Film drainage and interfacial instabilities in polymeric systems with diffuse interfaces

A.N. Zdravkov, G.W.M. Peters *,1, H.E.H. Meijer

Dutch Polymer Institute, Materials Technology, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

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Abstract

We report an experimental investigation on the effect of mutual diffusion in polymeric systems on film drainage between two captive drops. The main objective is to study the influence of diffuse interfaces on film drainage. This is done by using material combinations with different interfacial properties and interferometric visualization of the film between two interacting drops. For highly diffusive systems film drainage is observed to be, in contrast to immiscible systems, non-axisymmetric and unstable immediately after the film formation (at a few micrometers film thickness). Depending on whether the total thickness of the diffusion layers in the film is smaller or larger than the thickness of the film, Marangoni convection is found to enhance or delay film drainage. Enhanced film drainage is determined to be in order of 100 times faster than predicted by the current models, while delayed film drainage is observed after a drainage period where experimental and predicted results (assuming, a partially mobile interface) are in close agreement.

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Keywords: Film drainage; Film drainage instability; Polymer–polymer inter-diffusion; Diffuse interface layers; Drop coalescence; Marangoni convection

1. Introduction

Interfacial phenomena govern, to a large extent, processes like drop break-up and coalescence, and thus structure development in emulsions and polymer blends. Drop coalescence, besides its importance for producing new tailored materials, is of fundamental interest given the complexity of the phenomena involved. In combination with an external bulk flow that governs the frequency, strength and duration of drop collisions, the drainage of the film between the drops up to a critical film thickness is considered to be the rate-determining step in drop coalescence [1].

In this work we will focus on polymer blends, both, because of their practical importance and because of the convenient time scales of the observed phenomena. Mutual diffusion in polymer blends is mostly considered negligible for practical purposes [2–7] and this assumption seems reasonable, regarding their high viscosities and the fact that mixing of long molecules is thermodynamically unfavorable [8,9]. However, the molecular weight polydispersity of most (commercial) polymers will enhance mutual solubility, because the asymmetry across the interface is enlarged and because the small molecules diffuse faster than the large ones [10].

The discrepancies between predicted and experimentally determined drop coalescence rates (in particular in the film drainage step) as reported in the literature [2–4,11–13] are, most likely, due to a small but still non-zero mutual solubility in polymer systems. Even a small solubility can, analogous to the effect of surfactants, substantially alter the interface response to a deformation [14,15]. The effect of mutual diffusion becomes even more important during the film drainage step where small length scales are involved; i.e., film thicknesses of the order of 1 µm and less. It is known that for systems with pure interfaces, i.e., the absence of an excess of surface active molecules, film drainage depends on the interface mobility, which, in turn, is determined by the dispersed to matrix phase viscosity ratio, the drop radius and the film radius. All three parameters
have a known impact [1,16–19]. However, for systems with surfactants and/or diffuse interfaces, these parameters can become less meaningful and new specific parameters like the interface surfactant concentration and interface thickness come into play and can determine, to a large extent, the film drainage process.

In such systems, film drainage alters the drops interfaces in the film region, leading to an inhomogeneous surfactant distribution or an inhomogeneous thickness of the diffuse layer along the drops interfaces. This produces interfacial tension gradients that induce (Marangoni) stresses [20]. These interfacial stresses can have a substantial influence on film drainage and they even can overrule it. While these effects are well investigated for systems with surfactants and for thermally induced gradients [14,15,21–24], they are hardly studied for diffuse systems. MacKey and Mason [25] were the first to point out the importance of the diffusion of a third component (a mutual solvent) on the coalescence of a drop against an interface. They found that diffusion of this third component from the drop into the film increases the rate of film thinning and thus shortens the coalescence time. The opposite was found for diffusion into the drop. More recently, in agreement with these results, a jump-like coalescence between two captive oil drops in a water phase was observed [26,27] where again a third component was diffusing from the drop to the matrix phase. Both cases of diffusion from the drop into the film and vice versa were investigated theoretically by Saboni et al. [28,29]. For a similar case, but this time a surfactant diffusing across the interface towards the film, the opposite effect, thick and very stable aqueous films between oil phases were observed by Velev et al. [30].

