

Pressure–volume–temperature dependencies of polystyrenes

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Abstract

The pressure–volume–temperature (*PVT*) dependencies of four molten polystyrenes (PS) were determined at $T=450\text{--}530\text{ K}$, and $P=0.1\text{--}190\text{ MPa}$. In addition, five sets of published *PVT* data for PS were examined. The Simha–Somcynsky (S–S) lattice-hole equation of state (eos) was used to analyze the data. Fitting the data to eos yielded the characteristic reducing parameters, viz. P^* , V^* , T^* , where from the Lennard–Jones measures of energetic (ϵ^*), and volumetric (v^*) interactions were calculated. It was found that: (1) the values of the interaction parameters for PS resins varied, viz. $27.7 \leq \epsilon^* \leq 35.2$, and $35.5 \leq v^* \leq 50.2$; (2) ϵ^* was dependent on v^* , and (3) ϵ^* and v^* linearly increased with the logarithm of molecular weight. In addition, these volume-averaged interaction parameters depend on the chain configuration, as well as the presence of additives.

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1. Introduction

The pressure–volume–temperature (*PVT*) dependence of polymers has been measured to determine compressibility and the thermal expansion coefficients, important for process designing. However, these measurements, combined with adequate theoretical description, may provide an insight into the internal structure and the volume-averaged interactions. Several equations of state (eos) for liquids have been proposed [1–7]. In addition Tait empirical relation has been used [8]. Curro [9], Zoller [10], Rodgers [11], Rudolf et al. [12], reviewed and evaluated the suitability of several eos to describe the *PVT* behavior. Of the six mentioned theoretical expressions [11] the two: Dee and Walsh (D–W) modified cell model (MCM) [7], and Simha and Somcynsky (S–S) lattice-hole theory [4] performed well.

D–W modification of the Prigogine et al. cell model amounts to increasing the Lennard–Jones hard-core volume universally by 7%. The resulting eos provides good fit of data, with a set of characteristic reducing parameters (P^* , T^* , and V^*), and a single ‘adjustable’ quantity, M_0/c , where M_0 is segmental molecular weight, and $3c$ is the external degree of freedom [13].

The S–S theory has been used to provide description of the cohesive energy density [14,15], internal pressure, *PVT* behavior [16–20], etc. The great advantage of the S–S derivation is direct incorporation of the free volume parameter, h , which in turn may be used to interpret variety of dynamic properties, e.g. viscosity [21,22]. Considering the fundamental nature, precision, and wide applicability of the S–S theory, the following text will focus on the use of S–S eos. Fitting the experimental data to the eos yields the P^* , T^* , and V^* parameters, which are related to the Lennard–Jones 6–12 interaction quantities [23]: the maximum attractive energy, ϵ^* , and the segmental repulsion volume, v^* . For single-component polymeric liquids the *PVT* behavior is fully described by these two parameters through an adequate eos.

Over the years a large number of polymeric systems has been studied and the P^* , T^* , and V^* reducing parameters have been tabulated, e.g. see [9–12]. However, the P^* , T^* , V^* values published by various authors for supposedly the same polymer are different. Thus, this work aims to analyze the variability of the derived from S–S eos interaction parameters. Three potential sources will be examined: the method of testing (e.g. procedure, reproducibility), the computational methods, and variability of the tested material, viz. molecular weight and its distribution, additives introduced by the manufacturer, etc. Since the problem is general, for simplicity PS was selected. *PVT* data for several PS resins were measured in the author’s laboratory, while additional sets were taken from literature.

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2. Theory

The Simha–Somcynsky lattice-hole theory [4] considers an amorphous, condensed system as a mixture of occupied (by chain segments or small molecules) and empty sites. For macromolecules, the statistical segments are defined as $M_s = M_n/s$, where M_n is the number average molecular weight of a statistical macromolecule, composed of s statistical segments. The authors incorporated the configurational entropy of mixing as derived by Huggins and Flory for linear chains, and the inter-segmental interactions via the Lennard–Jones [23] (L–J) potential with the characteristic segmental energy, ε^* , and volume, v^* , per statistical segment:

$$E_0 = \lambda_{\text{repuls}} r^{-m} - \lambda_{\text{attract}} r^{-n}; \quad m = 10 \text{ to } 13; \quad (1a)$$

$$n = 6 \text{ or } 7$$

The form of L–J potential (Eq. (1a)) was originally adopted because it provided satisfactory description for the second virial coefficient of a gas with $m, n > 4$. Later, the second attractive interactions term was derived using quantum mechanics (for hydrogen and helium, $n=6$ and 7 was found, respectively). The first empirical term of Eq. (1a) has been identified as originating in repulsive interactions. Over the years the L–J potential (Eq. (1a) with $n=6$, and $m=12$) was applied to many condensed systems, quite different than these considered by L–J.

