. The parameter a_2 in the definition of Y_s only linearizes the dependence.

For n -paraffins and their mixtures, good superposition was found in wide ranges of T (e.g., 20 to 204 °C) and P (e.g., 1 to 5,000 bars). Furthermore, the values of the key parameters in Eq. 3 were found to be constant (Utracki 1983a,b, 1986).

Application of Eq. 3 to η of 15 polymers (Utracki 1983c, 1985; Utracki and Simha 2001b) was less straightforward. For example, molecular weight distribution (MWD) affected the magnitude of the a_1 slope. Furthermore, within wide range of T and P (e.g., $1 < T/T_g < 1.6$, where T_g is the glass transition temperature), some liquids undergo a secondary liquid–liquid transition, $T_{tr}/T_g = 1.20 \pm 0.05$ (Boyer 1977, 1980a,b, 1985, 1987). To superimpose the viscosity data below and above T_{tr} different characteristic pressure reducing parameters of Eq. 3 had to be used. Furthermore, to achieve superposition of rheological data onto a master curve, the characteristic pressure reducing parameter, P^* , was redefined as $P^*_R = \kappa P^*$, where the factor κ depends on the substance. It has been found that while for low viscosity liquids (e.g., paraffins and their mixtures, silicone oils, etc.) $\kappa=1$ gave good superposition, for most polymer melts $\kappa \geq 1$ had to be used.

Modification of the pressure reducing parameter might be examined from the perspective of the S–S theory and dynamics and flow. Because the theory is formulated in reduced variables, the assumption that P^*_R is larger in flow than P^* determined at thermodynamic equilibrium means that in flow the reduced pressure, $\bar{P}$, is smaller than at equilibrium; hence, in flow the effective reduction of h with P is smaller by a factor of κ . The theory also expresses the molecular weight of statistical segments as: $M_s \propto RT^*/P^*V^*$ (see below). For most vinyl polymers $M_s \approx 1/2 M_0$, where M_0 is molecular weight of the mer (Utracki 2005), i.e., statistically vinyl mer with two C-atoms in the main chain

occupies two lattice cells. Thus, replacing P^* by $P^*_R = \kappa P^*$ reduces M_s by a factor of κ . In short, the effective free volume in flow is larger than its value at the thermodynamic equilibrium.

For testing the validity of Eq. 3 measurements of η and h within the same range of T and P are required. For the chemically pure solvents the physical properties at any T and P are well defined, thus excellent data fit to Eq. 3 was obtained using viscosities from one source, and PVT data from another. However, for polymers this strategy is dangerous. There are many polymer grades, and the commercial resins contain plethora of different additives (Utracki 2005)—taking data from different sources may lead to serious errors. Furthermore, initially the method used to fit the PVT data to S–S eos was sequential (first, determine T^* and V^* from data at ambient pressure, and then compute P^* from data at $P>0$), resulting in a T and P dependence of P^* ; the current simultaneous fit of data eliminates this ambiguity.

In a recent publication, Sedlacek et al. (2005) reported η and PVT data for several commercial polymers determined within the same range of T and P . The data fitted to Eq. 2 showed that viscosity at higher pressure was lower than expected from the low-pressure behavior, i.e., the η vs $1/f$ dependence did not follow the expected pattern.

In the present paper, we reanalyze the data and attempt to identify the reasons for the reported lack of superposition. Accordingly, the paper examines the S–S eos, its reliability to predict the free volume fraction within full range of T and P . Next, the characteristic reducing parameters (P^* , T^* , and V^*) are computed from the coupled S–S equations, and the parameter h is calculated for T and P at which η was determined. The pressure effects on flow are also analyzed, and replacement of η_0 by the constant stress viscosity is discussed. For the sake of reliability, only interpolated viscosity data at selected constant stresses are used. The results are analyzed in terms of Eq. 3, and general conclusions are drawn.

The paper touches several domains of science, thus a large number of references. However, this is not a dispassionate and complete review of one or another of these, but rather presentation of observed molten polymer behavior and its proposed interpretation.

Simha–Somcynsky lattice–hole theory

The S–S theory

The theory (Simha and Somcynsky 1969; Somcynsky and Simha 1971) considers an amorphous, condensed system as a mixture of occupied and empty sites. It incorporates the Huggins and Flory configurational entropy of mixing

(Flory 1953), and the Lennard-Jones (L-J) intersegmental interactions (Lennard-Jones 1931; Lennard-Jones and Devonshire 1937) with the characteristic segmental energy, ε^* , and volume, v^* , per statistical segment, the latter defined as $M_s = M_n/s$, where M_n is the number-average molecular weight (Utracki 2005). The authors also introduced the number $3c$ of the external, volume-dependent degrees of freedom (Prigogine et al. 1953a,b, 1957), which for linear, flexible molecules is (Simha 1977):

$$3c = s + 3 \quad \therefore \text{for } s \gg 3; 3c/s \approx 1 \quad (4)$$

The variables of state and derived quantities are scaled by the three characteristic scaling parameters of pressure, temperature, and volume:

$$\left. \begin{aligned} P^* &= zq\varepsilon^*/(sv^*) \\ T^* &= zq\varepsilon^*/(Rc) \\ V^* &= v^*/M_s \end{aligned} \right\} (P^*V^*/T^*)M_s = Rc/s \quad (5)$$

where $zq = s(z-2) + 2$ is the number of interchain contacts in a lattice of coordination number z , and R is the gas constant. Using reduced variables (indicated by tilde), S–S eos is expressed by the coupled equations:

$$\begin{aligned} 3c \left[(U - 1/3)/(1 - U) - yQ^2(3AQ^2 - 2B)/6\tilde{T} \right] \\ + (1 - s) - (s/y)\ln[(1 - y)] = 0 \end{aligned} \quad (6)$$

$$\tilde{P}\tilde{V}/\tilde{T} = (1 - U)^{-1} + 2yQ^2(AQ^2 - B)/\tilde{T} \quad (7)$$

with the occupied lattice site fraction $y=1-h$, and the notation: $Q = 1/(y\tilde{V})$, $U = 2^{-1/6}yQ^{1/3}$. The L-J coefficients, $A=1.011$, and $B=1.2045$, are for face-centered cubic lattice with the coordination number $z=12$. Thus, Eqs. 6 and 7 describe the PVT surface, as well as the associated with it free volume function, $h = h(\tilde{P}, \tilde{T})$.

The P^* , T^* , and V^* parameters are determined by fitting the PVT -surface of a liquid to Eqs. 6 and 7, using a simultaneous nonlinear least squares fit. Rapid convergence is obtained in two steps: (1) fitting data to the polynomial expression, $\tilde{V} = \tilde{V}(\tilde{P}, \tilde{T})$ (Utracki and Simha 2001a), provides the initial values of P_{in}^* , T_{in}^* , and V_{in}^* , and (2) fitting the data to Eqs. 6 and 7. The computations give the P^* , T^* , and V^* parameters, as well as the values of $h = h(\tilde{P}, \tilde{T})$. However, because the temperature and pressure at which η was determined (T_R and P_R , respectively) may be different than those used in PVT measurements, the exact values of $h=h(P_R, T_R)$ have to be computed from Eqs. 6 and 7 for T_R and P_R , using the set of P^* , T^* , and V^* parameters of given polymer.

During the 30 odd years, the S–S theory has provided description of the PVT behavior in a single- and multicomponent systems, e.g., see (Simha et al. 1984, 2001;

Papazoglou et al. 1989; Utracki et al. 2003; Tanoue et al. 2004; Utracki and Simha 2004a; Utracki 2004a, 2006a) as well as that of the cohesive energy density and internal pressure (Utracki and Simha 2004b; Utracki 2004b). Its great advantage is the explicit incorporation of the free volume parameter, h , which in turn may be used to interpret variety of dynamic properties, e.g., shear viscosity of neat liquids, their blends, composites, or foams (Utracki and Simha 2001b).

For many decades, the free volume was an intellectual concept that helped interpretation of the experimental data, but which could not be measured. This situation improved with the advent of the Positron Annihilation Lifetime Spectroscopy (PALS), and the molecular modeling (Jean et al. 2003; Binder et al. 2003). Based on quantum mechanical calculations, the interpretation of PALS data provides the size of individual free volume cells, their distribution, as well as the total free volume that might be correlated with the free volume determined by other means at the same T and P .

Application of S–S theory to PALS

Positrons, e^+ , annihilate by interacting with electrons, e^- , following at least three mechanisms distinguished by different lifetimes. In polymers a *meta*-stable e^+e^- *ortho*-positronium (*o*-Ps) is formed. Its diameter is similar to that of hydrogen atom, i.e., of ca. 0.1 nm, and its lifetime depend on the size of the free volume cell. Thus, the lifetime of *o*-Ps (τ_3) is a measure of a single cavity, whereas both the lifetime and intensity (I_3) provide information of the total free volume content.

