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Document status and date:
Published: 01/01/1990

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Link to publication

# The measurement of interfacial tension in polymer/polymer systems: The breaking thread method

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## Synopsis

When blending incompatible polymers in the melt, the resulting morphology is strongly dependent on the interfacial tension. One stage of the mixing process is now used to determine this interfacial tension: in the absence of an overall flow field, extended liquid threads in a liquid matrix exhibit sinusoidal disturbances which cause the threads to disintegrate into lines of droplets. From the growth rate of these disturbances, the interfacial tension between the thread phase and the matrix phase is calculated. For molten polymers, this so-called "breaking thread method" is relatively fast and simple since it does not require density data for the two phases. Upon addition of a diblock copolymer to the thread phase, a considerable decrease in interfacial tension is measured.

## INTRODUCTION

To attain a polymeric material with specific properties, often a blend is made of different, mostly incompatible, polymers. During the mixing process of incompatible polymers in the molten state, the interfacial tension between the liquid phases is of major influence on the development of the blend morphology (Elmendorp, 1986a). Since the material properties are dependent on this morphology, it is important to have a method for measuring the interfacial tension between polymer melts. In the present paper, one stage of the mixing process of incompatible polymers is in fact used to measure the interfacial tension.

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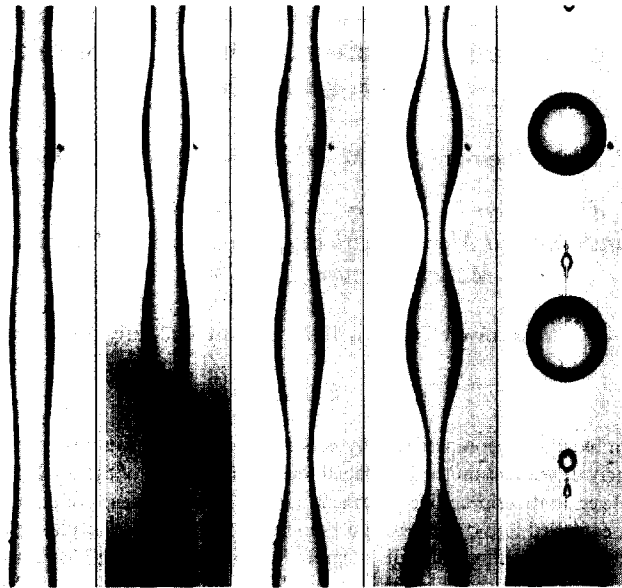[a]Present address: DSM Research, P. O. Box 18, 6160 MD Geleen, The Netherlands.

FIG. 1. Sinusoidal distortions on a nylon (PA-6) thread, with diameter 55 $\mu$m, embedded in a polystyrene (PS 638) matrix. The measurement was performed at 230 °C; the times at which the subsequent photographs were taken are: $t = 0$, 15, 30, 45, 60 s.

It is known that during the mixing of two incompatible fluids, e.g., in a shear flow, droplets are highly extended into long threads. Upon cessation of the flow, these liquid threads exhibit sinusoidal distortions which finally cause the threads to break up into a number of smaller droplets (see Fig. 1 ). By analyzing this process of disintegration of a liquid thread in a liquid matrix, it is possible to determine the interfacial tension between the two liquid phases. This so-called "breaking thread method" is only applicable if no yield stresses are present and if both fluids have a loss angle of 90° as the shear rate approaches zero.

Chappelear (1964) was the first who applied this method for measuring the interfacial tension between some polymer melts. Unfortunately, his experimental error was considerable since his zero shear rate viscosity was obtained by extrapolating data from a capillary viscometer into the low shear rate region. Today, a proper determination of the zero shear rate viscosity significantly contributes to the accuracy of the method.
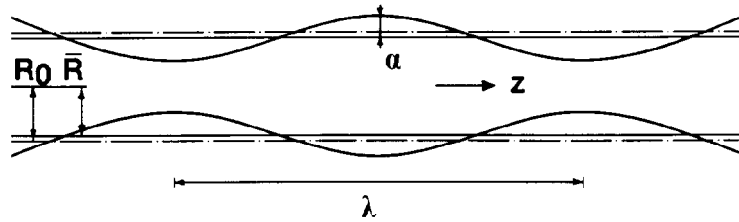
FIG. 2. Sinusoidal distortions on a liquid cylinder (Elmendorp, 1986b), where the radius $R(z) = \bar{R} + a\sin(2\pi z/\lambda)$ and the average radius is given by $\bar{R} = (R_0^2 - a^2/2)^{1/2}$. Reprinted with permission of The Society of Plastics Engineers.

