MATERIALS AND INTERFACES

Simultaneous Determination of the Surface Tension and Density of Polystyrene in Supercritical Nitrogen

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In this paper we present a simple procedure for calculating the mass density of polymers at high temperature and pressure conditions. The proposed method entails the integration of a pendant drop volume from an axisymmetric drop image profile; this same pendant drop profile can be used to determine the surface tension using axisymmetric drop shape analysis (ADSA). Our approach yields both density and surface tension data simultaneously and is advantageous since it does not require any additional procedure or module to calculate the density of polymers in a fluid. This integration method provides a set of density data for the sample polymer, polystyrene, in supercritical fluid nitrogen, which is similar to the data derived from the empirical Tait equation and the semiempirical Sanchez−Lacombe equation of state when the temperature is above the polymer glass transition point. The results corroborate the use of all three approaches in determining the mass density of polymers at high temperatures. The comparable surface tension data are obtained at temperatures above the glass transition temperature of polymer with the densities generated by the three density determination approaches. We expect that the approach based on ADSA in conjunction with the mass density determination by the current integration method can be applied to the surface tension measurements of many other polymer melts in various fluid environments.

Introduction

Surface tension is one of the most important parameters in polymer engineering processes, such as foaming, suspensions, wetting, and blending,[1] and there are many methods available for measuring surface tension. Among them, the pendant drop method has many advantages because of the simplicity of the apparatus and the versatility of its applications.[2,3] The latter is shown in surface tension measurements for many fluid systems, such as low molar mass liquids, liquid crystals, and polymers. This method includes the determination of a dense liquid drop profile in another liquid at the equilibrium interface of two liquids.[4,5] One of the pendant drop techniques, the axisymmetric drop shape analysis (ADSA) method, relies on the numerical integration of the Laplace equation of capillarity and determines the surface tension value through a best fit of the experimental profile with the theoretical one. However, there are several obstacles in carrying out such experiments with polymers. One is to do with the experimental difficulties in handling viscous polymer melts at high temperature and pressure; it is a challenge to ensure that the equilibrium of the polymer interfaces is maintained during the measurement.[6–8] It has been difficult to determine polymer mass densities precisely at extreme conditions (i.e., high temperature and pressure conditions), which often poses challenges to obtaining accurate surface tension measurements.[9] For polymer melt systems, one can, in principle, measure the mass density and surface tension separately, and then obtain the density data through interpolation. The density

is usually required as an input parameter in the procedure of determining the surface tension by fitting the experimentally observed profile of the pendant drop. For this procedure to be successful, however, one requires accurate density data as well as the ability to replicate the identical experimental conditions for both the density and surface tension measurements, which is not always feasible in given experiments.[10–16]

Several theoretical approaches, both empirical and semiempirical, have been essayed to calculate the mass density of polymer melts at high temperature and pressure, such as those that use the Tait equation[17–19] and the Sanchez−Lacombe equation of state (S-L EOS).[20] These equations relate the pressure, temperature, and volume of polymer melts; the density of the polymer can in turn be calculated as a function of pressure and temperature. In fact, these theoretical predictions of polymer mass densities have been used by us in a number of recent publications.[21,22] Nonetheless, these approaches have entailed certain errors (see below), since most of the current theoretical models used to calculate the pressure, volume, and temperature (PVT) relationship of polymer melts employ approximations that have not been justified experimentally or using first principles.[23]

On the other hand, there have been several experimental attempts to measure the mass density of polymer melts and their surface tension simultaneously. These approaches are based on a sessile drop method;[14–16] however, it has also been reported[8–10] that the sessile drop profile based methods are less accurate for determining surface tension as compared to the pendant drop methods, possibly because of the significant influence exerted by the solid substrate supporting the fluid sample drop.

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Table 1. Polystyrene Molecular Weights

polystyrenes (PS)	maker	M_w (g/gmol)[a]	M_n (g/gmol)[b]	M_w/M_n
polydispersed PS	Dow Chemicals	312000	120000	2.60

[a] M_w (g/gmol): weight-average molecular weight. [b] M_n (g/gmol): number-average molecular weight.