Excepting the recent publications (Srithawatpong et al. 1999; Olson et al. 2002; Olson 2004; Schmidtke et al. 2004; Consolati et al. 2005), it has been assumed that the free volume cells, V_3 , are spherical. The quantum mechanical calculations (Tao 1972; Eldrup et al. 1981) gave a semiempirical equation, relating the free volume cell radius, R , to the measured *o*-Ps lifetime, τ_3 :

$$\frac{1}{\tau_3(ns)} = 2 \left[1 - \frac{R(nm)}{R + R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + R_0} \right) \right]; \quad V_3 = \frac{4\pi R^3}{3} \quad (8)$$

where $R_0=0.1656$ nm is an empirical thickness of the electronic layer. The total free volume fraction, f_{PALS} , has been expressed as (Jean et al. 1986; Wang et al. 1990; Liu and Jean 1995):

$$\begin{aligned} f_{PALS}(-) &= V_3(nm^3)C_f \\ &= V_3[A I_3(\%) + B]; \quad \begin{cases} A = 0.018 \pm 0.002 \text{ when } B = 0 \\ B = 0.39 \pm 0.03 \text{ when } A = 0 \end{cases} \end{aligned} \quad (9)$$

The above relation is based on rough assumptions and must be considered approximate. The quoted constant values were determined from the experimental PALS data and the thermal expansion coefficient.

Schmidt and Maurer (2000) calculated A of Eq. 9 assuming that f_{PALS} is equal to h calculated from S–S eos; the A -values were found to vary from one polymer to the next, viz. $A=0.038$ for PVAc, 0.02 for PC, and 0.0152 to 0.0167 for PS. Documented dependence of I_3 on other factors than free volume fraction (Schmidt 2000), distance from T_g (Kisliuk et al. 2000), and the void geometry (Consolati et al. 2005) may be a reason for this variability. Another approach was proposed by Dlubek et al. (1998, 2004–2006). The authors calculated free volume cell size from Eq. 8, and then from S–S relation the hole fraction, h , what lead to the number of averaged cells in the melt. However, because the current aim is to examine consistency of h and the free volume computed from PALS data, the use of Eq. 9 seems to be the most neutral.

Comparison of free volumes from PALS and PVT

Because the aim of this paper is examination of the relation between the free volume parameter, h , and viscosity, η , it is important to compare the theoretical $h=h(T, P)$ dependence with free volume fraction measured by PALS: $f_{\text{PALS}}=f_{\text{PALS}}(T, P)$. Previous analyses demonstrated that the predicted $h=h(T)$ behavior at ambient pressure is correct (Yu et al. 1994; Higuchi et al. 1995; Srithawatpong et al. 1999; Schmidt and Maurer 2000; Schmidt 2000; Olson et al. 2002; Olson 2004; Dlubek et al. 2004, 2006; Consolati et al. 2005). Assuming that at $T \approx T_g + 20$ to 25°C $h=f_{\text{PALS}}$, superposed the two sets of data in full range of temperature. However, so far the relation, $h=h(P)$, has not been examined.

PALS measurements at higher than ambient P are scarce. One of the exceptions is a study of cured epoxy resin at different of T and P (below and above T_g) (Jean et al. 1986; Wang et al. 1990; Liu and Jean 1995). The published graphs reporting variations of τ_3 and I_3 with T and P were digitalized and from the extracted data V_3 , and f_{PALS} (Eq. 9 for $B=0$) were computed. Because the original authors did not measure the PVT , this information was taken from another publication (Dunne et al. 2001). Fitting these data to the S–S eos yielded the parameters listed in Table 1. Next, these parameters were used to compute $h=h(T, P)$ —these along with $f_{\text{PALS}}=f(T, P)$, are shown in Fig. 1. The behavior of $h=h(T, P)$ and that of $f_{\text{PALS}}=f(T, P)$ is similar, but the computed h values are higher by 0.0093. Shifting vertically the PALS data resulted in superposition; hence, here: $h(T, P) = f_{\text{PALS}}(T, P) + 0.0093$.

Thus, for cured epoxy resin, the values of h and f_{PALS} are consistent within the full range of T and P . However,

Table 1 The S–S eos fit to cured epoxy data (Dunne et al. 2001)

Parameter	Value
Standard deviation of V , σ (ml/g)	0.00109
Correlation coefficient squared, r^2	0.999998
Coefficient of determination, CD	0.996877
P^* (bar)	11,819±140
T^* (K)	12,626±76
V^* (ml/g)	0.6910±0.0010

because both types of measurements are prone to errors, and the theories for the free volume calculation contain several assumptions, the thermodynamic free volume fraction f is expected to linearly relate to either h or f_{PALS} :

$$f(T, P) \equiv V_f/V = b_0 + b_1 h(T, P) \\ = c_0 + c_1 f_{\text{PALS}}(T, P) \quad (10)$$

where b_i and c_i are equation parameters. The recent studies of the free volume in fluoro elastomers also indicate that PVT and PALS data are consistent with each other (Dlubek et al. 2005).

Experimental

Eight commercial resins are listed in Table 2. Their PVT behavior was studied using fully automated pressure dilatometer (SWO Polymertechnik GmbH, Germany), in a range of T and P . The viscosities were measured in modified capillary and dynamic rheometers (Göttfert and Rheometrics, respectively). The average error in V was ± 0.001 ml/g (i.e., $\pm 0.1\%$), and in $\log \eta$ was $\pm 5\%$. For the present calculations only data from the capillary instrument at three temperatures and at $P=1$ to 700 bars were used.

Full details of the experimental procedure, instrumentation, and precision of data acquisition are provided in the preceding articles (Sedlacek et al. 2004, 2005). Briefly, the standard capillary rheometer was modified by addition of a second pressurized reservoir below the capillary. Two capillaries with length-to-diameter ratio of 0.12 and 20, and two pressure transducers (upstream and downstream) were used. Using the “zero length” capillary data, the entrance pressure drop (Bagley) correction was determined. The results from the long capillary (corrected for the end effects) were used to compute the shear viscosity. The computations took into account the Rabinowitsch correction. The hydrostatic pressure for which the data are reported is the mean of the two pressure readings upstream and downstream of the capillary.

Fig. 1 The computed h (full squares) and f_{PALS} (full circles) data for epoxy (Dunne et al. 2001) at $P=1.0132$ bar (1A) or at $T=373.15$ K (1B). Shifting f_{PALS} data by 0.0093 (open squares) resulted in good superposition. The lines represent the least squares fit with $r^2=0.999$ and 0.995, for the T and P dependencies, respectively

Calculations

PVT data fit

The characteristic reducing parameters for the eight resins in Table 2 were computed (using MicroMath *Scientist*™ software) by simultaneously fitting the coupled Eqs. 6 and 7 to experimental data, with initial values of P^* , T^* , and V^* taken from the paper of Sedlacek et al. (2005). Examples of the fit for semicrystalline and amorphous polymers are displayed in Fig. 2.

The computed values of P^* , T^* , and V^* are listed in Table 3, along with the fitting statistics. Evidently, the S–S eos well represents the observed dependencies. The recomputed values of P^* , T^* , and V^* slightly differ from those reported previously (e.g., see Rodgers 1993; Utracki and Simha 2004a; Utracki 2005). The smallest difference is for LDPE60 (0.05, 2.03, and 0.68% for P^* , T^* , and V^* , respectively), while the largest for PP (−6.4, 7.9, and 2.7%

for P^* , T^* , and V^* , respectively). The largest random scatter was observed for PS, where the standard deviation of V : $\sigma=0.00108$.

Determination of the constant stress viscosities

The capillary viscosities were measured at the wall shear rates from $\dot{\gamma} = 35$ to 2,500 (s^{-1}), at three levels of T and six levels of P from 1.0325 to 700 bar (Sedlacek et al. 2004, 2005). The isobaric shear viscosity, η , was plotted as a function of the wall shear stress, σ_{12} . To determine the constant stress viscosity, $\eta=\eta(P, T, \text{ and } \sigma_{12}=\text{constant})$, first η (measured at the middle T) was plotted vs σ_{12} . Next, the viscosities at lower and higher T were computed at the selected levels of σ_{12} . Figure 3 demonstrates that while for some polymers three sets of $\eta=\eta(P, T, \text{ and } \sigma_{12}=\text{constant})$ data could be determined, for others only one was possible; extrapolation would increase uncertainty.