In contrast to other methods for measuring interfacial tension, such as a pendent or spinning drop, the breaking thread method does not require data on the density difference between the two phases, which is often difficult to measure with sufficient accuracy. The method is also suitable for systems consisting of polymers with small density differences and for systems with extremely high viscosities where a pendent or spinning drop requires several hours to attain an equilibrium shape.

## THEORETICAL BACKGROUND

Lord Rayleigh (1879) developed a theory for the growth of distortions on viscous jets in air. Tomotika (1935) extended this theory to the breakup of (Newtonian) liquid cylinders in a (Newtonian) liquid matrix for the case in which no overall flow field is present. Initially, a liquid cylinder of radius $R_0$ is subject to very small sinusoidal distortions of, in principle, arbitrary wavelengths $\lambda$ (see Fig. 2). As a consequence of the decrease of the total interfacial area with increasing amplitude (Lord Rayleigh, 1879), only distortions with a wavelength larger than the original circumference of the cylinder grow. Defining the dimensionless wave number $X$ by

$$X = \frac{2\pi R_0}{\lambda}, \tag{1}$$

means that only distortions with $X < 1$ grow.

All amplitudes $a$ grow exponentially with time $t$,

$$a = a_0 e^{qt}, \tag{2}$$

where the growth rate $q$ is given by

$$q = \frac{\sigma \Omega(\lambda, p)}{2\eta_c R_0},$$  (3)

with

$\alpha_0 =$ original amplitude (m),

$\sigma =$ interfacial tension (N/m),

$\eta_d =$ viscosity of the disperse (thread) phase (Pa s),

$\eta_c =$ viscosity of the continuous (matrix) phase (Pa s),

$p =$ viscosity ratio $(\eta_d/\eta_c)$,

$\Omega(\lambda, p) =$ a tabulated function [Tomotika(1935)].

For a given viscosity ratio $p$, there will be one dominant wavelength $\lambda_m$, at which the amplitude grows fastest; the distortion having this wavelength consequently causes the thread to break up into droplets. The dominant wave number $X_m(=2\pi R_0/\lambda_m)$ and its corresponding value $\Omega_m$ are graphically presented as a function of the viscosity ratio (Fig. 3).

For an incompressible fluid and assuming that no satellite droplets are formed, the radius $A$ of the newly formed droplets can be calculated from the original thread radius and the dominant wave number (Chappelear, 1964)

$$A = R_0(1.5\pi/X_m)^{1/3}.$$  (4)

For example, if $p = 1$, then $X_m = 0.56$ and thus $A = 2.0 \, R_0$.

Knowing the growth rate $q$ of a distortion, the breakup time $t_b$ can be derived from Eq. (2),

$$t_b = \frac{1}{q} \ln(\alpha_b/\alpha_0),$$  (5)

where $\alpha_b$ is the amplitude at breakup $(\alpha_b = 0.81 \, R_0)$. This theoretical value of $\alpha_b$ is based on the fact that for sinusoidal waves the smallest diameter of the thread reaches zero when the amplitude $\alpha$ equals the average thread radius $\overline{R}$ (Elmendorp, 1986a).

To calculate the breakup time, one has to estimate the original amplitude $\alpha_0$. Kuhn (1953) derived an expression for $\alpha_0$, based on fluctuations of the interface caused by Brownian motion
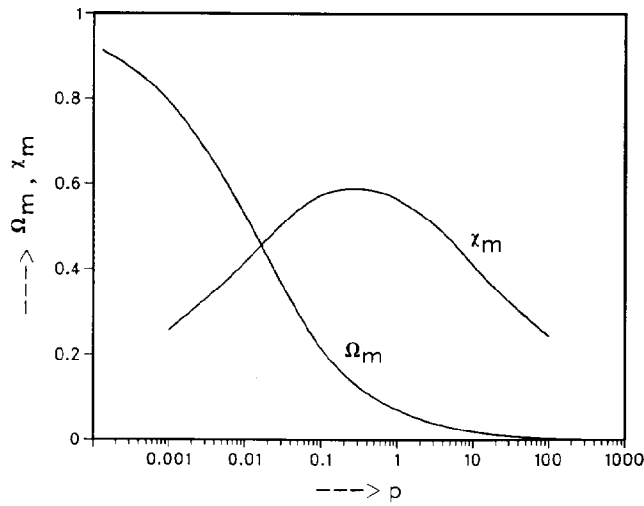
**FIG. 3.** Dominant wave number $X_m$ and its corresponding growth function $\Omega_m$ as a function of the viscosity ratio $p$ (Elmendorp, 1986b). Reprinted with permission of The Society of Plastics Engineers.