This work is an extension of our previous work [22] on film drainage for oil/water systems with polymeric surfactants and presents experimental results on film drainage for polymer–polymer combinations with diffuse interfaces, using direct observations of the film drainage process and of the film thickness evolution. The aim is to increase the understanding of film drainage in polydisperse polymeric systems with an asymmetry of the molecular weights across the interface and thus with mutual diffusion.

2. Materials and methods

The polymers used in this work are polybutene (PB, BP Chemicals, UK), polyisobutylene (PIB, Infinium, UK) and polybutadiene (PBD, Aldrich) as the dispersed phase and polydimethylsiloxane (PDMS, United Chemical, USA) as the matrix phase. These materials have been frequently used in experiments on structure development [5,7,12,13,31,32], mainly because they are considered to be ideal model systems, regarding their viscosity at room temperature and mutual solubility that is considered to be negligible. In Ref. [33] we reported a detailed characterization of the bulk and interface properties of these material combinations. For this study the materials were chosen in such way that a broad range of interfacial properties (interfacial tension and diffuse interface thickness) was covered, see Table 1. The coding of the combinations is kept the same as in Ref. [33]. After each of the polymer abbreviations, the number molecular weight, $M_n$, is given. The zero shear viscosities ($\mu_d$ for the dispersed phase and $\mu_c$ for the continuous phase) were measured with a rotational viscometer (Rheometrics, ARES) using a plate–plate configuration and applying steady shear. At shear rates below 30 s$^{-1}$ and at 20°C, all polymers show Newtonian behavior. To ensure Newtonian behavior of the materials during the coalescence experiments, slow collision rates were used (with approach velocities of the order of 1–3 μm/s). The interfacial tension, $\gamma$, of the polymer pairs was measured as a function of time with a pendant/ sessile drop apparatus (PAT-1, Sinterface, Germany). The mean values (accuracy ±0.1 mN/m) at two successive moments ($\gamma_{fresh}$, few minutes after the drop is formed and $\gamma_{old}$, 4 h later) are given in Table 1. The arrows in Table 1 indicate the tendency of the change in time of $\gamma$. The change of the volume of a sessile drop after 0.5 and 4 h, due to mutual diffusion, was used as an estimate for the length scale of the diffusion, $\Delta R = (V_{f,0})^{1/3} - (V_{f,4})^{1/3}$, see Table 1. In this work the volume, $V_{f,0}$, was determined by extrapolating the data to zero time, avoiding in this way the effect of changes due to some initial relaxation of the drop. The accuracy of the method is ±0.5 μm. The thickness of the diffusion layer around a drop is estimated to be of the order of magnitude of $\Delta R$. For the combinations A5 and B3, the thickness of the diffusion zone was measured also by means of confocal Raman spectroscopy [33,34]. For A5 the thickness of the diffuse layer was, after 4 h,

Table 1

<table>
<thead>
<tr>
<th>Polymer combination</th>
<th>Dispersed phase/matrix phase</th>
<th>$\mu_d/\mu_c$ (Pa s/Pa s)</th>
<th>$\gamma_{f,0}$ (mN/m)</th>
<th>$\gamma_{o,0}$ (mN/m)</th>
<th>$\Delta R_{1/2,0}$ (μm)</th>
<th>$\Delta R_{4,0}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>PB635/PDMS28k</td>
<td>6/1.2</td>
<td>1.9</td>
<td>2.5</td>
<td>60</td>
<td>237</td>
</tr>
<tr>
<td>A3</td>
<td>PB950/PDMS60k</td>
<td>51/0.1</td>
<td>2.6</td>
<td>2.5</td>
<td>15</td>
<td>67</td>
</tr>
<tr>
<td>A5</td>
<td>PB950/PDMS63k</td>
<td>51/12</td>
<td>2.8</td>
<td>2.4</td>
<td>8</td>
<td>34</td>
</tr>
<tr>
<td>A6</td>
<td>PBD1000/PDMS63k</td>
<td>130/12</td>
<td>3.2</td>
<td>3.0</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>B1</td>
<td>PB1800/PDMS28k</td>
<td>1/1.2</td>
<td>4.0</td>
<td>4.0</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>B3</td>
<td>PB68k/PDMS68k</td>
<td>17/0.1</td>
<td>4.2</td>
<td>4.2</td>
<td>–</td>
<td>2</td>
</tr>
</tbody>
</table>