Table 2 Polymers studied in this work

Number	Polymer code	Manufacturer and grade	MFR (dg/min)	ρ (g/ml)	Transition T (°C)	
					Melting	Glass
1	LDPE60	ExxonMobil LD600 BA	20.5	0.92	110	ND
2	LDPE65	ExxonMobil LD650 BA	22.0	0.91	102	ND
3	LLDPE	ExxonMobil LL6101 XR	20	0.92	120	ND
4	HDPE	ExxonMobil HMA 014	4	0.96	134	ND
5	PP	ExxonMobil PP 1374	22	0.90	160	ND
6	PS	Kaucuk–Unipetrol Krasten 137	17–19	1.06	–	86
7	PMMA	Asahi–Kasei Corp. Delpet80N	2	1.19	–	145
8	PC	Teijin Chem Panlite AD5503	57 ^a	1.20	–	117

LDPE low-density polyethylene, LLDPE linear low-density polyethylene, HDPE high-density polyethylene, PP polypropylene, PS polystyrene, PMMA poly(methyl methacrylate), PC polycarbonate of bisphenol-A, MFR melt flow rate given by the manufacturers, ρ density—manufacturers' data, ND not determined

^a At 280 °C

Fig. 2 Fitting experimental $V=V(T, P)$ data of LLDPE and PMMA (Sedlacek et al. 2005) to S–S eos. Experimental data are shown as *filled points*, while those computed as *open squares*. In both figures, P ranges from 150 (*top*) to 700 bar

Shear viscosity/free volume dependence

Once the $\eta=\eta(\sigma_{12}=\text{constant})$ values were determined at the specified level of $P=P_R$, and $T=T_R$, the hole fractions, $h=h(T_R, P_R)$ were computed from Eqs. 6 and 7. It is noteworthy that once the parameters: P^* , T^* , and V^* , are known for high molecular weight polymer melts ($s \gg 3$) the coupled equations predict the V and h at any P and T . Thus, using the P^* , T^* , and V^* from Table 2, the values of $h=h(T_R, P_R)$ were computed. An experimental plot for HDPE of $\ln \eta$ vs $1/h$ is displayed in Fig. 4 as an example. It is evident that at each stress level, the data for the three temperatures do not follow a single dependence predicted by Eq. 3. In Fig. 5, the data of Fig. 4 are replotted replacing the original P^* by the modified pressure reducing parameter, P^*_R . Thus, as before (Utracki 1985; Utracki and Simha 2001b), for the rheological application of the S–S eos the pressure reducing parameter P^* in Eqs. 6 and 7 is replaced by: $P^*_R = \kappa P^*$, where κ is an adjustable factor; its optimized value for HDPE is $\kappa=1.80$.

Optimization of κ values was carried out for all T and P data using the middle stress viscosities, e.g., for HDPE at $\sigma_{12}=147$ kPa. As illustrated in Fig. 6, the optimum was easy to determine, using any goodness of fit parameter. The very worst superposition was found for PP (see Fig. 7); in

spite of two different values of κ -factor, the superposition was poor.

A test for adequacy of the procedure is presented in Fig. 8, where data for two LDPE resins at the same stress level of $\sigma=33$ kPa are plotted vs $1/h$. Fitting the data to Eq. 3 resulted in excellent fit with $r^2=0.9999$ for either resin. The parameters of Eq. 3, and the statistics of data fit are listed in Table 4. The parameters were computed using data for the middle-stress level at three T and six P levels fitted to Eq. 3; column 2 lists the wall shear stress for which the viscosity data were obtained, while column 3 presents the values of κ required for superposition. A summarizing plot in Fig. 9 illustrates the linearization of data by Eq. 3. Figure 10 displays variation of κ with the reduced temperature: T/T_g for the amorphous polymers, and T/T_m for the semicrystalline.

Discussion

Correlation between the free volumes from PALS and PVT measurements

According to analysis of PALS data for polymers the values of the parameters b_i in Eq. 10 are not universal. On the one

Table 3 The characteristic reducing parameters and the statistical data fit for polymers listed in Table 2

Number	Polymer	P^* (bar)	T^* (K)	$10^3 \times V^*$ (ml/g)	CD	σ	r^2
1	LDPE60	6,174 $\pm$ 10	10,479 $\pm$ 7	1,171.3 $\pm$ 2.2	0.99965	0.00046	0.9999999
2	LDPE65	6,092 $\pm$ 12	10,484 $\pm$ 8	1,171.6 $\pm$ 2.5	0.99949	0.00059	0.9999998
3	LLDPE	6,220 $\pm$ 10	10,571 $\pm$ 7	1,173.5 $\pm$ 2.4	0.99968	0.00041	0.9999999
4	HDPE	6,189 $\pm$ 17	9,022 $\pm$ 10	1,189.3 $\pm$ 5.3	0.99909	0.00091	0.9999995
5	PP	5,480 $\pm$ 13	9,042 $\pm$ 7	1,175.3 $\pm$ 3.7	0.99933	0.00098	0.9999995
6	PS	6,725 $\pm$ 19	9,923 $\pm$ 8	957.5 $\pm$ 2.7	0.99901	0.00108	0.9999990
7	PMMA	8,588 $\pm$ 23	9,663 $\pm$ 7	836.6 $\pm$ 2.1	0.99923	0.00080	0.9999993
8	PC	7,776 $\pm$ 20	9,739 $\pm$ 7	816.0 $\pm$ 2.3	0.99909	0.00085	0.9999992

CD Coefficient of determination, σ standard deviation, r^2 correlation coefficient squared—all of the specific V volume

Fig. 3 Examples of the isothermal viscosity data plotted vs the wall shear stress for LDPE60 and PC at $P=1$ to 700 bar; *solid points* are experimental, *open* are interpolated for selected shear stresses

hand, C_f in Eq. 9 is not constant (Schmidt and Maurer 2000) (hence, b_1 and b_2 are expected to vary), and on the other the vertical shift required to superimpose data in Fig. 1 might depend on the substance (hence, b_2 may vary). The variations, implicit in the form of Eq. 9, may originate in different geometry of the free volume cells for macromolecules with different chain stiffness (Consolati et al. 2005), or in others free volume influences that affect intensity of PALS (Schmidt 2000).

Good correlation between the free volumes computed from PALS and the PVT behavior is displayed in Fig. 1. The agreement has been obtained in spite of several complications, viz digitalization of reported data and recalculation of $f_{PALS} = f_{PALS}(T, P)$ using Eqs. 8 and 9, as

well as extracting the free volume parameter h from PVT data of different cured epoxy resin than that used in PALS experiments. There is also an inherent difference in the free volumes accessible for the PALS and the PVT experiment; while in the former, o -Ps is capable to access free volume cells of ca. 0.1 nm diameter; the latter test is related to volume compressibility and thermal expansion, hence segmental motion. These problems notwithstanding it is evident that similar agreement between the two sets of free volumes was obtained for the T as for the P dependencies. In short, under the thermodynamic equilibrium conditions, within a wide range of independent variables the S–S eos provides reliable, quantitative measure of free volume.

Fig. 4 Interpolated constant stress isothermal viscosity vs reciprocal free volume parameter h for HDPE at $P=1$ to 700 bar, and $T=170$, 190, and 210 °C; *points* are experimental, *lines* to guide the eye

Fig. 5 The same data as in Fig. 4, but now the free volume parameter h is recomputed assuming: $P_R^* = 1.80P^*$

Fig. 6 Selecting the optimum κ -value for PC at $\sigma_{12}=60$ kPa

Relationships between the shear viscosity and free volume

In earlier publications on the relationships between shear viscosity and a measure of free volume (Batchinski 1913; Doolittle 1951a,b, 1952; Doolittle and Doolittle 1957; Utracki 1974, 1983a–c, 1985, 1986) the liquids of interests were low molecular weight solvents or oils. For these substances, the zero-shear viscosity, η_0 , followed the

Fig. 7 Plot of $\ln \eta$ vs $1/h$ for PP at $\sigma_{12}=36, 60$, and 99 kPa, and $T=190, 210$, and 230 °C. While for the two lower temperatures, $\kappa=1$ for 230 °C $\kappa=1.7$ was used

Fig. 8 Comparison of viscosity vs hole fraction dependence for two LDPE resins; the solid lines represent Eq. 3 with parameters listed in Table 4

empirical equations relating it to density, $\rho=1/V=\rho(P, T)$, as proposed by Batchinski and by Doolittle, or to the hole fraction, h , computed from the PVT surface. It is particularly significant that Eq. 3 provided excellent superpositions of data onto “master” curves. Furthermore, for n -paraffins and their mixtures the relation was found valid within a wide range of independent variables: $T=20$ to 204 °C, and $P=1$ to $5,000$ bar, with common value of the two constants, $a_1=0.79$, and $a_2=0.07$ (Utracki 1983b, 1985, 1986). In short, the capillary flow data for these liquids were found to be directly related to the thermodynamic equilibrium quantity, h .

