A New Method to Determine Simultaneously Density and Surface Tension of Polymeric Liquids Including Reactive Systems

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INTRODUCTION

The surface (interfacial) tension of polymeric liquids is an important thermodynamic parameter that plays a decisive role in many technological processes, such as wetting, printing, painting or bonding. For example, the surface tension can be regarded as the "driving force" of wetting and levelling of powder coatings[1], and the adhesive strength between polymers and lacquers is related to their interfacial tension.[2] However, only very little reliable surface tension data are available. One reason is the fact that technical systems are complex multicomponent systems (binder, hardener, additives, pigments) which cause difficulties in surface tension measurements. In addition, high viscosities and limited thermal stability in the case of polymer melts as well as reactive systems cause also several difficulties in the experimental determination of their surface tension. Thus, sophisticated measuring techniques are needed.

Using drop shape methods, the surface tension is obtained directly. However, since gravity influences the drop shape as well, one has to know the density of the polymeric liquids, often at elevated temperatures. Usually, it has to be evaluated separately by time-consuming methods of dilatometry. By employing a new strategy, we could show that axisymmetric drop shape analysis (ADSA) can be applied to determine simultaneously the density and surface tension of polymeric melts from sessile drops.[3-5] With respect to the measuring technique, a high-temperature chamber whose temperature could be precisely controlled and a sample holder that allowed the formation of highly axisymmetric sessile drops at elevated temperatures were developed.

Results will be reported regarding the influence of additive properties, like molecular weight and chemical compositions, on the surface tension of a typical epoxy binder and, for the first time, the influence of hardener on the surface tension of an epoxy resin representing a reactive system.

AXISYMMETRIC DROP SHAPE ANALYSIS - BASIC PRINCIPLES AND MODIFICATION FOR DENSITY DETERMINATION

Drop shape methods are based on the idea that the shape of a sessile or pendant drop is determined by a combination of surface tension and gravity effects. When gravitational and surface tension effects are comparable, it is possible, in principle, to determine the surface (interfacial) tension from the measurement of the shape of a drop. In the past, the precision of drop shape methods was strongly dependent on the measurement of some selected critical points of the drop shape which had to be interpreted using different sets of tables.[6,7] By means of this classical calculation procedure accurate and consistent results are difficult to obtain. Recent developments utilize video digital image processing techniques to extract the entire experimental drop profile with subsequent numerical procedures to calculate the surface (interfacial) tension based on the Laplace equation of capillarity.[9-14] The surface tension measurements of polymeric liquids using drop shape methods are typically based on pendant drop experiments, both in the older, e.g.[15] as well as in the recent literature, e.g..[16,17] There are, in essence, two reasons for using pendant rather than sessile drops. Generally, perfect axisymmetry can be realized more easily for pendant than for sessile drops. Additionally, some of the computer based approaches are limited to pendant drops.[9,10]

In our study, axisymmetric drop shape analysis (ADSA), an approach started by Rotenberg et al.,[11] was used. This nu-

merical procedure unifies both methods of sessile drops and of pendant drops. In a previous study,[3] it was shown for polystyrene that sessile drops can be used to determine the surface tension of polymer melts interchangeably with pendant drops. The strategy employed is to fit the shape of an experimental drop to the theoretical drop profile according to the Laplace equation of capillarity using a least-square algorithm with surface (interfacial) tension as one of the adjustable parameters: γ is the surface (interfacial) tension; R_1 and R_2 are the principal radii of curvature of the drop; ΔP is the pressure difference across the curved interface. ADSA requires the local gravity, the densities between the liquid and fluid phases and several arbitrary but accurate coordinate points selected from the drop profile as input parameters.