^a^ Few minutes after the drop is formed.

^b^ Four hours after the drop is formed.

^c^ The data are processed in different way than in Ref. [33], see text for explanation.
determined to be \( \approx 70 \text{ µm} \), while for B3, within the accuracy of the technique (±15 µm) no diffusion was detected, for 2–3 days. For more detailed results on these material combinations, the reader is referred to Ref. [33].

Film drainage experiments were performed with two captive drops of radius \( R_d \approx 750 \text{ µm} \), formed at the ends of two tubes that are incorporated in a stainless steel box filled with the continuous phase, see Fig. 1. The bottom tube can be moved towards the upper one by means of a motor (for a more detailed description of the set-up see Refs. [22,35]). A film is formed during the approach with a constant velocity (1–3 µm/s) and when flattening between the drops is observed, the approach is stopped. The films are interferometrically visualized with reflected laser light (\( \lambda = 632.8 \text{ nm} \)) and the images are recorded by means of a CCD camera and a video recorder (Fig. 1). The difference in film thickness between two neighboring interferometric rings of the same intensity is 226 nm. The recorded images were processed to obtain information on the time evolution of the film thickness and of the film profile [22]. In contrast to [22] here the film drainage is non-axisymmetric and the minimum film thickness, \( h_{\text{min}} \), can be localized in certain region of the film. For example, \( h_{\text{min}} \) for system B1 is localized in the region denoted by the white arrow and it can be tracked in time by counting the rings that show up from this point (Fig. 1b). For some of the experiments, the thickness at rupture is determined by using the changes in intensity of the reflected light [36].

3. Results and discussion

In the following, first the visualization of film drainage is shown for some representative cases that demonstrate the influence of the diffuse layer thickness on film drainage behavior. Next, a schematic explanation of the observed phenomena is given, which is followed by more quantitative experimental results of the evolution of the minimal film thickness. The results are discussed on the basis of predictions of the available film drainage models.

3.1. Film drainage: observations

Fig. 2 shows the film evolution for two relatively fresh systems, A1 and B1, i.e., observations obtained a few minutes after the drops are formed (Figs. 2a–2c and 2d–2f, respectively). The A1 combination is representative for a system with a thick diffuse layer (\( \Delta R_{1/2} h = 60 \text{ µm} \), see Table 1) and B1 for a system with a relatively thin diffuse layer (\( \Delta R_{1/2} h = 2 \text{ µm} \)). The interferometric visualization reveals that for both systems the film drainage is non-axisymmetric and unstable already at thicknesses of the film formation, i.e., a few micrometers. This is in contrast with many previous experimental observation with immiscible systems, e.g., Refs. [22,37]. For system A1 many peristaltic instabilities are observed during the drainage, which grow until film rupture occurs (at \( t = 20 \text{ s} \), see Fig. 2c). In contrast, the instabilities in the B1 system are more restricted and the film drainage time is much longer. The interfacial tension \( \gamma \) and the drop viscosity \( \mu_d \), known to influence the film drainage [19], have values that favor faster drainage of system B1. However, the drainage for system A1 is at least 10 times faster. This discrepancy is ascribed to the fact that most drainage theories [1,18,19] assume sharp interfaces while in reality a small solubility substantially changes film drainage. For diffuse systems, parameters like the film radius and the drop radius most likely loose their importance. For system B1, it should be stressed that although \( \gamma \) is constant (at least during the first 4 h) within the accuracy ±0.1 mN/m, see Table 1, the film drainage is also unstable. Therefore, one can say that the thickness of the diffusion layer (in our case the relevant parameter is \( \Delta R \)) together with the value of the interfacial tension are the relevant parameters that are influencing the film drainage and the interfacial instabilities.
Fig. 2. Comparison between the film drainage behavior of system A1 (a–c) and B1 (d–f). The reference bar on picture (a) corresponds to 100 µm. Note the difference in pattern and time (bottom of the pictures). The white arrows point out regions in the film where the drop interfaces are in closer contact, i.e., the film pimples, which are surrounded by the film dimples (not indicated).