However, for high molecular weight commercial polymers, rarely the viscosity data vs free volume follow Eq. 3. In most cases a modification has been required (Utracki 1983b, 1985; Kadijk and van den Brule 1994; Sedlacek et al. 2005). The origin of this different behavior (between the simple and macromolecular liquids) needs to be discussed. Several sources might be postulated, viz error of the measurements, incorrect interpretation of the thermodynamic and/or the rheological data, or an inherent difference of liquid structures. Because several research groups have reported similar deviations, evidently, the error of measurements is not the culprit. Similarly, validity of S–S eos has been well documented and the method of the free volume computation in a wide range of P and T was confirmed with independent PALS results. Thus, in the following text, the remaining possibilities, the rheological, and structural aspects of polymer behavior need to be discussed.

Table 4 Parameters of Eq. 3 [$\ln\eta=a_0+a_1/(h+a_2)$], and the statistical data fit

Polymer	σ_{12} (kPa)	κ	a_0	a_1	a_2	CD	σ	r^2
LDPE60	33	1.35	-0.952 ± 1.76	0.986 ± 0.44	$(-7.41\pm 0.03)\times 10^{-5}$	0.992	0.052	0.99989
LDPE60	66	1.35	-18.2 ± 15.3	11.4 ± 14.8	0.36 ± 0.31	0.994	0.052	0.99992
LDPE65	33	1.50	-6.28 ± 0.96	3.17 ± 0.10	0.143 ± 0.008	0.984	0.057	0.99988
LDPE65	60	1.50	-10.1 ± 3.6	4.87 ± 2.27	0.19 ± 0.07	0.998	0.026	0.99998
LLDPE	81	1.60	-1.98 ± 2.16	1.77 ± 0.96	0.101 ± 0.061	0.996	0.029	0.99998
HDPE	147	1.80	-0.16 ± 0.46	1.81 ± 0.25	0.095 ± 0.019	0.999	0.006	0.99999
PP	60	1.0 & 1.7	-7.77 ± 5.21	5.53 ± 4.39	0.244 ± 0.167	0.993	0.063	0.99988
PS	89	1.70	-20.7 ± 11.1	6.03 ± 5.16	0.069 ± 0.099	0.988	0.175	0.99915
PMMA	220	2.10	-31.5 ± 40.6	11.2 ± 23.9	0.102 ± 0.315	0.980	0.180	0.99935
PC	60	1.27	-11.2 ± 21.4	5.27 ± 13.8	0.110 ± 0.420	0.950	0.192	0.99888

Pressure effects on flow

The total stress tensor may be written as:

$$\pi = P\delta + \sigma = \begin{pmatrix} P + \sigma_{11} & \sigma_{21} & 0 \\ \sigma_{12} & P + \sigma_{22} & 0 \\ 0 & 0 & P + \sigma_{33} \end{pmatrix} \quad (11)$$

where P is isotropic or hydrostatic pressure, δ is unit tensor, and σ is the deviatoric part that vanishes at equilibrium (Bird et al. 1987; Carreau et al. 1997). In consequence, while the first invariant yields P , the individual normal stresses have the form: $P + \sigma_{ii}$, indicating that the hydrostatic pressure of sheared liquid is modified by the normal stresses. During the flow through a tube, the only normal stress of concern is $N_1 = \sigma_{11} - \sigma_{22} \cong \sigma_{11}$, which reaches its maximum value at the tube wall, $N_1(R)$. Within the terminal zone $N_1 < \sigma_{12}$, with $\sigma_{12} \leq 250$ kPa; thus, the

deviatoric component is most important at the ambient pressure $P = 100$ kPa. However, in the pressure-driven, capillary flow experiments the pressure gradient is:

$$\Delta P = \Delta P_0 + \sigma_{12}(4L/D) \quad (12)$$

where ΔP_0 is the end effects pressure drop, and L/D is the capillary length-to-diameter ratio (in the present work $L/D = 20$ was used). Thus, according to Eq. 12 the deviatoric component constitutes less than 2.5% of hydrostatic pressure drop in the ambient pressure tests, and it can be neglected in the present studies where $0.1 \leq P \leq 70$ MPa. The general validity of this conclusion is supported by the agreement between data from the pressure driven experiments (e.g., capillary flow), and those with mechanically imposed shearing analysis (e.g., in cone-and-plate rotational tests). Furthermore, it should be mentioned that the Bagley end effects correction, ΔP_0 , mainly depends on the normal stresses. Agreement between the shear flow data obtained from the capillary flow with those from a slit rheometer (with several pressure transducers that measure the pressure drop within the fully developed flow region, and thus not requiring the Bagley-type correction) provide another indication of a minor role the normal stresses play in capillary flows.

Evidently, for the Newtonian fluids, the normal stresses are zero; thus, the diagonal stress components are identical to P . The good predictability of the zero-shear viscosity dependence on h for solvents might be considered as indicating that only η_0 should be used in Eqs. 2 or 3. Unfortunately, for molten polymers of industrial interest η_0 is rarely experimentally accessible, and in the present work it was replaced by the constant stress viscosity, $\eta = \eta(\sigma_{12} = \text{constant})$. The strategy is based on the time–temperature superposition of the flow curves, $\eta = \eta(\dot{\gamma})$ (Fesko and Tschoegl 1971; Ferry 1980). A similar procedure might be used for the pressure effects (Tschoegl 1981). Fundamentally, the time–temperature superposition starts with a series of isothermal plots of $\log \sigma_{12}$ vs $\dot{\gamma}$. Shifting the constant temperature dependencies onto a reference curve (usually

Fig. 9 Linearization of $\ln\eta$ vs $1/h$ dependence by means of Eq. 3 for the eight polymers (see Table 4)

the midtemperature one) is accomplished by multiplying σ_{12} by b_T and $\dot{\gamma}$ by a_T :

$$a_T = b_T \eta_0 / \eta_{0r} \quad \text{and} \quad b_T = T_r V / T V_r \quad (13)$$

where the subscript r indicates the reference quantities. Within the range of temperatures used in the present work the value of b_T is close to unity, e.g., in the full range of T and P for HDPE $b_T = 1.00 \pm 0.03$; hence, the deformation rate shifting factors for temperature and pressure superposition: $a_T, a_P \propto \eta_0(T, P)$. In day-to-day rheological practice, a simplified procedure has been used, neglecting b_T altogether; the isothermal flow curves, $\log \eta = \eta(\log \dot{\gamma})$ are shifted by dividing η by η_0 and multiplying the deformation rate by η_0 , i.e., by sliding the flow curves at 45° angle, along the constant stress lines. Note that this procedure shifts the whole curves, including the zero-shear viscosity region; hence, there is equivalence between behavior of $\eta_0 = \eta_0(P, T)$ and that of $\eta = \eta(P, T)|_{\sigma=\text{constant}}$. In conclusion, the rheological measurements and interpretation of data cannot be used for explaining the lack of superposition implied by Eq. 3.

Structures and relaxations in molten polymers

During the last decade there has been significant progress in understanding of the liquid structures dependence on T , stemming mainly from the molecular modeling and neutron scattering experiments (Jäckle 1986; Kanaya et al. 1999; Kanaya and Kaji 2001; Binder et al. 2003; Bicerano 2003). An existence of the dynamic crossover has been demonstrated at $T > T_g$, which affects temperature and pressure dependencies of liquid viscosity or relaxation time.

Several mechanisms have been used to explain the phenomena (Casalini and Roland 2005). For example, the mode-coupling theory (MCT) considers a liquid as an assembly of particles enclosed in cages formed by their neighbors. The molecular dynamics indicates a two-step relaxation—segmental and structural: at $T > T_c$ vigorous vibrations of molecular units in cages (from which they are able to escape) dominate the liquid behavior, and the temperature dependence of the relaxation time follows power-law dependence. By contrast, at $T < T_c$ the α -relaxation of the cages dominates. The crossover temperature, T_c , of these two mechanisms takes place at about constant T/T_g ratio—for PS and PIB the event was observed at $T/T_g = 1.15$ and 1.35, respectively (Kisliuk et al. 2000). The polymer dynamics at temperatures below T_c is complicated by the presence of two other relaxation processes: the fast and the elementary. The former, which originates is backbone chain vibrations or side groups motion, starts near the Vogel–Fulcher–Tammann–Hesse (VFTH) temperature in the glassy state, and stretches to $T > T_c$. The elementary relaxations have been observed only in macromolecular liquids. Their origin has been traced to a

host of conformational transitions, documented by the quasielastic neutron scattering studies. These relaxations extend to temperatures well above T_c (Ngai 2000).