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \qquad (1)$$

However, determination of the density of a polymeric liquid, especially a polymer melt, is not a trivial task. Therefore, the ADSA algorithm was modified in such a way that the density would be replaced by the mass of the drop as input parameter.[3-5] Conceptually, this was readily feasible, since the ADSA algorithm also yields the volume, so that the density became output rather than input. The mass of a sessile drop is available through weighing the polymer granulate before and after the experiment at elevated temperatures, which is difficult for pendant drops since some of the polymer material is inside the capillary from which the drop is hanging down. Therefore, from the experimental perspective, use of a sessile rather than a pendant drop is required. Figure 1 shows schemes of two experimental setups for elevated temperatures, which contains
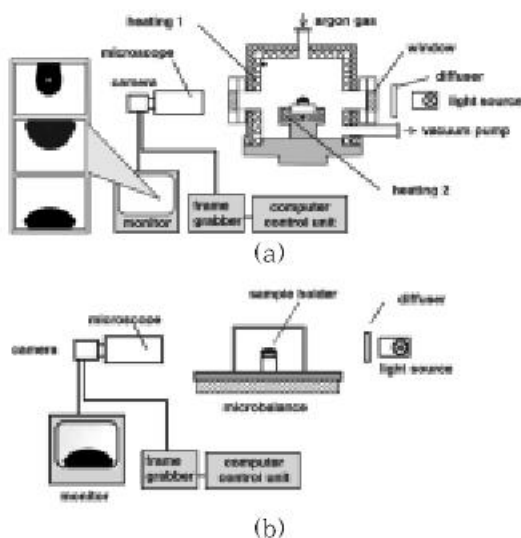
(a)

(b)

Figure 1. **Scheme of two experimental setups for surface tension measurements using sessile liquid droplets: (a) high-temperature apparatus to measure the density and surface tension of polymer melts; (b) setup to measure the density and surface tension of polymeric liquids and mixtures at room temperature.**

Figure 2. **A typical image of a sessile drop (DER 664 UE at 166 ℃) on top of a stainless-steel cylinder reproduced by a laser printer. From this profile, ADSA determines the surface tension to be 38.14 ± 0.26 mJ/m².**

a high-temperature cell (Figure 1a), and for room temperature measurements where a microbalance was integrated to register the weight of the sessile liquid droplet during the experiment (Figure 2b).

Surface tension measurements with sessile drops require, apart from good axisymmetry, relatively large contact angles. Hence the underlying substrate has to be very smooth and homogeneous (for good axisymmetry) and, if possible, should be hydrophobic (to prevent spreading). At high temperatures of the experiment it is certainly not an easy task to find such a material. To overcome these difficulties a different strategy was employed: the sessile drops were formed by putting polymer granulates or droplets on the top of a small stainless-steel cylinder (h=10 mm, ∅=5 mm). If the mass of the polymer is chosen properly, it will spread to the

edge of the cylinder but not beyond. Hence the drop will be axisymmetric (due to the axisymmetry of the cylinder) and, due to the barrier effect of the edge, can have a conveniently large contact angle.

From a practical perspective another aspect becomes relevant: In conventional sessile drop experiments with flat and smooth surfaces the camera is slightly tilted out of the horizontal in order to create a drop "tip" or cusp in the apparent profile at the point of contact with the solid. Thus, the baseline of the drop can be detected much easier. However, if a cylinder is used as a substrate, tilting the camera would be meaningless. Therefore, in order to get a "tip" in the apparent profile as well, the design of our cylinders was improved: The upper part of the cylinder was made cone shaped. In this way, the image of a sessile drop on top of this cylinder looks similar to the conventional case with a reflection of the drop on a flat and smooth surface ($\theta < 90°$). A typical image is shown in Figure 2.

Figure 3 shows the density results for a typical sessile drop experiment using DER 664 UE (DOW, Germany), an epoxy resin based on bisphenol-A with a molar mass of
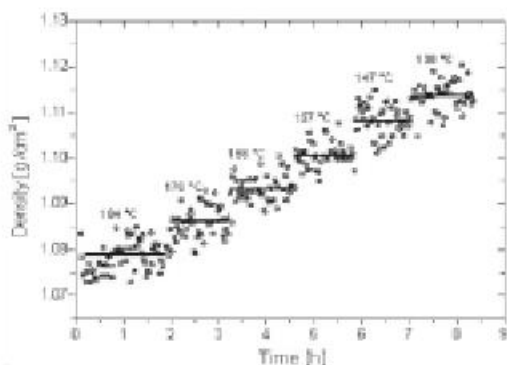
Figure 3. Density vs. time for a sessile drop experiment using the epoxy resin DER 664 UE. The error bars are the 95% confidence limits calculated from ADSA for each image. The bold lines are the mean densities at a specific temperature.
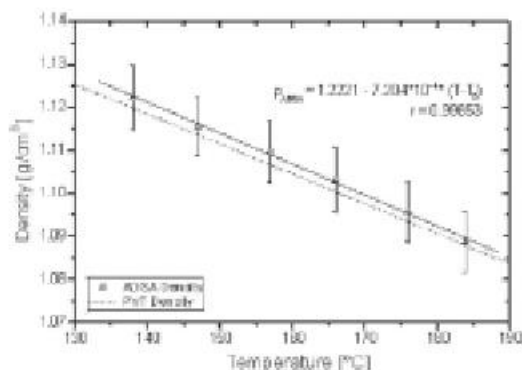

