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Determination of interfacial tension between two immiscible polymers with and without surfactants at the interface

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Abstract

A second-order drop deformation method for inferring interfacial tension between two immiscible polymers is proposed and shown to improve the accuracy of tension estimate appreciably. A small step-strain method, which uses a strong flow (capillary number >1) and short flow time $\sim O(0.1\ \text{s})$, is successfully developed to avoid complications caused by the surfactants for surfactant-laden drops. This method is demonstrated to give good tension estimates for a range of viscosity ratios and surface coverage.

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Keywords: Drop deformation; Drop retraction; Interfacial tension; Surfactants

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1. Introduction

The accurate determination of interfacial tension between two immiscible polymers is not trivial and has been subjected to numerous studies. For example, Xing et al. compared five popular techniques for a polymer model system and found that most techniques have an uncertainty of ±20–30% except the pendant drop technique, which has an uncertainty of only ±1.4% [1]. Unfortunately, the pendant drop technique needs very long sample preparation and test time for typical viscous polymers. The drop retraction method, on the other hand, was found to be convenient but suffers from a large uncertainty (±26%). The difference between the average results obtained by different methods is more than 10%. In other comparative studies of polymer systems, it is common to see similarly large discrepancies [2–5]. Thus it seems desirable to improve the accuracy of the drop deformation and retraction methods for estimating interfacial tension.

For interfaces with surfactants or copolymers, it is more difficult to measure the interfacial tension accurately. The tedious pendant or sessile drop method [6–9], and the spinning drop method [10] were used in some studies. One potential drawback associated with these techniques is that the drop shape is coupled to the surfactant adsorption/desorption, making it very difficult to reach the true equilibrium. This is not expected to be a problem for the drop deformation or retraction method since the change of drop shape is usually much faster than the surfactant adsorption or desorption time for polymers. However, there are other potential issues that may make the drop deformation and retraction methods invalid for surfactant-laden drops. The surfactant influences drop deformation through dilution, Marangoni, and tip-stretching effects [11–17]. These effects are not included in the Taylor's small deformation theory, on which the drop deformation and retraction methods are based. Indeed, recent computer simulation results have raised doubt on the suitability of these methods for surfactant-laden surfaces [18, 19].

The purpose of this study is two-fold. First, we would like to improve the accuracy of the drop deformation and retraction methods for surfactant free drops. This is achieved by adding a second-order term to the Taylor theory. The second goal is to investigate experimentally the impact of surfactants on the applicability of drop deformation and retraction methods. We show that under certain well-controlled conditions, the drop retraction method can provide reasonable tension estimates even for surfactant laden drops.

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Table 1
Model fluids and their properties at 22.0 ± 0.2 °C

Suspending fluid	η_s (Pa s)	Drop fluid	η_d (Pa s)	λ
PDMS	60.0	PBd	5.6	0.093
		PBd	140	2.3
PIB	103	PDMS	110	1.07
Castor oil	44.4	PDMS	0.05	0.00112

2. Experiment

2.1. Materials

Various drop and suspending fluids were chosen to cover a wide range of viscosity ratios (Table 1). Polyisobutylene (PIB), polybutadiene (PBd), and polydimethylsiloxanes (PDMS) were obtained from Exxon Mobile, Aldrich, and Corning, respectively. The lower Newtonian plateau viscosity of these fluids was measured with a commercial rheometer (ARES-LS, TA Instruments). The interfacial tension was determined from drop deformation as described in Section 4. Surfactants were generated at the interface by reaction between end-functionalized PBb and PDMS [14]. Less than 1% of amine-functionalized polydimethylsiloxane (PDMS-HN$_2$, $M_n = 27$K, United Chemicals) was mixed with an inert PDMS ($M_n = 62{,}700$) in a small vial. A drop of PBd containing 0.17% carboxyl-functionalized polybutadiene ($M_n = 10$K, Polymer Sources) was introduced into the vial with a syringe and allowed to react at room temperature. This produced a "salt-like" complex of PDMS-PBd at the interface that we refer to as the surfactant. The surfactant concentration at the interface was controlled by the reaction time and/or concentration of PDMS-NH$_2$. The PBd drop with surfactant at the interface was then transferred via pipette into the flow cell.