$$a_0 = \left( \frac{21kT}{8\pi^{3/2}\sigma} \right)^{1/2}, \tag{6}$$

where $k$ is the Boltzmann constant and $T$ the absolute temperature. Distortions with an amplitude of $a_0$ are always present on a fluid cylinder; they are the smallest possible perturbations. For a polymer thread in a polymer matrix, assuming $R_0 = 1$ $\mu$m, $\sigma = 5 \times 10^{-3}$ N/m, and $T = 473$ K, this means that the relative distortion $a_0/R_0 = 0.0004$. However, measurements of the amplitude can be started only from $a_0/R_0 \geqslant 0.1$ since smaller amplitudes are not visible. Substitution of $q$, $a_b$, and $a_0$ in Eq. (5) yields

$$t_b = \frac{\eta_c R_0}{\Omega_m \sigma} \ln(1.39\sigma R_0^2/kT). \tag{7}$$

This expression for the total breakup time of a liquid cylinder at rest is not tested in the present paper; only Eqs. (2) and (3), which concern the growth rate, are necessary to determine the interfacial tension. However, from Eq. (7) the typical time scale of the experiments can be

TABLE I. Zero shear rate viscosity $\eta$ and corresponding loss angle $\delta$ of the homopolymers used in the interfacial tension measurements.

| Material code | $T$ (°C) | $\eta$ (Pa s) | $\delta$ (deg) |
|---|---|---|---|
| HDPE (DSM): | | | |
| Stamylan 7058 | 200 | 1800 | 90 |
| Stamylan 7058 | 230 | 1590 | 90 |
| Stamylan 7359 | 200 | 250 | 90 |
| LDPE (BP Chem.): | | | |
| BP 33 | 190 | 83 000 | 90 |
| PS (DOW Chem.): | | | |
| Styron 638 | 200 | 1400 | 90 |
| | 230 | 1000 | 90 |
| PS (BP Chem.): | | | |
| HH 101 | 190 | 31 200 | 88 |
| PA-6 (BASF): | | | |
| B 3 | 230 | 425 | 90 |

estimated. Using $\eta_d = \eta_c = 1000$ Pa s (yielding $p = 1$ and consequently $\Omega_m = 0.1$), $\sigma = 5 \times 10^{-3}$ N/m, and $T = 473$ K, threads of diameters $D_0 = 0.1, 1, 10,$ and $100 \,\mu$m will break up after, respectively, $t_b = 1, 12, 170,$ and $2000$ s.

## MATERIALS

The materials used in the experiments were high and low density polyethylene (HDPE and LDPE), polystyrene (PS), and nylon (PA-6). The rheological properties were measured by a Rheometrics Mechanical spectrometer (RMS-2) and are listed in Table I. For all materials given in this table, the loss angle $\delta$ is close to 90°, implying Newtonian behavior during the experiments.

## EXPERIMENTAL PROCEDURE

Threads of the desired polymer are spun, e.g., from a melt-index apparatus, from a single screw extruder, or simply from a molten granule on a hot plate. A typical thread has a diameter of 20 $\mu$m and a length of 10 mm. After 24 h at 80 °C, the thread is placed (at room temperature) between two films of the second polymer, each with dimensions $10 \times 10 \times 0.6$ mm. The system is enclosed between two glass sheets, placed under an optical microscope (Zeiss) in a Mettler FP2 hot
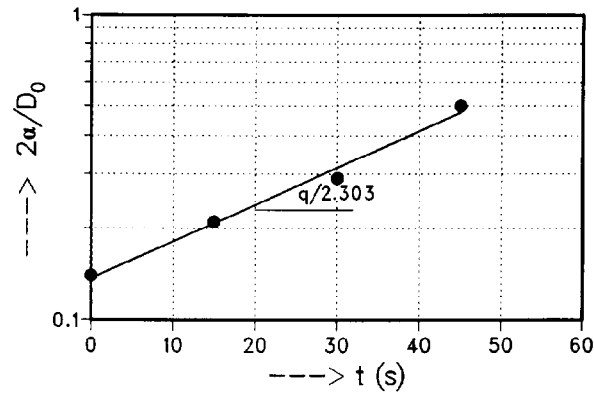
**FIG. 4.** Plot of the relative amplitude $(2\alpha/D_0)$ vs time, from the experiment shown in Fig. 1. Experimental and theoretically dominant wave number: $X_{\mathrm{expl}} = 0.6$; $X_m = 0.61$.

