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Wetting by polymer solutions

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Abstract

Very small droplets of polystyrene dissolved in toluene were placed on a glass slide and studied under a goniometer microscope. The drops were allowed to spread and dry and their extent of spreading is plotted as a variation of the concentration of the polymer in the solution. It was observed that drops of polystyrene in a volatile solvent such as toluene, spread to some extent and then gets dried up thus preventing the contact line from moving further. When liquid PDMS in non-volatile solvent, HMDS, and in volatile solvent, toluene, was used, the droplets continued to spread. One conclusion among others, is that even if the droplet dries but leaves behind a mobile contact line then the solution spreads out, on the other hand if the droplet dries and the contact line loses its mobility, the spreading automatically comes to a stop.

Keywords: Wetting; Polymer solutions; PDMS

1. Introduction

The knowledge of wetting kinetics of polymer solutions is of considerable practical interest [1]. The kinetics of wetting of polymer melts were initially studied by Schonhorn et al. [2] who studied both high and low energy surfaces wetted by drops of polymer melts. Investigations of this kind for polymer melts and solutions still continue [3].

Four systems of polymer solutions are classified here as follows:

1. Polymer that is solid in pure form at room temperature, that is, has no mobility, and solvent that is non-volatile.
2. Polymer that is solid in pure form at room temperature and solvent that is volatile.
3. Polymer that is liquid in pure form at room temperature and solvent that is non-volatile.
4. Polymer that is liquid in pure form at room temperature and solvent that is volatile.

The first of these categories was studied by Nieh et al. [4] extensively. Solutions of low-molecular weight polystyrene (45,000) in dibutyl phthalate (b.p. 350 °C) did not wet clean glass although pure dibutyl phthalate did. Glass is a high-energy substrate and polymer solutions should have wet it. Wetting behavior was restored when the higher molecular weight polymer solutions were used (although at low polymer concentrations). Ybarra et al. [5] proposed that the thin film behavior of polymer solutions was responsible. It was also found [4] that there was no quantitative difference between the spreading behavior of Newtonian and non-Newtonian fluids. The rates of wetting appeared to be the same as for a wetting liquid, however, they observed a sudden stop or equilibration in the spreading of these drops, a feature also noted by Zosel [6]. Theoretical calculations by Saritha et al. [7] have shown that the bulk of the liquid reaches equilibrium, that is, stops moving during the surface tension driven phase, while there is a thin pre-cursor film dominated by the disjoining pressure formed ahead of the bulk that continues to spread. It is only the former that is measured with resolution under microscopy.

While studying the evaporation of a sessile droplet of water from a surface, Hu and Larson [8] found that in a droplet containing DNA, drying takes place in two phases. In the first

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phase, the contact angle decreases as the contact line remains stationary, that is, the contact line remains pinned. In the next phase, the contact line begins to recede and the contact angle remains quite small. Hu and Larson [9] have shown that in a pure liquid drop the very large evaporative flux near the contact line gives rise to a cooling effect. The resulting temperature gradient gives rise to a Marangoni effect. The Marangoni forces pin the contact line which would otherwise have receded under evaporation. In the case of a solution which contains dissolved solute, there is also an increase in the concentration of the solute at the edge of the drying droplet which leads to a gradient in surface tension. It is noteworthy that wettability does not appear to play a role in the pinning process. Ehrhard and Davis [10] showed that pinning happened in wetting but non-volatile liquid drops under heating. Spreading was shown to be opposed by Marangoni forces. In this case the Marangoni forces are pointed inwards in contrast to the case above where they are pointed outwards.

We have emphasized here on the systems 2–4 that have not been studied fully or not studied at all. For the case 2, we have polystyrene, both low and high molecular weights, in toluene which is a volatile solvent. This is aimed at supplementing the observations of Hu and Larson, particularly at high polymer concentrations and high solvent volatility. Presently there are no results for the third and the fourth categories. For case 3, we have liquid polymer polydimethyl siloxane (PDMS) in toluene and for case 4, polydimethyl siloxane (PDMS) in a non-volatile solvent, hexamethyl disiloxane (HMDS). In an earlier review [11], it has been argued that 3-dimensional mobility/viscosity and the 2-dimensional mobility/surface diffusion are the key features in governing the wetting kinetics. We show here how important they can be.