The influence of the interface age on film drainage behavior and film drainage time was studied in more detail for system A5 for which the diffuse layer is less developed than for the A1 but more than for the B1 systems (see $\Delta R_4$ in Table 1). Two drops were formed and left in the matrix for different times before being brought into contact. In Fig. 3 a comparison is made between a fresh system, with only a few minutes of drop residence time before starting the experiments (Figs. 3a–3d) and an old system, with a few hours of drop residence time (Figs. 3e–3h). These results illustrate that film drainage in the fresh system is stable and axisymmetric. The time of drainage is approximately 30 min after which film rupture occurs and the two captive drops merge into a filament. In contrast, the film drainage in the old system is unstable, non-axisymmetric and the time of drainage is 10 times shorter. Obviously, the thickness of the diffuse layer plays an important role and an increasing thickness is in favor of the film drainage. An interesting feature can be observed; the film rupture event is much slower compared to systems with apolar/polar interactions (where it is an instant event) and can be followed for several seconds (Figs. 3d and 3h). This is due to the relatively low interfacial tension, $\gamma$, and the high viscosities, $\mu_d$ and $\mu_c$ of the dispersed and continuous phase, respectively (see Table 1).

3.2. Mechanisms of film drainage in systems with diffuse layers

When diffuse layers of two drops overlap during a collision, the concentration of the diffusing molecules in this zone becomes higher, resulting in a lower interfacial tension in the film region, relative to the interfacial tension of those parts of the drops that are not in contact. Moreover, film drainage also enhances the thickness variation of the diffuse layers along the drop interfaces in the film region. The induced gradients in interfacial tension produce tangential (Marangoni) stresses along the interface that result in convection from areas with low to areas with high interfacial tension. According to Lucassen and van den Tempel [38] the tangential forces generate in the region of non-uniform interfacial tension (in this work the film region) longitudinal and transversal waves of different wave length and propagation velocity. Which wave length will be developed, for the longitudinal waves, depends mainly on the interfacial di-
latational elasticity while for the transversal waves it depends on the interfacial tension. Higher values of these two parameters lead to larger wave length. Such interfacial waves could be the source of the observed instabilities (see Figs. 2 and 3). However, whether the instabilities will grow depends on the total thickness of the interfacial layers in the film region. If the total thickness is larger than the film thickness the Marangoni convection will locally promote the instabilities. Otherwise the instabilities will be damped either by the interfacial tension or by the interfacial elasticity. In another words, depending on the thickness distribution of the diffuse layers, Marangoni convection can promote or reduce film drainage [20,25]. Fig. 4a shows schematically the contribution of Marangoni convection to film drainage for the case where there is no overlap of the diffuse layers, i.e., the total thickness of the diffuse layers is still less then the minimal film thickness. This mechanism is thought to be responsible for a stabilization of the film by opposing the film drainage. When there is an overlap in the diffuse layers, see Fig. 4b, the Marangoni convection promotes locally the film drainage. The unstable and non-axisymmetric film drainage observed in Figs. 2 and 3 is ascribed to this local film thinning behavior which leads to faster drainage in regions of overlap accompanied with growing dimples in the neighboring regions. Considering Fig. 2 again one can see the difference in the length
scale of the instabilities for system A1 and B1. A systems have a dilatational elastic modulus in the range of 3–5 mN/m [33] and an interfacial tension in the range of 1.5–3 mN/m, while B systems have a modulus in the range of 13–18 mN/m [33] and an interfacial tension in the range of 4–5 mN/m. Obviously both parameters are larger for the B systems, which will lead to less pronounced instabilities (i.e., larger wave length) than for A systems, see Fig. 2. It should be mentioned here that in this, rather simple, description of how gradients in diffuse interfaces cause Marangoni convection, the ongoing process of diffusion during the film drainage process is neglected. Only the age of the interface, giving a certain interfacial thickness, and film formation effects are taken into a count. In reality, depending on the time scales of the different processes, ongoing diffusion might also contribute to the film drainage process, e.g., by reducing the value of the interfacial elasticity [33].