stage, and brought to the desired temperature. Care is taken that no pressure is exerted on the system, to avoid deformation of the thread. Then, in the molten state, distortions start to grow at the interface.

At a given position of the thread, the distortion is photographed at regular intervals of time (see Fig. 1). As long as the distortion remains sinusoidal, its amplitude $\alpha$ can be obtained from the expression

$$\alpha = \frac{b - a}{4}, \tag{8}$$

where

$a$ = the smallest diameter,

$b$ = the largest diameter.

According to Eq. (2), the growth rate $q$ of the distortion can be calculated from the slope of the line, obtained by plotting $\log(2\alpha/D_0)$ against time, where $D_0$ is the original thread diameter. The time $t = 0$ may just coincide with the first measurement. A typical plot is shown in Fig. 4.

From Eq. (3) and Fig. 3, the interfacial tension $\sigma$ can now be calculated:

$$\sigma = \frac{q\eta_c D_0}{\Omega_m}. \tag{9}$$

**TABLE II.** Interfacial tension (experimental and reference data) between some incompatible homopolymers, having zero shear rate viscosities $\eta_{d,c}$. The first three reference data were taken from Wu (1979); the last value was obtained from Elmendorp (1986a) and was measured at 250 °C.

| Thread phase | Matrix phase | $T$ (°C) | $\eta_d$ (Pa s) | $\eta_c$ (Pa s) | $p$ | $X_{\text{expt}}$ | $X_m$ | $10^3\sigma_{\text{expt}}$ (N/m) | $10^3\sigma_{\text{ref}}$ (N/m) |
|---|---|---|---|---|---|---|---|---|---|
| HDPE | PS | 200 | 250 | 1 400 | 0.179 | 0.59 | 0.59 | 4.9 | 4.7 |
| HDPE | PS | 200 | 1 800 | 1 400 | 1.290 | 0.55 | 0.56 | 4.1 | 4.7 |
| PS | LDPE | 190 | 31 200 | 83 000 | 0.375 | 0.55 | 0.59 | 4.3 | 4.9 |
| PA-6 | PS | 230 | 425 | 1 000 | 0.425 | 0.60 | 0.61 | 20.0 | ⋯ |
| PA-6 | HDPE | 230 | 425 | 1 590 | 0.267 | 0.60 | 0.59 | 13.5 | 10.7 |

The experimental wave number ($X_{\text{expt}}$) must be compared to the theoretical one ($X_m$) to give a control on the quality of the experiment.

## RESULTS FOR HOMOPOLYMERS

The interfacial tension between some incompatible homopolymers, measured via the breaking thread method, can be found in Table II. Where possible, reference data taken from the literature are given.

From the results shown in Table II, a few remarks can be made concerning the applicability of the breaking thread method. A straightforward evaluation of the tabulated function $\Omega(\lambda,p)$ is only possible if thread breakup is generated by a distortion having the dominant wavelength $\lambda_m$. It is therefore essential to compare the experimental wavelength to the theoretical one. If these two values are close enough, an accuracy of 10% may be reached. If not, see the third experiment (PS/LDPE), larger errors in the values of the interfacial tension result. In general, if breakup might occur at some wavelength $\lambda$ other than the dominant wavelength $\lambda_m$, the complete graphical representation of $\Omega(\lambda,p)$, covering a range of $10^{-3} < p < 10^2$ and $0.1 < X < 0.9$, as given in Figs. 1 and 2 of Chappelear (1964), might be of help.

To avoid end pinching (Stone and Leal, 1989) or relaxation (see Fig. 5 ), the thread should be highly elongated and have a constant diameter; in the present experiments, the ratio of length to diameter $L/D_0 > 60$. For the same reason, systems with a viscosity ratio $\eta_d/\eta_c \ll 1$ can be expected to give the best results.