Stickel et al. (1995, 1996) demonstrated that none of the proposed equations provides description of the dynamic behavior in the full range of T . The authors linearized the empirical VFTH expression:

$$\log \eta_0(T) = A + B/(T - T_0) \quad \text{linearized:} \quad (14)$$

$$[d \log \eta / d(1/T)]^{-1/2} = B^{-1/2}(1 - T_0/T)$$

The data plotted according to Eq. 14 followed three approximate straight lines, which defined two transition temperatures, $T_A > T_B$. The former is the lower limit of the Arrhenius-type dependence, whereas the latter indicates a dynamic change from VFTH-1 to VFTH-2 dependence. According to the coupling model (CM) the change is caused by different intermolecular coupling within the two domains (Ngai 2003).

In short, in macromolecular liquids at $T > T_g$, there are several relaxation processes, often different from those of simple, low molecular weight liquids. The difference diminishes as the temperature increases. It is noteworthy that the crossover transition at ca. $1.2T_g$ falls within the range of the so-called liquid–liquid transition temperature, $T_{LL}/T_g = 1.2 \pm 0.1$, described by Boyer (1977, 1980a,b, 1985, 1987) as: “ T_{LL} is a molecular level transition–relaxation associated with the thermal disruption of segment–segment contacts”. Initially, Boyer considered T_{LL} to be a third order thermodynamic transition (Boyer 1980a,b), the idea accepted by several researchers, while others suggested a dynamic nature (Patterson et al. 1976), or denied its existence (Plazek 1982; Plazek and Gu 1982, Chen et al. 1982; Orbon and Plazek 1982, 1985). For example, Murthy tabulated T_{LL} and T_c values for a series of nonpolymeric liquids finding that indeed: $T_{LL} \cong T_c$, where the latter parameter indicates empirical deviation from power-law dependence (Murthy 1988a,b, 1990, 1993; Murthy and Kumar 1993; Murthy et al. 1994). In later days, Boyer was not convinced of the thermodynamic nature of T_{LL} , as he classified it also as “intermolecular relaxation transition”, calling the one that occurs ca. 50°C above T_{LL} the “intramolecular relaxation transition” T_{Lp} (Boyer 1985, 1987). The latter transition separates “true liquid” from a structural polymer melt.

Over the years the thermodynamic origin of T_{LL} has been loosing support—the MCT derivation of T_c provided strong argument for the relaxation-based, dynamic nature of the transformation. However, there is no doubt that liquids above T_g have structures that within the specific T regions there are diverse relaxation modes. A change of liquid structure and behavior at $T > T_g$ does exist, independently how one may call it. For decades, this was known to

process engineers who empirically established that amorphous polymers should be processed at $T > 1.2T_g$, within the zone where an Arrhenius-like activated flow dominates (Bicerano 2003). Recent *PVT* data of a series of PS samples well followed Eqs. 6 and 7, without any apparent deviation. However, calculation of the compressibility parameter, K , demonstrated a dramatic change of $K=K(T)$ dependence at $T/T_g = 1.22$ to 1.23 (Utracki 2006b).

The diversity of liquid structures is also reflected in their classification as strong or fragile. Initially, that was based on the η vs T dependence, then on the relaxation time near T_g (Angell 1985, 1995, 1997; Ito et al. 1999; Böhmer et al. 1993). The fragility index m is defined as:

$$m \equiv \lim_{T \rightarrow T_g} (d(\log \tau) / d(T_g/T)) \quad (15)$$

Relaxations of strong liquids cooled from high temperature to T_g follow the Arrhenius equation with low values of $m \approx 20$, while those of fragile liquids (m up to 200, to which most polymers belong) follow a more complex behavior. For strong liquids $m = \Delta H_a / RT_g$, i.e., it is proportional to the activation energy of molecular relaxation, ΔH_a . Ngai and Roland (1993) pointed out the correlation between m and the Kohlrausch–Williams–Watts parameter n , which is a measure of intermolecular coupling. Molecular modeling has shown that fragility depends on the entropic barrier that governs the conformational transitions (Buhot and Garrahan 2002).

Flow of molten semicrystalline polymers is also complicated by the presence of ordered structures at temperatures well above the melting point, e.g., at $T \leq T_m + 50$ °C. It is worth recalling that the transition temperatures are pressure-sensitive, e.g., $d\tilde{T}_g/d\tilde{P} = 26$ (McKinney and Simha 1974, 1976), $d\tilde{T}_m/d\tilde{P} = 42$, and $d\tilde{T}_{LL}/d\tilde{P} = 72$ (K/kbar) (Boyer 1980a,b). Thus, at $T = \text{constant}$, an increase in P may induce transition of kinetic or thermodynamic liquid structure.

The idea of correlation between liquid behavior at thermodynamic equilibrium and that in flow originates in the mean-field approach, which assumes that liquids are structureless. This approach that for decades well served the polymer physics is unable to explain several phenomena, such as polymer–polymer miscibility and other transformations. Thus, recognizing the diversity of polymeric liquids structures it is important to consider how these affect the free volume and the flow behavior.

The S–S lattice-hole mean field theory does not consider polymeric chain structure—its effects are only reflected in the values of the characteristic reducing parameters, P^* , T^* , and V^* , and the Lennard-Jones interaction parameter. Characteristically, the eos well fits the *PVT* data even across the transformation temperature at

ca. $1.2T_g$. It seems that at thermodynamic equilibrium the hole distribution is not seriously affected by chain configuration. However, as evident from the temperature–viscosity relationships on both sides of the crossover temperature, the polymeric chain structures significantly affect the flow. In all postulated models of flow, viz reptation, cell structures, hole jumping, it is implicit that configurational or conformational changes do affect liquid dynamic behavior.

Correlation between the shear viscosity and free volume

The static tests, such as in PALS or *PVT* measurements, are conducted under the thermodynamic equilibrium conditions. The tests are slow enough for the macromolecules to attain equilibrium conformation. During flow, the macromolecules are subjected to external forces and their conformation may change with the imposed stresses or deformation rates (Utracki 2004a).

According to the free volume theories, flow might be visualized as a coordinated series of jumps of flow elements to holes (Litt 1976; Jäcke 1986). Thus, only holes larger than of a critical size may participate in the process. Because the hole size depends on the locally available free volume, only large enough free volume cells are able to contribute to flow. The arguments based on the flow model and shape of the free volume cavity suggest that as T decreases or P increases the accessible free volume decreases faster than what would be expected from compressibility. Thus, at lower temperatures, the viscosity ought to increase faster than expected from the high-temperature behavior. Figure 4 confirms this expectation as the temperature decreases from 210 to 190 and 170 °C the viscosity vs $1/h$ dependencies shifts to progressively higher values.

It is noteworthy that Eq. 3 well described flow behavior for low molecular weight n -paraffins and lubricating silicone oils (viscosity span of ca. 6 decades). For these substances, excellent superposition has been obtained, but not for the molten polymers (Utracki 1985). In that publication, the superposition for molten polymers required introduction of different values of the characteristic reducing parameter $P^*_R = \kappa P^*$ for the flow behaviors. Replacing P^* by P^*_R effectively reduced the pressure effect on h . This approach was adopted in the current work. Optimized values of the κ parameter are presented in Table 4.

Accepting the free volume mechanism of flow, it is pertinent to consider the size and shape of the free volume cells. The quantum mechanical computations (Srihawatpong et al. 1999; Olson et al. 2002; Schmidtke et al. 2004; Olson 2004) showed that better description of the PALS data is obtained assuming nonspherical shapes (Consolati et al. 2005). It is reasonable to postulate that under pressure, the

Fig. 10 Parameter κ vs reduced temperature for glassy (T/T_g) and semicrystalline polymers (T/T_m). Data from Tables 2 and 4; the temperature is the middle of the three temperatures used in the studies (Sedlacek et al. 2005)

anisometric structures will coalesce easier than the spherical ones, thus increasing the availability of large-enough voids and facilitating the flow.

The data in Table 4 make it plain that as before (Utracki 1985; Kadijk and van den Brule 1994; Sedlacek et al. 2005), the polymer melts viscosity plotted as $\log \eta$ vs $1/h$ seldom results in superposition of $\eta = \eta(P, T)$ on a single curve. The simple relation between the equilibrium thermodynamic quantity such as hole fraction or free volume fraction cannot describe the flow behavior of polymer melts within a range of T and P . This conclusion is equally valid for Eq. 3 as for the previous empirical relations proposed by Batchinski or Doolittle. Furthermore, because the WLF (Ferry 1980) treatment is based on the latter postulate, one should question its general validity for polymer melts.