2. Experimental procedure

The solvents, toluene and HMDS, and the polymers, polystyrene and PDMS, were all used as purchased. Both high (280,000) and low (53,800) molecular weight polystyrenes (Aldrich) were used. Hexamethyl disiloxane was purchased from Aldrich. PDMS with a molecular weight of 17,000 was purchased from Polysciences.

As mentioned earlier, most of the experimental work concentrated on case 2 described above which was polystyrene dissolved in toluene. All experiments were carried out at room temperature. The substrates used were clean glass slides. No specific treatment was used to clean the glass slides as the liquids were found to wet them. A glass slide was placed on the stage of the Rame-Hart goniometer (Model 100-00) that was used to study the drops. Droplets of polymer solutions were deposited onto the glass slides using a micrometer syringe. The initial basal radius, r_0 (in mm) and the contact angle, θ (in degrees) were measured and recorded. The initial volume V_0 was then computed using the formula for the volume of a spherical cap:

$$V = \frac{\pi(1-\cos\theta)(2+\cos\theta)}{3\sin\theta(1+\cos\theta)} r_0^3 \qquad (1)$$

The drop was allowed to equilibrate and dry for 24 h and the final radius, $r_{0\infty}$, was then measured. For each weight percentage sample of the solution a minimum of 5 runs were carried out to obtain different initial volumes, except for the 5% case.

3. Results and discussion

Pure toluene completely wets clean glass, that is, the contact angle is zero. When polystyrene was dissolved in toluene, it was observed that for the lower weight percentage samples, the contact angle was only measurable as soon as the drop was introduced onto the slide. After that the drop spreads out too quickly and thins out till it was no longer in the view under the goniometer microscope. For the higher weight percentage samples, however, it was observed that the drops do not spread out completely to achieve a zero contact angle. The concentration of the residual polymer is also higher at the edge of the drop. This leads to a significant total loss of mobility of the contact line. Eventually the drop dried to form a donut-shaped ring, shown in Fig. 1, whose radius was measured. For the higher molecular weight samples, the rings were lot less prominent. In most cases, the drop evaporated to finally leave behind a smooth dry disc, probably because of the highly viscous nature of the sample which prevented the polymer solution from moving much upwards. The radii of the droplets were not measured as a function of time as they dried up and stopped moving too soon for any significant measurements to be taken.

Bascom et al. [12] have shown that the ridge near the contact line shown in Fig. 1 is due to Marangoni forces, where these forces are directed to cause spreading. Such cases have also been reported by Ruckenstein and coworkers [13–15] and validated in a model by Neogi [16]. We can invoke the same arguments by Hu and Larson [9] that cooling introduces Marangoni effect in this case. Further, the surface tension of polystyrene is about 35 mN/m and that of toluene is about

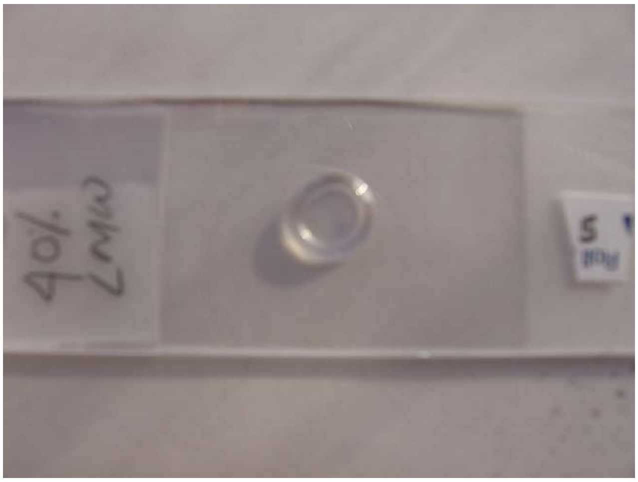

Fig. 1. A picture of the donut-shaped drop that is left behind after toluene evaporates from a solution of low-molecular weight polystyrene dissolved in toluene has been shown.

28 mN/m. That is, the solvent depleted contact line region will also contribute to the Marangoni effect and in the same direction as in the cooling effect above. However, the contact line does not move or does not move sufficiently fast, leading to an accumulation in that region.