The time needed to perform one experiment depends on the viscosities, the filament thickness, and the interfacial tension and may range (using the same thread diameter of 20 $\mu$m) from 50 s (PA-6/PS) to
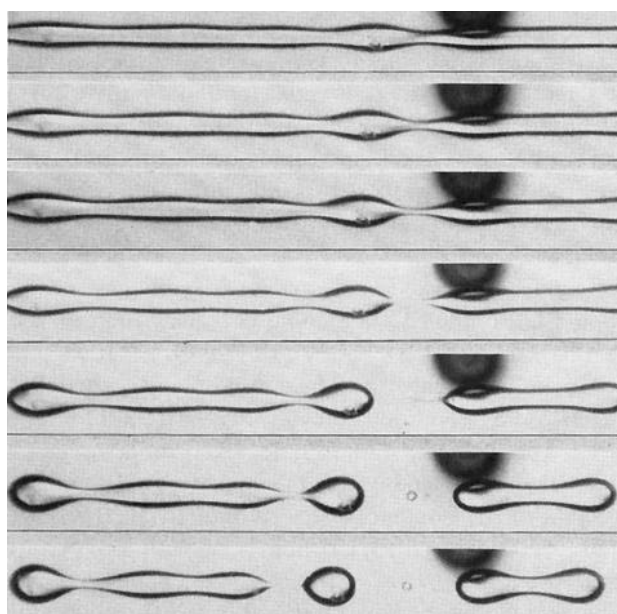
**FIG. 5.** Relaxation and breakup of a HDPE (Stamylan 7058) thread ($D_0 = 20\ \mu m$) in a PS (638) matrix at 200 °C. In this experiment, the time scales for end pinching and Rayleigh waves are comparable, so the experiment does not give a reliable value for the interfacial tension. The photographs were taken at regular time intervals and cover a range of 216 s.

several hours (PS/LDPE). In systems where both polymers are highly viscous, it is therefore desirable to decrease the initial thread diameter as much as possible to accelerate the disintegration process and thus avoid boring experiments and a possible degradation of the polymers.

The theoretical background is in principle only valid in the case of negligible inertia effects. Furthermore, it is restricted to Newtonian liquids. During these slow breakup processes (shear rate $\approx 10^{-3}\ s^{-1}$; Elmendorp, 1986a) it can be assumed that the polymers behave Newtonian. This assumption is confirmed by measurements using the RMS-2, where the loss angle $\delta$ is equal or close to 90° in the zero shear rate regime.

## INFLUENCE OF DIBLOCK COPOLYMERS

Adding a diblock copolymer to a blend of two incompatible polymers results in a reduction of the interfacial tension (Wu, 1979). Also the interfacial tension-driven breakup process of a liquid thread may be retarded in the presence of diblock copolymer at the interface. Here the breaking thread method was used for measuring the effect of adding a diblock copolymer to the model system PS (DOW 638)/HDPE (DSM Stamylan 7058).

The copolymer used was a polystyrene–polyethylene diblock copolymer (PS-b-PE), obtained via anionic polymerization of styrene and butadiene (giving PS-b-PB), followed by hydrogenation of the polybutadiene block. The number averaged molecular weights of the blocks amount to $M_n$ (PS) = 8.5 kg/mol and $M_n$ (PB) = 11.5 kg/mol. All syntheses were performed by W. J. J. de Vet (Eindhoven University of Technology) at the Université Sart-Tilman, Liège (Belgium). The molecular weights of the homopolymers amount to $M_n$ (PS) = 51.2 kg/ mol and $M_n$ (HDPE) = 30.3 kg/mol, both with a polydispersity of about three.

The diblock copolymer was introduced in the thread phase (usually polyethylene) via melt blending, either on a two roll mill or on the extruder from which the thread was spun. The zero shear rate viscosities were slightly increased, upon addition of the diblock copolymer, while the loss angle $\delta$ remained between 85° and 90°.

Figure 6 shows the dependency of the interfacial tension on the amount of diblock copolymer added to the thread phase.

The wavelengths at which breakup occurs are less uniformly distributed along the thread than in the case of only two homopolymers, as was also reported by Rumscheidt and Mason (1962). Therefore, only the measurements with the best agreement between $X_{expt}$ and $X_m$ may be taken into account. From the results, it is clear that the interfacial tension is considerably reduced by small amounts of diblock copolymer ( < 1 wt. %). Further addition does not cause any more significant changes.