Figure 4. Density vs. temperature for sessile drop experiment with epoxy resin DER 664 UE in comparison with PVT densities. The error bars are the 95% confidence limits calculated for six experiments. T_0 = 273.15 K.

M_w = 2000 g mol^{-1}. Typically, about 20 mg of the polymer were used for one experiment. The densitiy values were averaged to obtain the density at a specific temperature. In Figure 4, the mean densities are plotted as a function of temperature together with PVT density. The calculation of the temperature dependent density from PVT data requires additionally the density at room temperature, which can be measured, e.g., with a helium pycnometer.[cf. 18] ADSA and PVT measurements yield comparable results. Moreover, there is actually no difference in surface tension values, if calculated with ADSA or with PVT density. For instance, at 147 ℃ the surface tension of the epoxy resin calculated with PVT density would be 39.59 mJ/m^2 (sessile drop) instead of 39.68 mJ/m^2 when calculated with ADSA density. The advantage of ADSA is that only a single experiment is required for the determination of both surface tension and density. Furthermore, the ADSA density measurement does not, unlike the PVT measurement, require a reference density. It is therefore an absolute method.
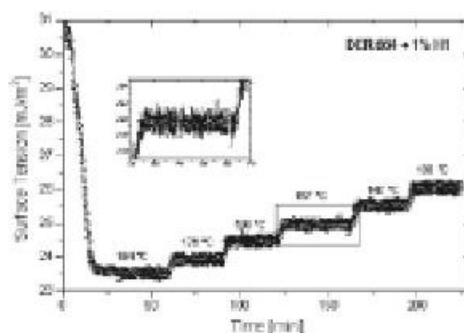

Figure 5. A plot of surface tension vs. time for a typical sessile drop experiment of an epoxy resin (DER 664) containing 1% of a levelling additive (homopolymeric acrylate H1).

SURFACE TENSION MEASURMENTS

Figure 5 shows the surface tension results for a typical sessile drop experiment of the epoxy binder containing an additive (DER 664 + 1% of a homopolymeric acrylate H1). The experiments were started at 184 ℃. During the heating of the chamber, the surface tension decreased
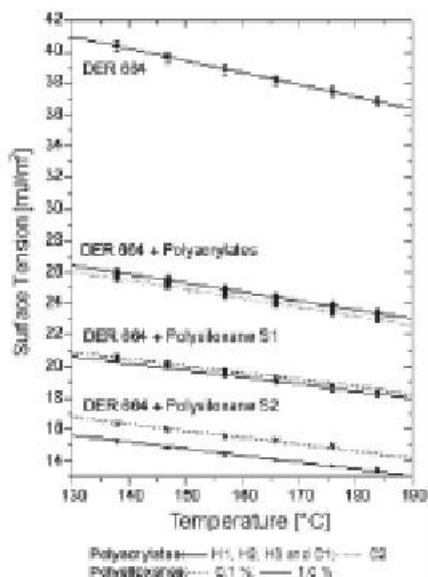
Figure 6. **A plot of surface tension vs. temperature of the pure epoxy resin, and additive containing mixtures. The error bars are the 95% confidence limits from six runs for each mixture.**

rapidly and then reached a constant value. When the temperature was lowered, the surface tension first increased and again reached a constant value. Constancy of the surface tension at each temperature indicates that no thermal degradation took place (see the insert in Figure 5). Thus, these values were averaged to obtain the equilibrium surface tension at each temperature. The error bars shown are the 95% confidence limits calculated by ADSA for each image.