$$E_0 = \frac{qz\varepsilon^*}{s} \left[1.0109 \left(\frac{v}{v^*} \right)^{-4} - 2.4090 \left(\frac{v}{v^*} \right)^{-2} \right] \quad (1b)$$

Prigogine et al. [1,2] used the L–J mean-field relation to describe interactions between statistical segments of s -unit molecules (see Eq. (1b), in which the radius, r , of Eq. (1a) is replaced by cell volume, v). The authors also introduced the number $3c$ of the external, volume-dependent degrees of freedom, given by geometry and environment of each solvent molecule or polymeric segment. For linear, flexible molecules [13]:

$$3c = s + K \quad (2)$$

Simha derived [24] $K=3$, and this value has been used with S–S eos applied to low molecular weight solvents. For other eos' K is empirical, changing from one eos to the next ($K=0.86$ or 1.78) [13]. However, for high molecular weight polymers, where the number of statistical segments $s \gg 3$, the simplifying relation, $3c/s \approx 1$, is usually employed.

In the S–S theory the variables of state, and derived quantities are scaled. The three characteristic scaling parameters of pressure, temperature, and volume are defined as [4]:

$$\left. \begin{aligned} P^* &= \frac{zq\varepsilon^*}{(sv^*)} \\ T^* &= \frac{zq\varepsilon^*}{(Rc)} \\ V^* &= \frac{v^*}{M_s} \end{aligned} \right\} \left(\frac{P^* V^*}{T^*} \right) M_s = \frac{Rc}{s} \quad (3)$$

In the cell model, $zq = s(z-2) + 2$ is the number of interchain contacts in a lattice of coordination number z , and R is gas constant. Using the reduced variables (indicated by tilde), SS expression for the configurational free energy is a function of specific volume, \tilde{V} , temperature, \tilde{T} , and the hole fraction: $h = h(\tilde{V}, \tilde{T})$:

$$\tilde{F} \equiv \frac{F}{F^*} = \tilde{F}[\tilde{V}, \tilde{T}, h(\tilde{V}, \tilde{T})] \quad (4)$$

Since the theory is general, describing a common $\tilde{P}\tilde{V}\tilde{T}$ surface, the reduced coordinates of the critical point are universal [25], thus: $\varepsilon^* \propto T_c$; $\varepsilon^*/v^* \propto P_c$; $v^* \propto V_c$. From Eq. (4), the eos is derived in form of coupled equations:

$$3c[(U-1/3)/(1-U) - yQ^2(3AQ^2 - 2B)/6\tilde{T}] + (1-s) - \left(\frac{s}{y} \right) \ln[(1-y)] = 0 \quad (5)$$

$$\tilde{P}\tilde{V}\tilde{T} = (1-U)^{-1} + 2yQ^2(AQ^2 - B)/\tilde{T} \quad (6)$$

with the occupied site fraction $y = 1 - h$, and notation: $Q = 1/(y\tilde{V})$, $U = 2^{-1/6} y Q^{1/3}$. The coefficients $A=1.011$, and $B=1.2045$ account for non-nearest neighbors interactions in face-centered cubic lattice with the coordination number $z=12$. The coupled equations describe the PVT surface, and associated with it free volume function, $h = h(\tilde{V}, \tilde{T})$.

The optimum value of the reducing parameters (P^* , T^* , and V^*) is determined by fitting the experimental PVT -surface in the molten state to Eqs. (5) and (6). Historically, two methods have been used, the sequential [26], and simultaneous. The sequential method obtains T^* and V^* from the ambient pressure V vs. T data, and then P^* is computed from the pressure dependencies. However, its values vary with the selected set of $V = V(P, T = \text{const})$; hence P^* has to be averaged over the range of P and T [27].

During the last two decades the simultaneous least-squares (lsq) fit of all data to S–S eos has been employed, Thus for example, Scientist™ from MicroMath has been used [14–20]. Rapid convergence is obtained in two-steps: (1) fitting data to the polynomial expression [16], $\tilde{V} = \tilde{V}(\tilde{P}, \tilde{T})$, provides the initial values of P^* , T^* , and V^* , and then (2) fitting the data to the coupled Eqs. (5) and (6). The computation provides numerical values of $h = h(\tilde{P}, \tilde{T})$, as well as the characteristic parameters: P^* , T^* , and V^* , from which the volume-averaged interaction parameters, ε^* and v^* , may be calculated using Eq. (3). It can be shown that h decreases as ε^* increases [20].

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