Especially for systems with diblock copolymers, there might be a yield stress in the zero shear rate range, which counteracts the driving force for breakup. If a pronounced yield stress is present (order of magnitude > 100 Pa), threads with a diameter > 10 $\mu$m will not break up at all. Because distortions grow in all our experiments, the influence of yield stresses, if present at all, is probably negligible. To verify this assumption for the present polymer system, the interfacial tensions were
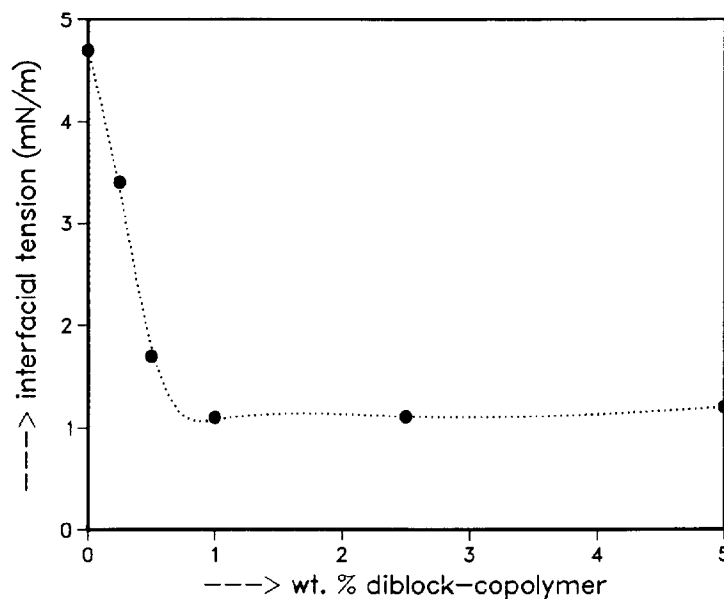
FIG. 6. Interfacial tension between PS 638 (matrix) and HDPE 7058 (thread) vs wt. % diblock copolymer added to the HDPE phase ($T = 200\,°C$).

also determined by a technique (in fact equivalent to a pendent drop technique), hereafter denoted as contact angle method (Hartland and Hartley, 1976). The equilibrium shape of a molten polymer droplet resting on a molten polymer substrate is related to the interfacial tension via the density difference between the two phases. The relevant equations governing this shape are briefly presented in the Appendix. Equilibrium is usually reached after about 1 h or more. The results show quite good agreement with the breaking thread measurements, as can be seen in Fig. 7; however, the decrease in interfacial tension becomes evident already at a smaller percentage of diblock copolymer.

## CONCLUSION

The breaking thread method is used successfully for measuring the interfacial tension between incompatible molten polymers, which exhibit Newtonian behavior as the shear rate approaches zero. An advantage of this (dynamic) method is the fact that density data are not
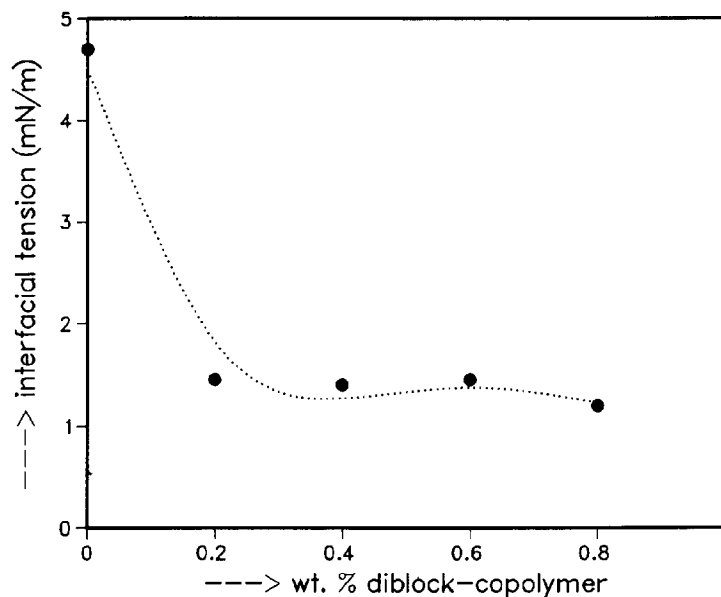
FIG. 7. Interfacial tension of the system of Fig. 6, measured with the contact angle method at 200 °C.

required. Moreover it is a simple, straightforward method which does not require special equipment or large quantities of materials.

