The Effect of Viscosity on Surface Tension Measurements by the Drop Weight Method

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ABSTRACT: Viscosity is one of the parameters affecting the measured surface tension, as fluid mechanics affects the measurement process using conventional methods. Several methods including the selected planes (SPM) and WDSM which combines the weight drop method (WDM) and SPM, are applied to surface tension measurement of high viscous liquids. Yet, none of them treats the viscosity effect separately. The current publication presents a simple, easy to apply empirical approach of satisfactory accuracy, for evaluation of surface tension of liquids having wide range of viscosities up to 10 Pa s. The proposed method is based on Tate's law and the ''drop weight'' method using calibration curves of known liquids having similar surface tensions but different viscosities. Drop weight of liquids having viscosity ≥ 0.05 Pa s, was found to be significantly affected by the liquid viscosity. The shape factor, f, of high viscosity liquids was found to correlate linearly with the logarithm of viscosity, pointing the importance of viscosity correction. The experimental correlation presented in the current work can be used as a tool for the evaluation of surface tension for high viscosity liquids such as prepolymers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1842–1846, 2007

Key words: surface tension; drop weight; viscosity; drop shape; calibration curves

INTRODUCTION

Highly viscous fluids, such as prepolymers, are used for various applications as adhesives and matrices for composites during their processing stage. In these applications, surface tension of the prepolymers is of great importance, affecting the composites processing and the final product properties. Despite its importance, insufficient attention has been given to the effect of the liquid viscosity on the measurement of its surface tension. In principle, surface tension, being a thermodynamic property, is independent of viscosity. However, the processes occurring during surface tension measurements, such as detachment from an orifice, which are viscosity dependent, may affect the resulting surface tension measurement.

Surface tension of liquids can be readily measured by various common methods, such as maximal bubble pressure, drop weight (WDM), drop profile (DPM), selected planes (SPM), Du-Nuouy ring and Wilhelmy plate.[1] The WDM was chosen owing to its simplicity and suitability in industrial practice. This method is based on Tate's law[1]:

$$W_T = 2\pi r\gamma, \tag{1}$$

where W_T is the ''ideal'' drop weight, γ is the surface tension, and r is the radius of the contact circumference between the drop and the capillary tip. The actual, measured weight, W, is lower than W_T, since only part of the drop detaches from the capillary tip. Therefore, it is customary to use a correction shape factor, f, such that $W = fW_T$. Harkins and Brown[2] concluded that f is a function of the dimensionless ratio r/a, or alternatively, $r/V^{1/3}$, where a is the capillary constant, and V is the drop volume. Lando and Oakley[3] analyzed the experimental results of Harkins and Brown[2] and developed a correlation of a shape factor defined as $F = 1/2\pi f$ with $x = r/V^{1/3}$ as follows:

$$F = 0.14782 + 0.27896x - 0.166x^2 \tag{2}$$

Based on eq. (2), in the x value range relevant to the present work, the following expression for f was calculated:

$$f = 0.7688x^2 - 1.0496x + 0.98707 \tag{3}$$

During detachment, the residual drop size is governed by fluid mechanics.[4] Zhang[5] described a drop formation as a two stage process. The first stage is the drop growth resulting from the continuous addi-

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tion of liquid. The second stage corresponds to a neck formation at the top of the drop followed by detachment of the drop from the nozzle or tube tip. Therefore, it is expected that the residual drop size will depend on the fluid viscosity and density.

Zhang[5] studied and simulated the drop formation process, considering also the liquid viscosity, and compared with experiments of 2-ethyl-1- hexanol dripping into water or water dripping into air. According to Zhang's model, an increase of the viscous force relative to the capillary force causes a longer thread of liquid prior to detachment. Jho and Carreras[6] studied the hydrodynamic effect in drop evolution, investigating the role of viscosity on this effect. For this purpose, they measured the drop weight of various liquids, including silicone fluids and polyethylene glycol (PEG), with viscosities in the range of 0.01–1 Pa s. They considered mainly the dripping rate effect, and used, however, the shape factors that were found and published by Harkins and Brown for low viscosity liquids. Retsos et al.[7] measured the surface tension of polymer melts, including polystyrene, polyisoprene, and their blends, using the drop weight method, but did not consider the effect of viscosity.