Table 2. Characteristic Parameters for the Sanchez−Lacombe Equation of State[28]

substance	P^* (MPa)	ρ^* (kg/m³)	T^* (K)
PS	387.0	1108	739.9
nitrogen	103.6	803.4	159.0

Table 3. Binary Interaction Parameters (k_{12}) of Polystyrene in Nitrogen at Different Temperatures

temp (°C)	interaction parameter (−)
30	0.245
50	0.239
70	0.233
90	0.227
110	0.221
130	0.215
150	0.209
170	0.203
190	0.197
210	0.191

The purpose of the present study was to find an effective way of obtaining the mass density and the surface tension of polymer melts simultaneously using the pendant drop method. Since the ADSA surface tension measurement entails visually capturing the pendant drop profile generated by a polymer melt, one can measure the volume of the pendant drop by reconstructing the 3-D structure of the drop. The method reported herein is based on a computer program created for axisymmetrical drops that is consistent with the requirements of the ADSA method for achieving a surface tension measurement. The experiment described in this paper used a drop profile that was obtained under high temperature and pressure experimental conditions to measure both the surface tension and the mass density of polystyrene in supercritical nitrogen, as both are commonly used in polymer materials and processing industry. We also examined the theoretical models represented by the Tait and S-L equations and present a comparison of all three approaches with respect to their efficiency at predicting densities of the polymer.

Materials and Methods

Materials. Polydisperse polystyrene (Styron 685D; weight average molecular weight (M_w) = 312 000; polydispersity index = 2.6) (Table 1) was obtained from Dow Chemical Co. Nitrogen (critical pressure = 492 psi; critical temperature = −147 °C) at 99.99% purity was purchased from PRAXAIR (Danbury, CT).

Density Determination: the Tait Equation of State. The density of polymers as a function of temperature and pressure plays an important role in many polymer engineering processes. The relation of pressure, temperature, and density is useful for optimizing processing parameters, predicting polymer−polymer miscibility, and correlating the parameters of polymer melt theories involving molecular structures. Among the theories of equations of state, the Tait equation is well-known as a successful empirical equation for predicting the density of amorphous polymers.[17–19] For polystyrene in nitrogen, the Tait equation can be written as[24]

$$v_p = v_0 \left[1 - 0.0894 \ln\left(1 + \frac{P}{B(T)}\right)\right] \quad (1)$$

where v_p is the specific volume (cm³/g), P is the pressure, and

$$v_0 = 0.7884 \exp(5.790 \times 10^{-4}T) \quad (2)$$

$$B(T) = 887.2 \exp(-4.323 \times 10^{-3}T) \quad (3)$$

Density Determination: the Sanchez and Lacombe Equation of State. Sato et al. employed the Sanchez−Lacombe (S-L) equation of state (EOS) to calculate the solubility of gas under high pressure and temperature.[20] The density of polystyrene saturated with nitrogen was determined using the following S-L EOS:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \quad (4)$$

where $\tilde{\rho}$ is the reduced density, $\tilde{P}$ is the reduced pressure, $\tilde{T}$ is the reduced temperature, and r is the number of sites occupied by a molecule. These parameters are defined as

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad r = \frac{MP^*}{RT^*\rho^*} \quad (5)$$

where ρ is the density, P is the pressure, T is the temperature, M is the molecular weight, R is the gas constant, and the characteristic parameters, P^*, ρ^*, and T^*, for the mixture were evaluated using the following mixing rules:

$$P^* = \sum_i \sum_j \varphi_i \varphi_j P_{ij}^*, \quad P_{ij}^* = (1 - k_{ij})(P_i^* P_j^*)^{0.5},$$

$$T^* = P^* \sum_i \frac{\varphi_i^0 T_i^*}{P_i^*}, \quad \frac{1}{r} = \sum_i \frac{\varphi_i^0}{r_i^0}, \quad \varphi_i^0 = \frac{(\varphi_i P_i^*/T_i^*)}{\sum_j (\varphi_j P_j^*/T_j^*)},$$

$$\varphi_i = \frac{(w_i/\rho_i^*)}{\sum_j (w_i/\rho_i^*)} \quad (6)$$

where T_i^*, P_i^*, ρ_i^*, and r_i^0 represent the characteristic parameters of the component i in its pure state. In particular, the first two characteristic parameters are defined as

$$T^* = \frac{\varepsilon^*}{k_B}, \quad P^* = \frac{\varepsilon^*}{v^*} \quad (7)$$

where ε^* is the interaction per mer and v^* is the close-packed mer volume.[21,22] The characteristic parameters for calculating the density using the S-L EOS are given in Table 2. The binary interaction parameter, k_{12}, was determined in order to minimize the relative experimental deviations at each given temperature; the determined binary interaction parameters at different temperatures are included in Table 3.