Evidently, one can always force the superposition by suitable selection of the adjustable parameters, viz $b \approx V_0$ in Doolittle method, or κ -factor employed in the earlier (Utracki 1985) and the present analyses (see Fig. 9). However, the value of either b or κ must be determined not only for each polymer, but as Fig. 8 demonstrates, for each polymer grade. In the present study, the superposition was obtained using a single κ -parameter for all values of shear stress, expected from the postulated equivalence of the zero-shear and constant stress viscosities. It is noteworthy

that superposition has been obtained by reducing only the pressure effect on flow—the superposition was achieved for all temperatures.

If the lack of superposition of $\log \eta$ vs $1/h$ data for molten polymers originates in the presence of structures, it is reasonable to expect that as the temperature increases the thermal motion will randomize distribution of lattice elements, improving superposition of data. In other words, it is expected that as T increases above T_c or T_B the value of the κ -factor should decrease. Figure 10 displays the κ vs the reduced temperature dependence for the glassy (triangles) and semicrystalline (squares) polymers. As the reference temperature, T_g was used for glasses, and the melting point, T_m , for semicrystalline polymers. In spite of chemical diversity of the three glassy polymers that data follow the linear dependence: $\kappa = 6.81 - 3.82 T/T_g$ with $r = 0.997$; hence, for the glassy resins $\kappa = 1$ at $T \approx 1.52 T_g$. The dependence for the semicrystalline polymers is more confusing, as T_m is more prone to variability due to changes in crystalline form, size, content, etc. However, the general tendency of the κ -factor to decrease with T is evident.

Was Ray Boyer correct postulating that “true liquid” is found at $T \geq 1.2 T_g + 50^\circ \text{C}$? Does this limit correspond to T_A ?

Summary and conclusions

The PVT behavior and shear viscosity of eight polymers was measured and analyzed using a Doolittle-type relation with free volume parameter extracted from the PVT surface by means of the Simha–Somcynsky equation of state (S–S eos). The results may be summarized as follows:

1. Comparison of the free volume fractions, h , from PVT and those from PALS measurements confirmed validity of the S–S eos in wide range of T and P .
2. Plots of viscosity as a function of h did not result in the expected superposition of data; the shear viscosity increased more rapidly with reduction of temperature, or less rapidly with increase of pressure than what could be expected from the reduction of free volume.
3. To achieve superposition the pressure effects were reduced by introducing the rheological characteristic pressure reducing parameter, $P^*_R = \kappa P^*$, with $\kappa = 1$ to 2.1. The resulting superposition was found valid within full ranges of P , T , and σ_{12} used in these studies.
4. One might postulate that the higher viscosity at lower temperatures (than expected from the higher temperature behavior) is related to reduction of the free volume cells below the size required for the segmental jump.
5. The need for selecting different κ -values for different polymers negates the universality of this approach—the relationships proposed by Batchinski, Doolittle, or

- Utracki (valid for simple liquids) might be used as empirical, with parameters to be determined for each system within the range of independent variables.
- The lack of universality of the viscosity-free volume dependencies is related to the recognized diversity of liquid structures, which affects molecular dynamics, but it is less evident in static tests.
 - The factor κ decreases with temperature; for the glassy polymers at $T > 1.52T_g$ $\kappa=1$ is expected, i.e., the behavior predicted by Eq. 3, valid for low molecular weight solvents and silicone oils, is expected to be equally valid for molten polymers at high enough temperatures.

Nomenclature

a_i, b_i, c_i	Parameters of Eqs. 2, 3, and 10, respectively
A, B	Numerical coefficients in Eqs. 6, 7, and 9
$3c$	External degrees of freedom
CD	Coefficient of determination
f, f_D	Free volume fraction and Doolittle' free volume fraction
f_{PALS}	PALS determined free volume; see Eq. 9
h	Simha–Somcynsky theoretical hole fraction calculated from PVT surface
I_3	Intensity of <i>ortho</i> -positronium annihilation
M_n, M_s	Number-average and segmental molecular weight
MWD	Molecular weight distribution
n	Number of carbon atoms per molecule of n -paraffin
P, P_R	Pressure, and its value for flow (bar)
P^*, P_R^*	Characteristic pressure reducing parameter, and its value for flow (bar)
r	Correlation coefficient
R	Gas constant, 83.1432 (bar ml/g mol ⁻¹ K ⁻¹)
R, R_o	Radius of the free volume cavity in PALS, and empirical thickness of electronic layer
s	Number of equivalent segments per molecule
T_A, T_B	Transition temperatures from Stickel's plot (°C or K)
T, T_R	Temperature, and its value for flow (°C or K)
T_{tr}, T_c	Transition and crossover temperature
T^*, T_R^*	Characteristic temperature reducing parameter, and its value for flow (K)
T_g	Glass transition temperature
$T_{LL}, T_{L\rho}$	Liquid–liquid transformation temperatures
T_m	Melting point
u	3c/s
V, V_f, V_o	Specific, free and occupied volume (ml/g)
V^*	Characteristic volume reducing parameter

v^*	Characteristic segmental repulsive volume
y	Lattice occupied site fraction
Y	Occupied site fraction
Y_s	Variable defined in Eq. 3
zq	Number of interchain contacts in a lattice of coordination number z
ε^*	Characteristic segmental energy
γ	Shear strain
$\dot{\gamma}$	Rate of shear
η_0, η	Zero-shear viscosity, and constant stress viscosity (Pa s)
K	Compressibility
$\kappa=P_R/P^*$	Pressure adjusting factor
ρ	Density (g/ml)
σ_{12}	Shear stress
σ	Standard deviation of data
τ_3	<i>o</i> -Ps lifetime
Superscript	Tilde Indicates reduced variables

Acknowledgements One of the authors (TS) wishes to acknowledge the financial support by AS GR Grant agency (Grant No. A2060202). We also thank Prof. Pierre J. Carreau for the useful discussions and encouragement.

References

- Angell CA (1985) In: Ngai KL, Wright GB (eds) Relaxation in complex systems. NRL, Washington, DC
- Angell CA (1995) Formation of glasses from liquids and biopolymers. Science 267:1924–1935
- Angell CA (1997) Entropy and fragility in supercooling liquids. J Res Natl Inst Stand Technol 102:171–185
- Batchinski AJ (1913) Untersuchungen über die innere Reibung der Flüssigkeiten. Z Physik Chem 84:643–706
- Bicerano J (2003) Glass transition. In: Mark HF (ed) Encyclopedia of polymer science and technology, 3rd edn, vol 2. Wiley, Hoboken, NJ
- Binder K, Baschnagel, Paul W (2003) Glass transition of polymer melts: test of theoretical concepts by computer simulation. Prog Polym Sci 28:115–172
- Bird RB, Curtiss CF, Armstrong RC, Hassager O (1987) Dynamics of polymeric liquids, 2nd edn. Wiley, New York
- Böhmer R, Ngai KL, Angell CA, Plazek DJ (1993) Nonexponential relaxations in strong and fragile glass formers. J Chem Phys 99: 4201–4209
- Boyer RF (1977) In: Mark HF (ed) Encyclopedia of polymer science and technology (supplement volume 2). Wiley, New York, pp 745–839
- Boyer RF (1980a) Dynamics and thermodynamics of the liquid state ($T > T_g$) of amorphous polymers. J Macromol Sci Phys B18 (3):461
- Boyer RF (1980b) Pressure dependence of T_{LL} . II. Isotactic PMMA. Colloid Polym Sci 258:760–767