Cerpa-Gallegos et al.[8] developed a new methodology to measure surface tension, that combining measurements of the weight and a shape parameter of pendant drops evolving at the tip of a capillary tube. They tested solutions of high molecular weights polymers and showed high dependency and correlation with molecular weight and concentration. Nevertheless, they did not consider directly the viscosity, and their methodology is based on the assumption that practically the total mass of a drop detaches from the capillary tip.

Since the effect of viscosity on the drop weight method is complex and not entirely understood, the objective of this communication is to present an empirical approach for evaluating the surface tension of high viscosity liquids, based on calibration curves of known liquids with similar surface tensions but different viscosities. The results are compared with earlier correlation of Oakly and Lando.[3]

EXPERIMENTAL

To evaluate the f factor of liquids of various viscosities, liquids of a wide range of viscosities for a given surface tension were required. Polydimethylsiloxanes (PDMS) of various molecular weights (MW) (analytical grade, Aldrich), with viscosities in the range of 0.02–10 Pa s were selected. The surface tensions and viscosities of the various PDMS and low viscosity liquids are shown in Table I. The viscosities were measured by a Brookfield viscosimeter DV2,

TABLE I
Viscosity, Surface Tension, Drop Weight, and Parameters Related to the Drop Weight Method of the Studied Liquids

Liquid	Viscosity η (mPa s)	MW	Surface tension γ^a (mJ/m^2)	Drop weight W (mg)	$r/V^{1/3}$	Shape factor f	Standard deviation for f
Heptane	0.4	–	20.14 [10]	8.2	0.437	0.64	0.041
DMF	0.79	–	37.3 [9]	16.6	0.384	0.69	0.016
Water	0.89	–	72.2 [9]	33.7	0.31	0.73	0.007
DMSO	1.98	–	43.6 [9]	18.7	0.389	0.67	0.001
Ethylene glycol	16.1	–	48 [9]	21.4	0.373	0.69	0.001
PDMS (10 cst)	31.8	1,000	19.4 [11]	8.1	0.489	0.63	0.002
PDMS (50 cst)	50.2	3,780	20.3 [11]	8.4	0.485	0.65	0.004
PDMS (100 cst)	9.3	5,970	20.4 [11]	8.5	0.483	0.66	0.003
PDMS (500 cst)	501	17,250	20.7 [11]	9.4	0.469	0.73	0.006
PDMS (1000 cst)	842	28,000	20.7 [11]	9.8	0.463	0.76	0.034
PDMS (10000 cst)	10,800	62,700	20.8 [11]	10.5	0.452	0.82	0.074

MW data were obtained from Sigma-Aldrich.
^{a} Data were retrieved from Refs. 9–11.
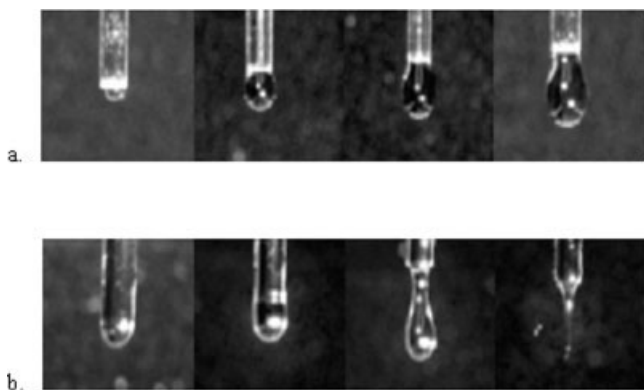
Figure 1 Drop evolution process. (a) Water (b) PDMS 10 Pa s.

while the surface tensions values were retrieved from literature.[9–11] The surface tensions of the different MW PDMS were calculated based on the following correlation of surface tension with MW of homologous series (eq. 4) described by Wu,[12] while the values for the constants of the equation were taken from Ref.[11]:

$$\gamma = \gamma_{\infty} - k/M_n^{2/3} \qquad (4)$$

where γ_{∞} is the surface tension at infinite molecular weight (20.9 mJ/m^2 for PDMS), and k is a constant (154 for PDMS), M_n is the number average molecular weight.