Density Determination: the Integration Method. In the integration method proposed herein, a known amount of mass of polymer sample was used to form a pendant during the experiment. The volume of the polymer was then calculated from the drop image profile once desired high temperatures and pressures were achieved in the experiment. For the volume calculation, the drop profile was modeled using a left profile $P_L(y)$ and right profile $P_R(y)$ (Figure 1). The drop volume was "cut" into a series of discs that were perpendicular to the vertical axis, y, of the drop (note: this axis does not necessarily coincide with the direction of gravity action). The midpoint rule was used for the integration along the y-axis:

$$\text{volume of drop} = \pi \int R(y)^2 \, dy \quad (8)$$
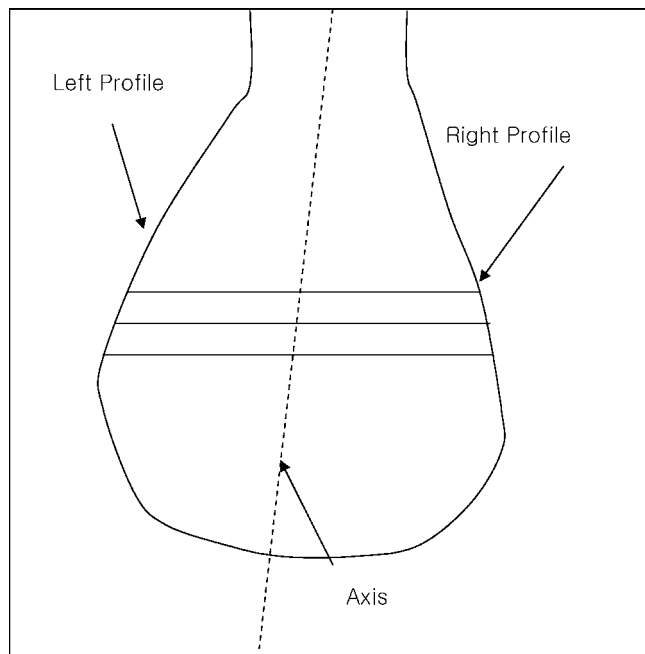
where the radius of each disk is

Figure 1. Volume integration along the *Y*-axis of a drop image.

$$R(y) = \frac{P_R(y) - P_L(y)}{2} \tag{9}$$

centered at

$$C(y) = \frac{P_R(y) + P_L(y)}{2} \tag{10}$$

For the volume calculation, it is also possible to use the trapezoid rule. When integration occurs at a pixel scale resolution, the difference between the two methods is the same as the discretization errors that occur during the drop profile extraction. In the experiment, the solid polymer sample was weighed and attached to the tip of a stainless steel rod. The sample was then heated up to 210 °C to generate the polymer melt and ensure equilibrium with the surrounding nitrogen supercritical fluid. The polymer melt formed pendant drop was generally axisymmetric and the density so obtained showed a small variation, less than 1%, in our experiments. The details were discussed in a previous publication.[20] Note that the weight changes of the polymer were corrected for the effect of nitrogen dissolving in the polymer melt during the experiment; the solubility values were obtained from those available in the literature.[21]

Volume and Surface Tension Measurements. The volume of polystyrene in nitrogen was calculated with the integration method at different temperatures ranging between 30 and 210 °C, and at a pressure of 500 psi. Figure 2a shows a typical cross-sectional drop profile, with a 3-D image in Figure 2b. For the density calculation, the volume was obtained through the integration by assuming that the drop was symmetric about the *Y*-axis. The polymer in pellet form was initially weighed before the experiment. The solubility data for nitrogen in polystyrene[21] was then used for correcting the density calculations.

To achieve the desired experimental conditions, a high-temperature and high-pressure sample cell was constructed in an earlier experiment[20] and used here. Briefly, the optical viewing cell consisted of a cylinder of stainless steel, which was heated by an electrical band heater during the experiment. The cylinder was hollow, with an inner diameter of 30 mm and length of 25 mm. Two optical-quality sapphire windows (Meller Optics, Inc.) permitted the illumination and observation of the
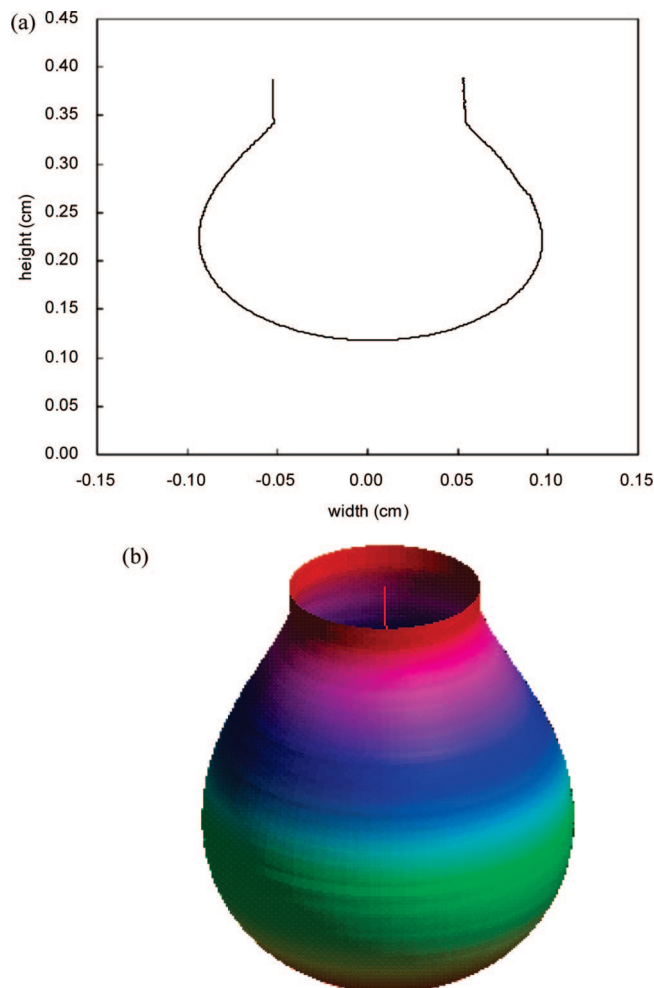