The limiting factors are the following. The viscosity should not exceed $10^5$ Pa s; otherwise degradation may occur during the breakup, unless the thread has an initial diameter of less than 1 $\mu$m. Furthermore, the polymer constituting the thread phase should not exhibit a yield stress. Finally, the method is not suitable for liquid crystalline polymers, due to their anisotropy.

Also the determination of the interfacial tension via the (static) contact angle method yields good results, although there is some scatter. The results from both methods should be compared to those from the spinning drop method.

The stability of (extended) molten polymer threads is considerably increased by the introduction of a diblock copolymer because this reduces the interfacial tension by a factor of about 4.
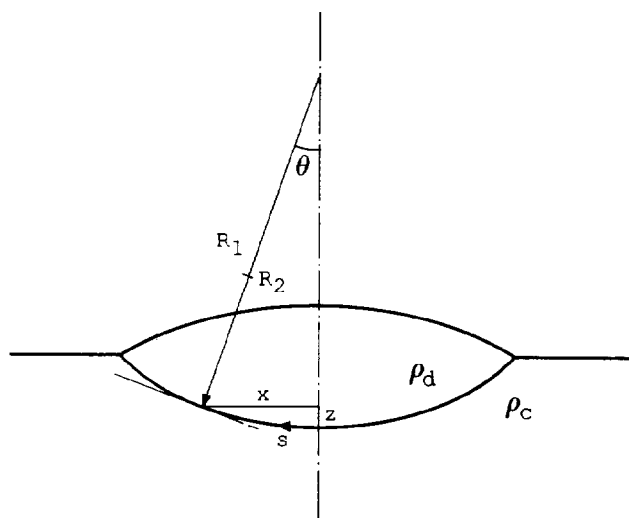
FIG. 8. Definition of some dimensions of an axisymmetric droplet resting on a liquid substrate $(\rho_d < \rho_c)$.

## ACKNOWLEDGMENTS

## APPENDIX: CONTACT ANGLE METHOD

The dynamical character of the breaking thread method requires a second static method to check the validity of the results. Direct application of pendent drop (Wu, 1969), however, proves to introduce many experimental problems if used for polymer melts (Trompetter, 1988). Determination of the interfacial tension is also possible from the dimensions of the pendent interface of an axisymmetric liquid drop resting on a liquid substrate (Neumann, 1894; Matijević and Eirich, 1969); see Fig. 8.

The principal radii of curvature are

$$R_1 = \frac{ds}{d\vartheta} \quad \text{and} \quad R_2 = \frac{x}{\sin \vartheta}. \tag{A1}$$

At any point $(x,z)$ the pressure difference across the interface must balance the Laplace pressure. This condition yields the Bashforth–Adams equation (Bashforth and Adams, 1892):

$$\sigma\left(\frac{d\vartheta}{ds} + \frac{\sin\vartheta}{x}\right) = \frac{2\sigma}{b} + \Delta\rho gz, \tag{A2}$$

where

$b$ = radius of curvature at the apex,

$g$ = constant of gravity,

$\Delta\rho = \rho_d - \rho_c$ = density difference between disperse (drop) and

continuous (substrate) phase.

Together with the boundary conditions

$$x = z = \vartheta = 0 \quad \text{at} \quad s = 0,$$

this equation can be solved numerically (Rotenberg et al., 1983).

Experiments are performed in the following way: a granule of the less dense polymer is placed on a compression molded plate of the denser polymer ($30\times30\times5$ mm) and placed in an oven under nitrogen. After 60 min at 200 °C, the sample is quenched in water. The drop is microtomed, after which the midplane is photographed; it is also possible just to photograph the entire drop in projection. From the drop shape the interfacial tension is calculated.

The results of these contact angle measurements are presented graphically in Fig. 7; they correspond quite well to the ones from the breaking thread method. Inaccuracies are mainly due to deviations in the measured contact angle $\vartheta$ or to the fact that some droplets do not attain a completely axisymmetric shape during the experiment. [A requirement for the method to be successful is that the shape factor $\beta = |\Delta\rho|gR^2/\sigma = O(10^{-1})$.] Finally, the error in the densities of the polymers is accumulated in the value for the interfacial tension. Densities of polymer melts can be determined by the method described by Laven (1985).

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