It can be seen from Table I, that for PDMS MW of 3780 (viscosity of 0.05 Pa s) and up, the change of surface tension is negligible. Therefore, the PDMS

liquids of viscosity ≥0.05 Pa s are considered as liquids of similar surface tension.

To evaluate the f factor for several liquids of known surface tension by the drop weight method, a quartz glass capillary, 20 mm long, 1.000 mm inner diameter, and 3.001 mm outer diameter was used. The diameters were measured by Mitotoyo Cordinate Measuring Machine (CMM), model EURO-C-A122010, with accuracy of 0.001 mm. The liquid was fed into the capillary through a funnel made of quartz glass. The funnel used for the low viscosity liquids was equipped with a valve and the dripping rate was set to ≤ 1 drop/min. According to the reported results of Harkins and Brown,[2] the said rate is low enough to minimize hydrodynamic effects, so that Reynolds number and capillary number effects on the measurements are negligible. Each reported result is an average value of 10 drops that dripped into a beaker, and weighed using an analytical balance (±0.02 mg).

RESULTS AND DISCUSSION

The process of drop formation and growth until a fraction of a second before detachment is shown in Figure 1. It can be seen that during the first stages, the shape of the growing drops is similar for both low- and high-viscosity liquids. They are different in their detachment kinetics, which most probably affects the detached drop volume. The high-viscosity drop forms a long neck that seems to contain a large fraction of the drop volume [Fig. 1(b)]. The low-viscosity drop develops a neck too rapidly to be captured by a normal video camera; however, based on
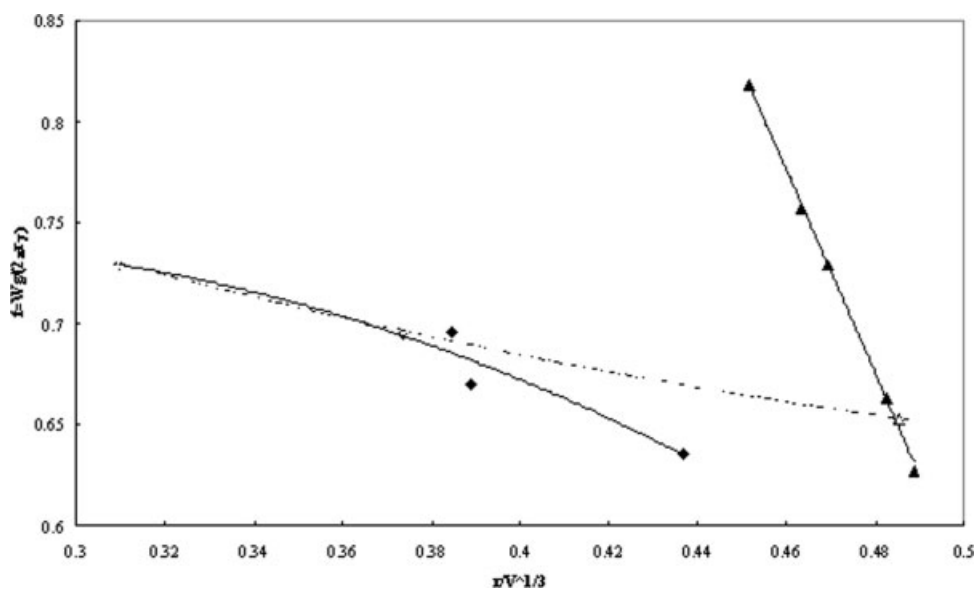
Figure 2 Correction factor for low- and high-viscosity liquids as a function of drop size. ◆ Low-viscosity liquids; ▲ high-viscosity liquids. The full lines represent the best fit of the experimental data to eqs. (5) and (6). The dashed line represents eq. (3).
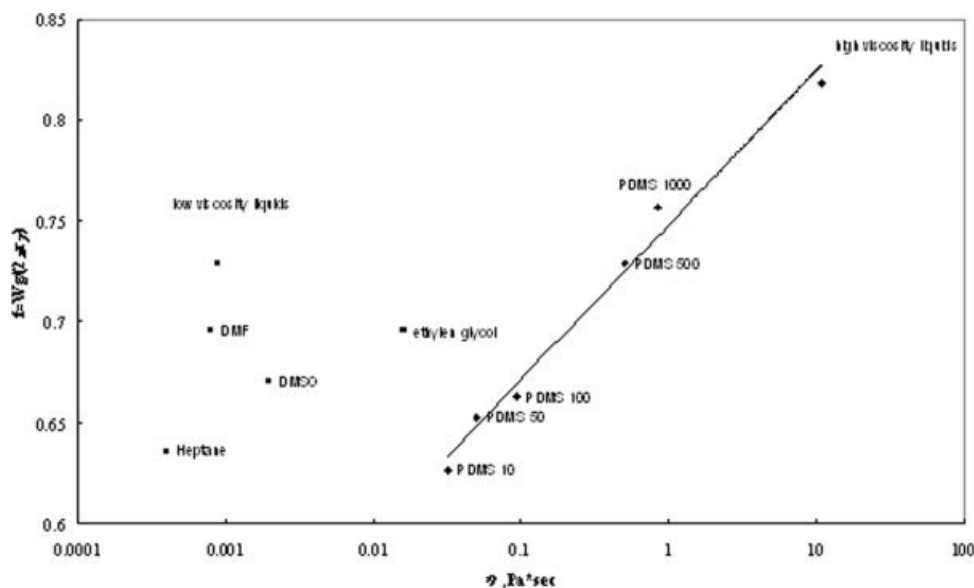
Figure 3 Correction factor for low- and high-viscosity liquids as a function of viscosity.