2.2. Methods

The drop deformation and retraction tests were carried out in planar elongational flow using a four-roll mill flow apparatus. The drop is imaged in the flow–flow gradient (x–y) plane. A derivative edge detection technique was implemented and the optics was calibrated with a precision sapphire ball of diameter 500.0 ± 0.6 μm (Edmund Industrial Optics). Typical drop sizes were less than 400 μm, much smaller than the effective flow field of about 14 × 14 mm^2. Drop dimensions were obtained directly from digital images in real time. The steady-state values were averaged over 100 points in order to reduce random errors. The temperature of the flow cell was controlled at 22.0 ± 0.2 °C by water channels embedded in the flow cell walls and was measured by a precision thermometer.

Two modes of flow were used in this study. (A) Step rate flow: A specified flow rate was applied and kept constant until the drop reached the steady state. In this study the shear rate was usually very small (Ca < 0.1) so that the steady state deformation was typically less than 0.15. This value was chosen because it is the limit below which the Taylor theory is accurate within 5%. The flow time was typically $O(100\ \text{s})$. (B) Step strain flow: A strong flow (Ca > 1) was applied briefly until the specified deformation was reached. In this study, the deformation was typically smaller than 0.15 and the flow time was $O(0.1\ \text{s})$.

Pendant drop experiments were carried out with a commercial pendant drop apparatus (First Ten Angstroms). This method is based on the principle that the shape of one liquid drop suspended in another liquid is governed by the balance between the interfacial tension and gravity. Fluid densities were measured using a Mettler Toledo balance (AG285) with the density kit. The interfacial tension was obtained by analyzing the drop profile. These measurements were performed at a controlled temperature of 22.0 ± 0.1 °C.

3. Theories

3.1. Steady deformation methods

A popular method of estimating interfacial tension from drop deformation is based on Taylor's small deformation theory [20,21]. For planar hyperbolic flow it predicts

$$D = \frac{f_2}{f_1}\frac{\eta_s R}{\sigma}\dot{\gamma}. \tag{1a}$$

Here the Taylor deformation parameter D is defined as $(L - B)/(L + B)$, where L and B are the drop length and breadth respectively.

$$f_1 = \frac{40(\lambda + 1)}{(2\lambda + 3)(19\lambda + 16)} \quad \text{and} \quad f_2 = \frac{5}{2\lambda + 3},$$

where λ is the viscosity ratio η_d/η_s, with η_d and η_s being the viscosity of the drop and suspending medium respectively. R is the drop radius, $\dot{\gamma}$ is the shear rate, and σ is the interfacial tension. Equation (1a) may be rewritten as

$$\sigma = \frac{f_2}{f_1}\eta_s R\left(\frac{\dot{\gamma}}{D}\right). \tag{1b}$$

Equation (1b) provides a convenient way to calculate the interfacial tension from drop deformation measured at a given shear rate. The result from Eq. (1b) will be referred to as the direct (Taylor) estimate. In practice, it is common to measure the steady state deformation for a range of shear rates and obtain the slope $D/\dot{\gamma}$ from a linear fitting of the D–$\dot{\gamma}$ curve. The tension is then calculated using the slope $D/\dot{\gamma}$, which will be referred to as the linear approximation or linear estimate.

An alternative model for estimating interfacial tension is the ellipsoidal model of Maffettone and Minale (MM model). For planar hyperbolic flow it predicts [22]

$$L^2 = \frac{(f_1^2 + 2f_1 f_2\,\mathrm{Ca})^{1/3}}{(f_1 - 2f_2\,\mathrm{Ca})^{2/3}}, \tag{2a}$$

$$B^2 = \frac{(f_1^2 - 2f_1 f_2\,\mathrm{Ca})^{1/3}}{(f_1 + 2f_2\,\mathrm{Ca})^{2/3}}, \tag{2b}$$

where Ca is the capillary number $\eta_s R\dot{\gamma}/\sigma$. From these two equations we can obtain

$$D_{\mathrm{MM}} = \frac{f_2}{f_1}\frac{\eta_s R}{\sigma}\dot{\gamma}, \tag{2c}$$

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