- Boyer RF (1985) T_{LL} and related liquid state transitions–relations: a review. In: Pethrick RA (ed) Polymer yearbook 2. Harwood Academic, Chur
- Boyer RF (1987) Evidence from T_{LL} and related phenomena for local structure in the amorphous state of polymers. In: Miller RL, Rieke JK (eds) Order in the amorphous state. Plenum, New York
- Buhot A, Garrahan JP (2002) Crossover from fragile to strong glassy behavior in the spin-facilitated chain model. *J Phys Condens Matter* 14:1499–1508
- Carreau PJ, De Kee DCR, Chhabra RP (1997) Rheology of polymeric systems: principles and applications. Hanser Publishers, Munich
- Casalini R, Roland CM (2005) Scaling of the supercooled dynamics and its relation to the pressure dependence of the dynamic crossover and the fragility of glass formers. *Phys Rev B* 71: 014210
- Chen J, Kow C, Fetter LJ, Plazek DJ (1982) Some evidence against the existence of the liquid–liquid transition, T_{ll} , in polymers. Part III the evolution of the T event by differential scanning calorimetry. *J Polym Sci B Polym Phys* 20:1565–1574
- Consolati G, Quasso F, Simha R, Olson BG (2005) On the relation between positron annihilation lifetime spectroscopy and lattice–hole-theory free volume. *J Polym Sci Part B Polym Phys* 43: 2225–2228
- Curro JG (1974) Polymer equations of state. *J Macromol Sci Rev Macromol Chem C11*:321–366
- Dee GT, Walsh DJ (1988a) Equation of state for polymer liquids. *Macromolecules* 21:811–815
- Dee GT, Walsh DJ (1988b) A modified cell model equation of states for polymer liquids. *Macromolecules* 21:815–822
- Dlubek G, Saarinen K, Fretwell HM (1998) The temperature dependence of the local free volume in polyethylene and polytetrafluoroethylene: a positron lifetime study. *J Polym Sci Part B Polym Phys* 36:1513–1528
- Dlubek G, Pionteck J, Kilburn D (2004) The structure of the free volume in poly(styrene-co-acrylonitrile) from positron life and pressure–volume–temperature (PVT) experiment. I Free volume from Simha–Somcynsky analysis of PVT experiments. *Macromol Chem Phys* 205:500–511
- Dlubek G, Wawryszczuk J, Pionteck J, Goworek T, Kaspar H, Lochhaas KH (2005) The high-pressure dependence of the free volume in fluoroelastomers from positron lifetime and PVT experiments. *Macromolecules* 38:429–437
- Dlubek G, Hassan EM, Krause-Rehberg R, Pionteck J (2006) Free volume of an epoxy resin and its relation to structural relaxation: evidence from positron lifetime and pressure–volume–temperature experiments. *Phys Rev E* 73:031803
- Doolittle AK (1951a) Studies in Newtonian flow I. The dependence of the viscosity on temperature. *J Appl Phys* 22:1031–1035
- Doolittle AK (1951b) Studies in Newtonian flow II. The dependence of the viscosity of liquids on the free-space. *J Appl Phys* 22: 1471–1475
- Doolittle AK (1952) Studies in Newtonian flow III. The dependence of the viscosity of liquids on molecular weight and free-space (in homologous series). *J Appl Phys* 23:236–239
- Doolittle AK (1954) The technology of solvents and plasticizers. Wiley, New York
- Doolittle AK, Doolittle DB (1957) Studies in Newtonian flow V. Further verification of the free-space viscosity relation. *J Appl Phys* 28:901–905
- Dunne RC, Sitaraman SK, Luo S, Wong CP, Estes WE, Periyasami M, Coburn J (2001) Thermal and mechanical characterization of ViaLux™ 81: a novel epoxy Photo-Dielectric Dry Film (PDDF) for microvia applications. *IEEE Trans Compon Packaging Manuf Technol* 24(3):436–444
- Eldrup M, Lightbody D, Sherwood N (1981) The temperature dependence of positron lifetimes in solid cyclohexane. *J Chem Phys* 63:51–58
- Ferry JD (1980) Viscoelastic properties of polymers. Wiley, New York
- Fesko DG, Tschoegl NW (1971) Time–temperature superposition in thermorheologically complex materials. *J Polym Sci C35*:51–69
- Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca, New York
- Flory PJ, Orwoll RA, Vrij (1964) Statistical thermodynamics of chain molecule liquids. I. An equation of state for normal paraffin hydrocarbons. *J Am Chem Soc* 86:3507–3514
- Fowler RH (1929) Statistical mechanics. Cambridge University Press, Cambridge
- Glasstone SN, Laidler K, Eyring H (1941) The theory of rate processes. McGraw-Hill, New York
- Hartmann B, Haque MA (1985) Equation of state for polymer liquids. *J Appl Polym Sci* 30:1553–1563
- Higuchi H, Yu Z, Jamieson AM, Simha R, McGervey JD (1995) Thermal history and temperature dependence of viscoelastic properties of polymer glasses: relation to free volume quantities. *J Polym Sci Part B Polym Phys* 33:2295
- Ito K, Moynihan CT, Angell CA (1999) Thermodynamic determination of fragility in liquids and a fragile-to-strong liquid transition in water. *Nature* 398:492–495
- Liu YC, Jean HY (1995) Free-volume hole properties of polymer blends probed by positron annihilation lifetime spectroscopy: miscibility. *Macromolecules* 28:5774–5779
- Jäckle J (1986) Models of the glass transition. *Rep Prog Phys* 49:171–231
- Jean YC, Sandreczki TC, Ames DP (1986) Positronium annihilation in amine-cured epoxy polymers. *J Polym Sci Part B Polym Phys* 24:1247–1258
- Jean YC, Mallon PE, Schrader DM (2003) Principles and applications of positron and positronium chemistry. World Scientific, New Jersey
- Kadijk SE, van den Brule BNAA (1994) On the pressure dependency of the viscosity of molten polymers. *Polym Eng Sci* 34:1535–1546
- Kanaya T, Kawaguchi T, Kaji K (1999) Local dynamics of some bulk polymers above T_g as seen by quasielastic neutron scattering. *Macromolecules* 32:1672–1678
- Kanaya T, Kaji K (2001) Dynamics in the glassy state and near glass transition temperature of amorphous polymers as studied by neutron scattering. *Adv Polym Sci* 154:87–141
- Kisliuk A, Mathers RT, Sokolov AP (2000) Crossover in dynamics of polymer liquids. *J Polym Sci B Polym Phys* 38:2785–2790
- Lennard-Jones JE (1931) Cohesion. *Proc Phys Soc* 43:461–482
- Lennard-Jones JE, Devonshire AF (1937) Critical phenomena in gases I. *Proc R Soc Lond* 163:53–70
- Litt M (1976) Free volume and its relationship to the temperature effect on zero-shear melt viscosity: a new correlation. *Trans Soc Rheol* 20:47–64
- McKinney JE, Simha R (1974) Configurational thermodynamic properties of polymer liquids and glasses. I Poly(vinyl acetate). *Macromolecules* 7:894–901
- McKinney JE, Simha R (1976) Configurational thermodynamic properties of polymer liquids and glasses. II Poly(vinyl acetate). *Macromolecules* 9:430–441
- Murthy SSN (1988a) Temperature dependence of the dielectric relaxation processes in glass-forming materials. *J Chem Soc Faraday Trans 2(6)*:671–677
- Murthy SSN (1988b) Temperature dependence of relaxation processes in amorphous polymers. *J Polym Sci C Polym Lett* 26:361–370
- Murthy SSN (1989) Secondary relaxations and the structure of glass. *J Chem Soc Faraday Trans 2(85)*:581–596
- Murthy SSN (1990) The nature of decoupling of various relaxation processes in glass-forming liquids. *J Mol Liq* 44:211–230
- Murthy SSN (1993) Liquid–liquid transition in polymers and glass-forming liquids. *J Polym Sci B Polym Phys* 31:475–480