the results shown below this neck is much smaller than for the high-viscosity liquid.

Table I depicts the measured drop weights and $r/V^{1/3}$ values as well as the shape factors and their standard deviation for the tested liquids. Shape factor values are calculated according to the definition of f in the introduction. The standard deviations are very small, pointing the good consistency and accuracy of the results.

For low viscosity liquids, the calculated shape factor values were in the range of 0.63–0.73. For the high viscosity PDMS, up to 10 Pa s, the shape factor value was found to be higher, up to 0.79. The higher value of the shape factor is related to the larger measured drop size.

As shown in Figure 2, the present experimental data for viscosities up to 0.016 Pa s can be very well correlated by the following empirical relationship:

$$f = -3.027x^2 + 1.5169x + 0.5494 \qquad (5)$$

where $x = r/V^{1/3}$. The slight deviation of some experimental points is restricted to a very narrow range of f and can result from sensitivity to operator's skill.[2]

For comparison, Figure 2 also shows that eq. (3) fits the present data, but only for low $r/V^{1/3}$ values. However, it can be readily seen in Figure 2 that the f values for the high viscosity liquids do not fit eq. (5). Thus, the results for low- and high-viscosity liquids cannot be fit by a single curve. In other words, f is not a unique function of $r/V^{1/3}$. The results for the high viscosity liquids can be correlated with $r/V^{1/3}$, using, however, the following function that is very different from eq. (5):

$$f = 43.825x^2 - 45.276x + 12.302 \qquad (6)$$

Moreover, Figure 3 demonstrates a strong dependence of f on viscosity, for the high- viscosity liquids. For these liquids, the shape factor correlates linearly with the logarithm viscosity.

$$f = 0.0266 \ \ln \ \eta + 0.729 \qquad (7)$$

For the low viscosity liquids, no unique correlation with viscosity could be found. It is interesting to note that the shape factor for two different nature materials, heptane and low viscosity PDMS, is similar. This indicates that although the measurements were conducted only for one series of high viscosity liquids, the viscosity effect is valid, and should be considered for a wider range of materials.

SUMMARY

A simple easily applied experimental method, of satisfactory accuracy, for evaluation of surface tension and shape factor of liquids having wide range of viscosities, was presented.

The present results indicate that the shape factor is, in general, a function of both, $r/V^{1/3}$ and η. For low-viscosity liquids, the shape factor is only a function of $r/V^{1/3}$ as was reported earlier by several authors, while for liquids with viscosity higher than 0.05 Pa s, the dependence of f on viscosity must be accounted for; f of high viscosity liquids was found to correlate linearly with the logarithm of viscosity.

Therefore, the viscosity correction is important especially when the surface tension of higher viscos-

ity liquids, such as prepolymers, or solutions of prepolymers in low molecular weight organic molecules, is studied.

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