



Equation of state and P–V–T properties of polymer melts based on glass transition data

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ABSTRACT

This paper addresses a method for predicting the participating constants in equation of state (EOS) for compressed polymeric fluids using two scaling constants. The theoretical EOS undertaken is Ihm–Song–Mason (ISM), which is based on the Weeks–Chandler–Anderson (WCA), and the two constants are the surface tension γ_g and the molar density ρ_g , both at the glass transition point. There are three temperature-dependent quantities that are required to use the EOS: the second virial coefficients $B_2(T)$, an effective van der Waals co-volume, $b(T)$ and a correction factor, $\alpha(T)$. The second virial coefficients are calculated from a two-parameter corresponding states correlation, which is constructed with two constants as scaling parameters, i.e., the surface tension γ_g and molar density ρ_g . This new correlation has been applied to the ISM EOS to predict the volumetric behavior of polymer melts including polypropylene (PP), poly(ethylene oxide) (PEO), polystyrene (PS), poly(vinyl methyl ether) (PVME), and polycarbonate bisphenol-A (PC) at compressed states. The operating temperature range is from 311.5 to 603.4 K and pressures up to 200.0 MPa. Other two-temperature-dependent parameters $\alpha(T)$ and $b(T)$ appearing in the ISM EOS, are calculated by scaling rules. It was found that the calculated volumes agree well with the experimental values. A collection of 421 data points has been examined for the aforementioned polymers. The average absolute deviation between the calculated densities and the experimental densities is of the order of 0.6%. The newly obtained correlation has been further assessed through a detailed comparison against previous correlations proposed by other researchers.

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1. Introduction

Macromolecular science has had a major impact on the way people live over the world. It is difficult to find an aspect of our lives that is not affected by polymers. Polymeric liquids are widely used for industrial and residential purposes. Polymer molecules may have a variety of architectural structures such as linear, ring, star, branched, and ladder chains as well as three-dimensional network structures. Polystyrene (PS) is one of the most widely used plastics, having applications in multiple industries for packaging, appliances, construction, automobiles, electronics, furniture, toys, housewares, and luggage. Major applications of polyethylene oxide (PEO) are related to textiles, cosmetics, antifoaming agents, and others (chemical intermediates, ink and dye solvents, demulsifiers, plasticizers, etc.) [1,2]. Low molecular weight atactic polypropylene is used as a component of hot melt adhesives and sealants. "Atactic" polypropylene which is produced as a

by-product of isotactic PP production is not ideally atactic or completely amorphous [3]. Ideally atactic polypropylene has been prepared by hydrogenation of poly 2-methyl-1, 3-pentadiene, that is, poly 1, 3-dimethyl-1-butenylene or PDMB [4]. Recently, directly synthesized atactic polypropylene and other amorphous poly α -olefins (APAO or APO) have been developed [3,4]. Versions with lower molecular weight are found in commercial products. Versions with high molecular weight are being evaluated as elastomers and as blend components for modification of isotactic polypropylene [3]. bisphenol-A polycarbonate (PC), is used in making canopies for supersonic aircraft, bubble helmets for astronauts, break-resistant windows, and bullet-resistant laminates for banks and armored cars. It is also used for computer housings where mechanical, electrical and fire-resistance properties are needed. It is also used in steam-sterilizable food-processing equipment. Interest properties of PC are good electrical, good thermal stability, and outstanding impact strength. High viscous and adhesion of PVME has made it applicable for coatings; aqueous tackifier; adhesion promoter of nonadhering materials to glass, metal, and plastics; copolymers used in pharmaceuticals; lens arrays for optical device (as thermographic copying material). Unquestionably, polymers have become the most important advanced materials not only because of their unique physical

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Table 1
Parameters for the polymer liquids.

Substance	MMW ^g	T _g (K)	ρ _g (kg/m ³)	γ _g (mN/m)
a-PP	42	260 ^a	842.85 ^b	31.23 ^c
PEO	44	232 ^a	1192.90 ^b	49.20 ^d
PS	104	373 ^a	1022.97 ^b	34.94 ^c
PVME	58	239 ^a	1066.44 ^b	35.77 ^c
PC	254	459 ^c	1192.66 ^c	32.94 ^c

^a Taken from Ref. [24].^b Taken from Ref. [25].^c Taken from Ref. [26].^d Taken from Ref. [27].^g Monomer molecular weight.

and chemical properties, which are unmatched by other materials, but also due to their process ability.

Fundamentally, melting is a transition that occurs in crystalline polymers. Melting happens when the polymer chains fall out of their crystal structures, and become a disordered liquid. The glass transition is a transition which happens to amorphous polymers; that is, polymers whose chains are not arranged in ordered crystals, but are just strewn around in any old fashion, even though they are in the solid.

A parameter of particular interest in synthetic polymer manufacturing is the glass transition state temperature (T_g), which describes the temperature at which amorphous polymers undergo a second-order phase transition. Glass transition is a method to characterize a property of a polymeric material. It denotes the temperature when the polymer goes from a hard, glass-like state to a rubber-like state.