Figure 2. Typical pendant drop profile of a polystyrene melt in supercritical nitrogen: (a) 2-D profile, (b) corresponding 3-D profile.
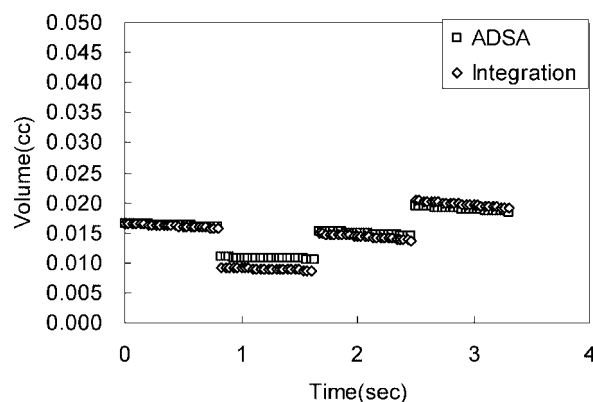

Figure 3. Comparison of the volume measurements of the integration method with the axisymmetric drop shape analysis (ADSA) method for various drops formed at different times.

pendant drop formed by the sample polymer melt. The experimental setup was tested for its accuracy and reproducibility with a range of polymer−gas combinations, and the details are described in our recent publication.[23] For the purpose of calibration, the volume was also obtained from the ADSA software and was compared with that of the integration method (see Figure 3). Note that the volume from ADSA was obtained after using the polymer density as an input in the surface tension calculations; thus, this volume determination was not indepen-
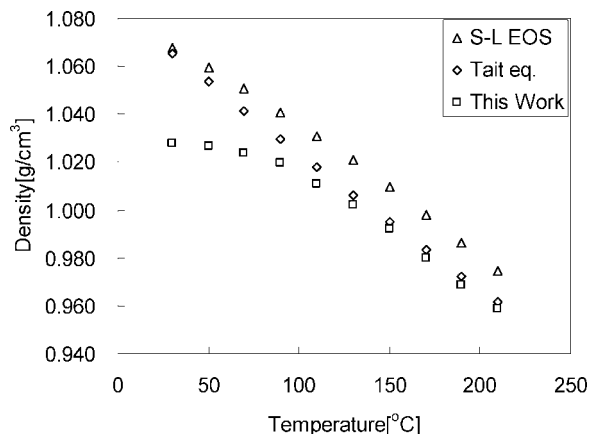
Figure 4. Temperature dependence of polystyrene density for all three density calculation methods. The current work is based on the integration method. The pressure used was 500 psi.

dent from the Laplace equation of capillarity fitting for surface tension determination.

Results and Discussion

Density Measurements. The density of polystyrene in supercritical nitrogen (critical conditions 493 psi and −147 °C) was determined using three approaches: two theoretical calculations based on the Tait and S-L equations of state, respectively, and the integration method. The integration method was verified when the results yielded by using this method were compared with those obtained from the ADSA program (Figure 3). The density results from the three approaches are shown in Figure 4. In the higher temperature range (i.e., above ∼100 °C), all three approaches yielded the same density change trend with respect to temperature. They appeared to have a similar negative slope of density change in relation to temperature, although the S-L EOS gave the highest density value at each temperature, while the integration method generated the lowest one. Nevertheless, relatively small differences among all three approaches indicated that at high temperatures, both approaches that use equations of state were valid for calculating polymer melt densities. These findings thus support earlier work that extracts the mass density of polymer melts based on either the Tait equation or S-L EOS.[21–23]