- Murthy SSN, Kumar D (1993) Glass formation in organic binary liquids studied using differential scanning calorimetry. *J Chem Soc Faraday Trans* 1993(14):2423–2427
- Murthy SSN, Sobhanadri J, Gangasharan G (1994) The origin of beta relaxation in organic glasses. *J Chem Phys* 100:4601–4607
- Ngai KL (2000) Dynamic and thermodynamic properties of glass-forming substances. *J Non-Cryst Solids* 275:7–51
- Ngai KL (2003) An extended coupling model description of the evolution of dynamics with time in supercooled liquids and ionic conductors. *J Phys Condens Matter* 15:S1107–S1125
- Ngai KL, Roland CM (1993) Chemical structure and intermolecular cooperativity: dielectric relaxation results. *Macromolecules* 26:6824–6830
- Olson BG (2004) Positron annihilation lifetime studies of polymers. Ph.D. thesis, Case Western Reserve University, Cleveland, OH
- Olson BG, Prodpran T, Jamieson AM, Nazarenko S (2002) Positron annihilation in syndiotactic polystyrene containing α and β crystalline forms. *Polymer* 43:6775
- Orbon SJ, Plazek DJ (1982) Some evidence against the existence of the liquid–liquid transition, TLL, in polymers. Part IV. Does the temperature dependence of shear viscosity indicate the existence of a liquid–liquid transition? *J Polym Sci B Polym Phys* 20:1575–1583
- Orbon SJ, Plazek DJ (1985) Rebuttal to “comments on ‘some evidence against the existence of the liquid–liquid transition. IV. The temperature dependence of shear viscosity’”. *J Polym Sci B Polym Phys* 23:41–48
- Ougizawa T, Dee GT, Walsh DJ (1989) PVT properties and equation of states of polystyrene: molecular weight dependence of the characteristic parameters. *Polymer* 30:1675–1679
- Papazoglou E, Simha R, Maurer FHJ (1989) Thermal expansivity of particulate composites: interlayer versus molecular model. *Rheol Acta* 28:302–308
- Patterson GD, Bair HE, Tonelli AE (1976) Thermal behavior of atactic polystyrene above the glass-rubber relaxation. *J Polym Sci Polym Symp Ed* 54:249–257
- Plazek DJ (1982) Some evidence against the existence of the liquid–liquid transition, T_{ll} , in polymers. Part I Transitions or dispersions. *J Polym Sci B Polym Phys* 20:1533–1550
- Plazek DJ, Gu GF (1982) Some evidence against the existence of the liquid–liquid transition, T_{ll} , in polymers. Part II Properties of and measurements with a torsional braid analyzer. *J Polym Sci B Polym Phys* 20:1551–1564
- Prigogine I, Trappeniers N, Mathot V (1953a) Statistical thermodynamics of r-mers and r-mer solutions. *Discuss Faraday Soc* 15:93–107
- Prigogine I, Trappeniers N, Mathot V (1953b) On the application of cell method to r-mer liquids. *J Chem Phys* 21:559–560
- Prigogine I, Bellemans A, Mathot V (1957) The molecular theory of solutions. North-Holland, Amsterdam
- Rodgers PA (1993) Pressure–volume–temperature relationships for polymeric liquids: a review of equations of state and their characteristic parameters for 56 polymers. *J Appl Polym Sci* 50:1061–1080
- Rudolf B, Kressler J, Shimomami K, Ougizawa T, Inoue T (1995) Evaluation of equation-of-state parameters from PVT data. *Acta Polym* 46(4):312–318
- Sanchez IC, Lacombe RH (1976) Elementary molecular theory of classical fluids–pure fluids. *J Phys Chem* 80:2353–2362
- Sanchez IC, Lacombe RH (1978) Statistical thermodynamics of polymer solutions. *Macromolecules* 11:1145–1156
- Schmidt M (2000) Macroscopic volume and free volume of polymer blends and pressure-densified polymers. Ph.D. Thesis, Chalmers University, Göteborg
- Schmidt M, Maurer FHJ (2000) Relation between free-volume quantities from PVT-EOS analysis and PALS. *Polymer* 41:8419
- Schmidtke E, Günther-Schade K, Hofmann D, Faupel F (2004) The distribution of the unoccupied volume in glassy polymers. *J Mol Graph Model* 22:309–316
- Sedlacek T, Zatloukal M, Filip P, Boldizar A, Saha P (2004) On the effect of pressure on the shear and elongational viscosities of polymer melts. *Polym Eng Sci* 44:1328–1337
- Sedlacek T, Cermak R, Hausnerova B, Zatloukal M, Boldizar A, Saha P (2005) On PVT and rheological measurements of polymer melts. *Int Polym Process* 20:286–295
- Simha R (1977) Configurational thermodynamics of the liquid and glassy polymeric states. *Macromolecules* 10:1025–1035
- Simha R, Somcynsky T (1969) On the statistical thermodynamics of spherical and chain molecule fluids. *Macromolecules* 2:342–350
- Simha R, Jain RK, Jain SC (1984) Bulk modulus and thermal expansivity of melt polymer composites: statistical versus macro-mechanics. *Polym Compos* 5:3–10
- Simha R, Utracki LA, Garcia-Rejon A (2001) Pressure–volume–temperature relations of a poly- ϵ -caprolactam and its nanocomposite. *Compos Interfaces* 8:345–353
- Somcynsky T, Simha R (1971) Hole theory of liquids and glass transition. *J Appl Phys* 42:4545–4548
- Srithawatpong R, Peng ZL, Olson BG, Jamieson AM, Simha R, McGervey JD, Maier TR, Halasa AF, Ishida H (1999) Positron annihilation lifetime studies of changes in free volume on cross-linking cis-polyisoprene, high-vinyl polybutadiene, and their miscible blends. *J Polym Sci Part B Polym Phys* 37:2754
- Stickel F, Fischer EW, Richert R (1995) Dynamics of glass-forming liquids. I. Temperature-derivative analysis of dielectric relaxation data. *J Chem Phys* 102:6251–6257
- Stickel F, Fischer EW, Richert R (1996) Dynamics of glass-forming liquids. II. Detailed comparison of dielectric relaxation, dc-conductivity, and viscosity data. *J Chem Phys* 104:2043–2055
- Tanoue S, Utracki LA, Garcia-Rejon A, Tatibouët J, Cole KC, Kamal MR (2004) Melt compounding of different grades of polystyrene with organoclay: compounding and characterization. *Polym Eng Sci* 44:1046–1060
- Tao SJ (1972) Positronium annihilation in molecular substances. *J Chem Phys* 56:5499–5510
- Tschoegl NW (1981) The theory of linear viscoelastic behavior. Wiley, New York
- Utracki LA (1974) Temperature dependence of liquid viscosity. *J Macromol Sci Phys B10(3):477–505*
- Utracki LA (1983a) Pressure and temperature dependent liquid viscosity. *ACS Polym Preprints* 24(2):113–114
- Utracki LA (1983b) Pressure dependence of Newtonian viscosity. *Polym Eng Sci* 23:446–452
- Utracki LA (1983c) Temperature and pressure dependence of liquid viscosity. *Can J Chem Eng* 61:753–758
- Utracki LA (1985) A method of computation of the pressure effects on melt viscosity. *Polym Eng Sci* 25:655–668
- Utracki LA (1986) Correlation between P–V–T behavior and the zero-shear viscosity of liquid mixtures. In: Hartmann B (ed) *Thermodynamics and rheology*. *J Rheol* 30:829–841
- Utracki LA (2004a) Clay-containing polymeric nanocomposites, vol 1. RAPRA, Shrewsbury–Shropshire, UK
- Utracki LA (2004b) Statistical thermodynamics evaluation of solubility parameters and polymer miscibility. *J Polym Sci Part B Polym Phys* 42:2909–2915
- Utracki LA (2005) Pressure–volume–temperature dependencies of polystyrenes. *Polymer* 46:11548–11556
- Utracki LA (2006a) Interphase between nanoparticles and molten polymeric matrix: pressure–volume–temperature measurements. *Compos Interfaces* 15 (in press)
- Utracki LA (2006b) Present-volume-temperature of molten and glassy polymers. *J Polym Sci Part B Polym Phys* (in press)

- Utracki LA, Simha R (1981) Viscosity of polymer solutions: scaling relationships. *J Rheol* 25(3):329–350
- Utracki LA, Simha R (1982) Relationships between viscosity and equilibrium properties of liquids. *ACS Polym Prepr* 23(2): 67–68
- Utracki LA, Ghijssels A (1987) Temperature dependence of the melt viscosity of epoxy resins. *Adv Polym Technol* 7:35–37
- Utracki LA, Simha R (2001a) Analytical representation of solutions to lattice-hole theory. *Macromol Chem Phys Molecul Theory Simul* 10:17–24
- Utracki LA, Simha R (2001b) Free volume and viscosity of polymer-compressed gas mixtures during extrusion foaming. *J Polym Sci Part B Polym Phys* 39:342–362
- Utracki LA, Simha R, Garcia-Rejon A (2003) Pressure–volume–temperature relations in nanocomposite. *Macromolecules* 36: 2114–2121
- Utracki LA, Simha R (2004a) Pressure–volume–temperature dependence of polypropylene/organoclay nanocomposites. *Macromolecules* 37:10123–10133
- Utracki LA, Simha R (2004b) Statistical thermodynamics predictions of the solubility parameter. *Polym Int* 53:279–286
- van der Waals JD (1873) Ph.D. dissertation, University of Leiden
- Wang YY, Nakanishi H, Jean YC (1990) Positronium annihilation in amine-cured epoxy polymers–pressure dependence. *J Polym Sci Part B Polym Phys* 28:1431
- Yu Z, Yahsi U, McGervey JD, Jamieson AM, Simha R (1994) Molecular weight dependence of free volume in polystyrene studied by positron annihilation measurements. *J Polym Sci Part B Polym Phys* 32:2637
- Zoller P (1989) PVT relationships and equations of state of polymers. In: Brandrup J, Immergut EH (eds) *Polymer handbook*, 3rd edn. Wiley, New York