The exact value of T_g is determined by analyzing the temperature dependence of a property. To accomplish this, some scientists use cooling curves. However, the overwhelming majority of scientists prefer to use solely heating curves [5,6]. The best ways to measure the transition glass temperature as reported in the literature are differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA). The first technique defines the glass transition as a change in the heat capacity as the polymer matrix goes from the glass state to the rubber state. The second technique defines the glass transition in terms of the change in the coefficient of thermal expansion (CTE) as the polymer goes from glass to rubber state with the associated change in free molecular volume.

The equation of state is the most fundamental equation in providing a basis for the accurate determination of the thermo-physical properties. The applicability of an equation of state to a given system is considered reliable if accurate input data are available. In practice, the input data may not be available for a given system or it may not be possible to measure the data accurately for some systems. The most suitable EOS to be used for practical applications are of semi-theoretical nature in which theoretically-based functional forms of the EOS are used by way of treating some of its parameters as quantities adjustable from experimental measurements. This procedure reduces considerably the amount of experimental data that is needed, and removes the direct dependence of the EOS on the chosen intermolecular potential model, and guarantees accuracy while maintaining relative simplicity and generality. Many theoretical equations of state such as the perturbed hard-chain theory (PHCT),

Table 2
Coefficients in Eq. (5).

Systems	a _λ	b _λ × 10 ²	c _λ × 10 ⁵	d _λ × 10 ⁸
a-PP	-0.5262	0.76 97	-2.1439	1.9531
PEO	-9.1764	7.7715	-20.9079	18.6818
PS	0.3071	0.0856	-0.2118	0.1686
PVME	0.1287	0.2686	-0.8111	0.7632
PC	0.4778	-0.0281	0.0807	-0.0601

Table 3

Percent deviation between the calculated specific volumes from the experimental specific volume [28] for a-PP.

Deviations of the calculated specific volume (PD) ^a					
P (MPa)	353.15 K	363.15 K	373.15 K	383.15 K	393.15 K
0.1	0.78	1.22	1.41	1.60	1.92
10	0.61	0.20	1.06	1.18	1.42
20	0.54	0.70	0.12	0.92	1.10
30	0.36	0.48	0.50	0.59	0.69
40	0.17	0.24	0.25	0.29	0.34
50	0.00	0.03	0.00	0.00	0.00
60	-0.14	-0.17	-0.19	-0.23	-0.28
70	-0.28	-0.34	-0.38	-0.47	-0.51
80	-0.39	-0.45	-0.56	-0.67	-0.75
90	-0.51	-0.65	-0.72	-0.87	-0.95
100	-0.60	-0.74	-0.86	-1.04	-1.13

^a PD = 100 × (exp - calc)/exp.

Flory–Orwoll–Vrij (FOV), lattice fluid (LF), statistical associated-fluid theory (SAFT), chain-of-rotator (COR) and perturbed hard-sphere-chain (PHSC) [7], and the polymer chain-of-rotator (PCOR) have been applied to liquid polymers and polymer melts [8]. Besides, the Ihm–Song–Mason (ISM) equation of state in conjunction with surface properties of polymers has been designed to apply to polymer melts by Sabzi and Boushehri [9].

In the present study a new version of the ISM EOS has been employed to obtain volumetric properties of five polymers consisting of polypropylene (PP), poly(ethylene oxide) (PEO), polystyrene (PS), poly(vinyl methyl ether) (PVME), and polycarbonate bisphenol-A (PC) at compressed states in the temperature range from 311.5 K to 603.4 K and pressures up to 200.0 MPa.

The second virial coefficient, which characterizes binary interactions between atoms and molecules, plays an important role in the ISM EOS. In the present work we use the most generally useful method of prediction of the second virial coefficient which corresponds to the use of the hypothesis of corresponding states. In this study a new corresponding state correlation for the second virial coefficient using molar density and surface tension, both at the glass transition point as two arbitrary constants is proposed.

The computed results are compared with a vast number of literature data, together with the original ISM EOS. From a total of 421 data points examined in reference to the aforementioned polymers, the average absolute deviations (AAD) between the calculated densities and experimental densities stayed within 0.6 %. For completeness, the present correlation has also been assessed by comparing it against several previously obtained correlations.

2. Theoretical Equation of State

We consider the statistical–mechanical equation of state derived by Song and Mason [10], which is based on the Weeks–Chandler–

Table 4

Percent deviation between the calculated specific volume from the experimental specific volume [28] for PEO.

Deviations of the calculated specific volume (PD) ^a					
P (MPa)	353.15 K	363.15 K	373.85 K	388.75 K	393.45 K
0.1	0.18	0.26	0.36	0.51	0.54
5	0.14	0.19	0.26	0.36	0.37
10	0.09	0.13	0.16	0.23	0.25
15	0.03	0.05	0.07	0.10	0.11
20	0.01	0.00	0.00	-0.01	0.00
25	-0.01	-0.03	-0.06	-0.09	-0.10
30	-0.03	-0.06	-0.10	-0.17	-0.18
35	-0.03	-0.08	-0.15	-0.24	-0.26
40	-0.01	-0.09	-0.18	-0.31	-0.34

^a PD = 100 × (exp - calc)/exp.

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