In Figure 6 plots of the surface tension vs. temperature of the the pure epoxy resin and of additive containing mixtures are shown. It is evident, that all additives decreased the surface tension of the epoxy resin considerably. The degree of the decrease depends on the type of the additives: the surface tension values of the polysiloxane systems were much lower than those of the polyacrylate systems. Furthermore, the difference between the two polysiloxanes was more pronounced than the differences between the polyacrylates.

With respect to film formation of powder coatings, the above surface tension results suggest some interesting differences in the performance of the polyacrylate or polysiloxane additives. As is well known, low surface tension of a coating improves wetting, while higher values improve levelling. Thus, if wetting of the substrate is a problem, polysiloxanes should be advantageous. On the other hand, the low surface tension values caused by the polysiloxanes have an adverse effect on levelling. Therefore rougher or wavier films should result compared to the polyacrylate systems ("orange peel" effect). This drawback of the polysiloxanes is probably part of the reason, why predominantly polyacrylates are used for powder coatings.[19] Nevertheless, in contrast to the polyacrylates, small modifications in the structure of the polysiloxanes lead to large differences in surface tension. Hence, the use of these materials seems to be promising for future developments of levelling additives for powder coatings. That is, to synthesize "suitable" modifications (e.g., with higher surface tensions) in order to improve the performance and to extend the applicability of powder coatings.

The effect of low molecular additives was studied in simple non-reactive, epoxy resin systems. There is still a lack of knowledge of the surface tension of epoxy-amine cross-linked systems. Curing of epoxy resins is one of the most common procedures of thermosetting materials. Because of their excellent mechanical and thermal properties, epoxy networks are used in a wide range of applications covering composite materials, adhesives, coatings, materials for encapsulation, etc.

The aim of a present study is, therfore,

Table 1. Surface tension and density values for separated components

N	System	Mean value of surface tension, mJ/m^2	95% CL	Mean value of density, g/cm	95% CL
1	HT 2, epoxy resin	44.9	0.69	1.11	0.01
2	HT 2a, hardener	36.1	0.28	0.97	0.01

The 95% CL confidence limits (CLs) were obtained by averaging over eight different drops (experiments)
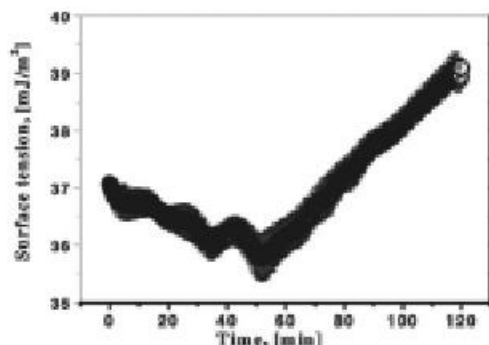

Figure 7. A plot of the surface tension vs. time for the reactive mixture HT2/ HT2a during curing reaction under air. The curve shown is an averaged curve from eight parallel sessile drop experiments.

the investigation of the bulk and surface properties of reactive systems of epoxy-amine cross-linked materials with different degree of reactivity during cross-linking reaction. For this purpose we have used FT-IR spectroscopy, viscosity measurements, and surface tension measurements. To study systematically the time dependence of the surface tension during the cross-linking reaction we have utilized the constrained sessile drop configuration in conjunction with axisymmetric drop shape analysis (ADSA) shown in Fig. 1b. The mean surface tension and density values of the separated components are summarized in Table 1. All surface tensions values were calculated with the real measured densities from the sessile drop experiments. HT2 (R&G Faserverbundwerkstoffe GmbH, Germany) is an epoxy resin based on bisphenol-A with a molecular weight of

M_w = 700 g/mol. (>50%) and epoxy derivate components (<50%). HT2a is a hardener based on isophorondiamin (>50%), benzyl-alkohol (<50%) and nonylphenol (<5%).

The surface tension of the reactive mixture HT2/ HT2a was monitored during the first 2 hours of curing reaction. Figure 7 shows the surface tension alteration as a function of curing time as an averaged curve obtained from eight parallel sessile drop experiments of epoxy-amine reactive mixtures HT2/ HT2a. Further experiments under different environments are presently carried out to explain the time-dependent alteration of the surface tension.

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