Larger density discrepancies emerged among the three approaches, however, when the temperature of the experiment was reduced below 100 °C. In this case, the integration method yielded a plateau while the two EOS approaches kept increasing as the temperature decreased. Since the glass transition for polystyrene in nitrogen is at approximately 100 °C,[27–31] the polymer adopts a glassy state and its molecular mobility becomes significantly limited as the temperature dips below 100 °C. Thus, at low temperatures, the density of the polymer should not change with temperature as significantly as when the polymer is in a liquid state at higher temperatures. In light of this important consideration, we believe that the values obtained from the integration method are more realistic than those obtained from the two theoretical approaches. Additionally, this outcome may not be surprising as both the Tait and the S-L equations were originally generated from experimental observations at high temperatures when polymers were still in a liquid state, as well as from mean field theories applied to the liquid state of polymer melts where sufficient molecular mobility was assumed.

Surface Tension Measurements. The surface tension of polystyrene in supercritical nitrogen was determined by the
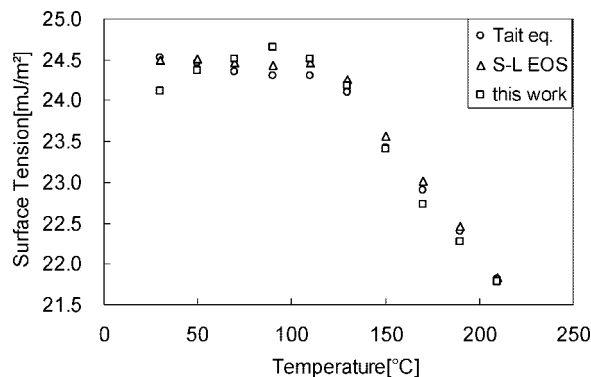

Figure 5. Temperature dependence of polystyrene surface tension for all three density calculation methods. The current work is based on the integration method. The pressure used was 500 psi.

ADSA technique with the mass density of the polymer melt as an input parameter. Three versions of the mass density were used, based on three density determination methods: the Tait equation, the S-L EOS, and the integration method proposed in the current work. The results are shown in Figure 5. It was observed that at high temperatures, above ∼100 °C, all three approaches yielded rather similar surface tension values at each temperature; they all increased with decreasing temperature, with the S-L EOS giving the highest value and the integration method generating the lowest value at a given temperature. These results indicate that all three approaches provide adequate mass densities for polymers in their surface tension measurements. However, discrepancies occurred when the temperature descended below ∼100 °C, the glass transition temperature. These large deviations were related to the large differences among the three density determination methods (Figure 4). On the basis of the surface tension change that typically occurs with respect to temperature, a clear break was observed around ∼100 °C for all three approaches. This break represented the direct effects of the glass transition temperature of polystyrene in supercritical nitrogen. When the temperature was below the glass transition temperature, the polymer adopted a solidlike state and its viscosity became extremely high. Under such situations, the pendant drop of the polymer was almost "powerless" to alter its shape. The surface tension measurement based on the drop shape analysis therefore showed becomes invalid.

It should be emphasized that, in the current experiments, the mass density of the polymer and its surface tension were obtained from the same pendant drop at a given high pressure and temperature, and the experiment did not require any additional procedure or module to obtain the density as an input parameter to determine the surface tension. The integration method proposed is robust and efficient at determining polymer densities when compared to other empirical or semiempirical equation of state models.

Summary

We have presented a simple method for obtaining the mass density of polymers at high temperature and pressure conditions. This procedure involved the integration of a pendant drop volume from an axisymmetric drop image profile that was simultaneously used for determining surface tension. The approach developed herein yielded both density and surface tension data simultaneously and was effective and advantageous since it does not necessitate the use of any additional procedure to calculate the density of polymers under a given experimental situation. For polystyrene in supercritical nitrogen, the integra-

tion method generated a set of density data similar to that calculated from both the empirical Tait equation and the semiempirical Sanchez–Lacombe equation of state when the temperature was above the polymer glass transition point. This corroborates the use of all three approaches in determining the mass density of polymers at high temperatures. However, at temperatures below the polymer glass transition point, large discrepancies in density were observed among the three approaches, reflecting the inability of the two theoretical models to predict accurately the polymer density while the integration method remained valid. The obtained density values can be used for ADSA surface tension calculations. At temperatures above the polymer glass transition point, similar surface tension data was produced by all three density determination approaches.

Acknowledgment

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