The extent of scatter of the radius of the drop as a function of $V_0^{1/3}$ for a droplet of polystyrene dissolved in toluene has been shown in Figs. 2 and 3. Two cases were considered, low-molecular weight polystyrene (MW 58,300) as shown in Fig. 2 for a weight percentage of 20% and higher molecular weight polystyrene (MW 280,000) as shown in Fig. 3 for a weight percentage of 25%. The distances spread have been fitted to a straight line. Figs. 2(a) and 3(a) show plots of the initial radius of the drop as a function of $V_0^{1/3}$. Figs. 2(b) and 3(b) indicate the basal radius measured after 24 h as a function of $V_0^{1/3}$. Fig. 4 shows a plot of the ratio $r_{0\infty}/V_0^{1/3}$ as a function of the weight percentage, ϕ for both the high and low MW polystyrenes in toluene. The lower molecular weight case is indicated by a dashed line. It is evident that the viscosity plays an important role in the wetting process.

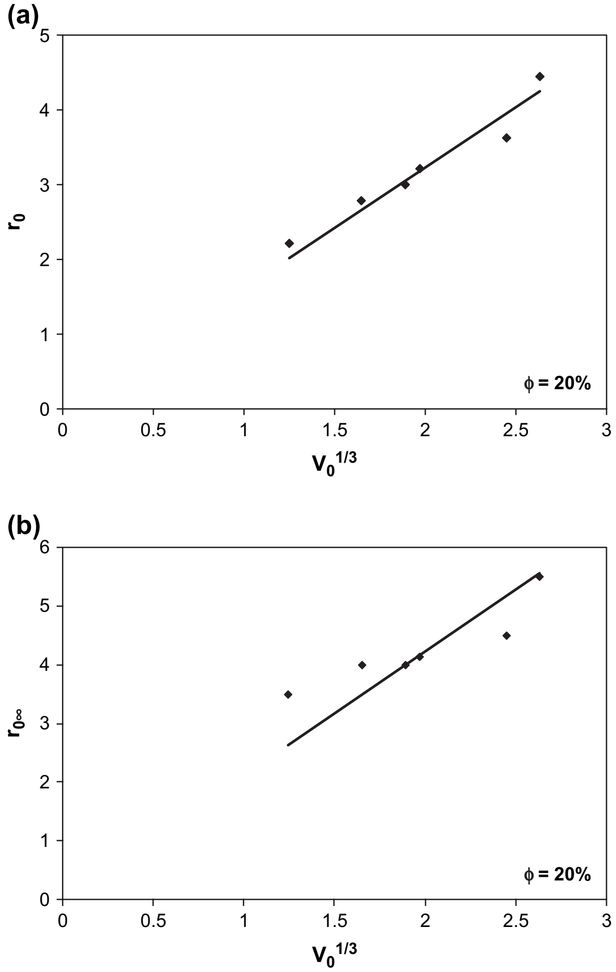

Fig. 2. (a) A plot of the initial basal radius, r_0, of the drop as it varies with $V_0^{1/3}$ has been shown for a sample of low-molecular weight polystyrene in toluene, 20% by weight. (b) A plot of the radius of the drop, measured after 24 h, $r_{0\infty}$, as it varies with $V_0^{1/3}$ has been shown for a sample of low-molecular weight polystyrene in toluene, 20% by weight.

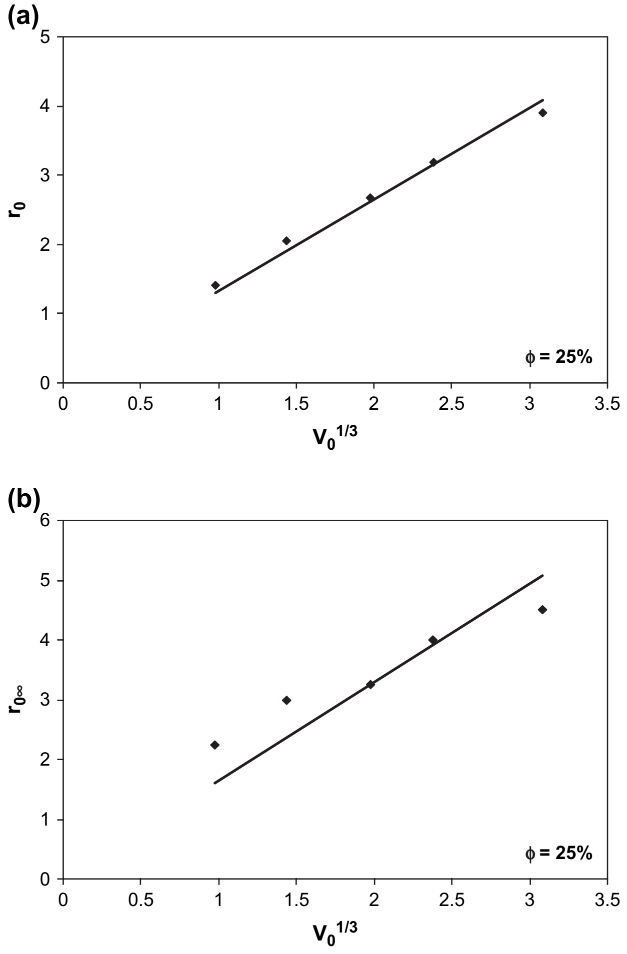

Fig. 3. (a) A plot of the initial basal radius, r_0, of the drop as it varies with $V_0^{1/3}$ has been shown for a sample of high molecular weight polystyrene in toluene, 25% by weight. (b) A plot of the radius of the drop, measured after 24 h, $r_{0\infty}$, as it varies with $V_0^{1/3}$ has been shown for a sample of high molecular weight polystyrene in toluene, 25% by weight.

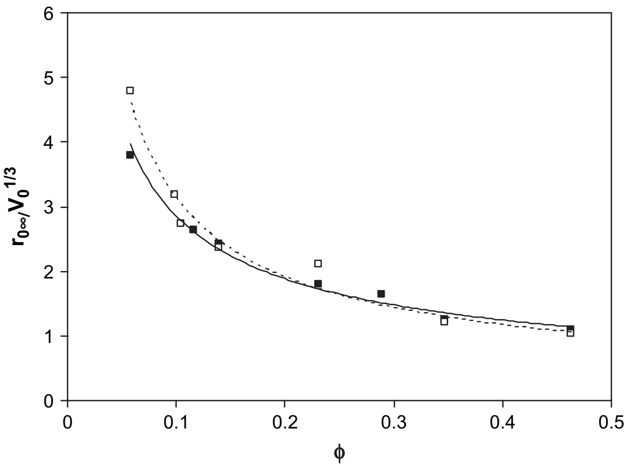

Fig. 4. A plot of the ratio $r_{0\infty}/V_0^{1/3}$ has been shown as a function of the sample weight percentages. The white squares represent the case of the low-molecular weight polystyrene dissolved in toluene. The dashed line indicates the best fit for the white squares. The black squares represent the case of the high molecular weight polystyrene dissolved in toluene while the solid line indicates the best fit for the black squares.

Experiments on systems 3 and 4 described earlier that involve liquid polymer PDMS in volatile solvent toluene and in non-volatile solvent HMDS, show only fast spreading results. These results can be understood in terms of thin film phenomena mentioned earlier briefly for the polystyrene–dibutyl phthalate (PS–DBP) system. The PS–DBP system shows a lack of wetting, not expected under phenomenological theories. According to Ybarra et al. [5], a thin film forms ahead of the contact line, with film thickness less than 100 nm. The potential in the film is different from the bulk by an amount that is expressed in terms of a disjoining pressure. In addition, the film is practically devoid of polymer. Starting from an initial condition during the spreading, this final configuration is realized in PS–DBP system because the mobility of the polymer is much lower than that of the solvent, but cannot be realized in the PDMS–HMDS system because of high mobility of PDMS. Consequently, PDMS–HMDS remains wetting. Because of the high mobility of the PDMS, it appears that it continues to spread even when the solvent is stripped off by evaporation. That is, Marangoni effect is not enough to arrest spreading in this case. (That the present theory of pinning by Marangoni forces does not include wettability has been alluded earlier.) PDMS by itself is not a special polymer in this context. Other polymer melts exhibit comparable spreading rates [11,17]. However, PDMS is distinguished by its low melting point because of which it is possible to find both a polymer melt and a non-volatile solvent at the same temperature. Both cases 3 and 4 (for practical reasons) are very special cases, the likes of which at least we have not been able to put together from another polymer.

Consequently it can be concluded that the spreading behavior of a polymer solution can be predicted if the mobility of the contact line can be determined. That is, the drop will only spread if the contact line is mobile.

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