3.3. Comparison with available film drainage models

Film drainage experiments provide information on the film behavior and on the evolution of the film thickness and, therefore, allow for a comparison with the available film drainage models. Hereafter, four asymptotic laws for the film thickness evolution for the limiting cases of immobile [16,19,39], partially mobile [16,19,39], parallel-film [40] and fully mobile [41] film drainage are used:

- immobile:
  \[ h = \left( \frac{0.36\mu_a}{\gamma} \right)^{1/2} \frac{R a^{1/2}}{t^{1/2}}, \quad \lambda a \rightarrow \infty, \quad (1) \]
- partially mobile:
  \[ h = \left( \frac{0.076\mu_a}{\gamma} \right)^{2/3} \frac{R a^{1/3}}{t^{2/3}}, \quad \lambda a \rightarrow 0, \quad (2) \]
- parallel-film:
  \[ h = \left( \frac{k_1\mu d_2}{2\gamma} \right) \frac{R a^2}{t}, \quad (3) \]
- fully mobile:
  \[ h = h_0 \exp \left(-\frac{t}{t_{ch}}\right), \quad t_{ch} = \frac{3\mu R_d}{2\gamma}, \quad \mu \rightarrow \infty, \quad (4) \]

where \( t \) denotes time, \( a \) the film radius, \( \lambda = \mu d_1/\mu c \) the drop to continuous phase viscosity ratio, \( k_1 \) is a constant (in this work in order of \( 1 \times 10^{-2} \)), \( h_0 \) the initial film thickness and \( \mu \) is the largest of the two viscosities of the drop and the continuous phase. In order to estimate the effect of the thickness of the diffuse layer on film drainage we will consider several systems with different interfacial properties, starting from the relatively diffusive system A3 proceeding with the (intermediate) less diffusive systems A5 and A6 and finishing with the slightly diffusive system B3 (see \( \Delta R \) in Table 1). Since in this work the aging of the systems is investigated, for fresh systems (few minutes after the two phases are brought into a contact) \( \Delta R_{1/2} \) is a more relevant parameter for estimation of the diffusion length scale, while for old systems (few hours after the two phases are brought into a contact) \( \Delta R_{4/3} \) is a more relevant. It should be mentioned here that the diffusion length parameter \( \Delta R \) is a better estimate for the more diffusive systems and it is only giving the order of magnitude of the thickness of the diffuse layer for the less diffusive ones.

3.3.1. Film drainage for systems with thick diffuse layers

The measured minimum film thickness versus time for system A3 is presented in Fig. 5. In this plot results from two experiments with the same experimental conditions but different system age are given; a ‘fresh’ (i.e., a few minutes after the two phases were loaded in the experimental set-up \( \equiv \) residence time) and an ‘old’ system (1 h residence time). The ‘fresh’ system shows a few times slower rate of drainage compared to the
‘old’ system. Moreover, Fig. 5 illustrates that the film drainage is approximately 100 times faster compared to the partially mobile model predictions (dashed line, Eq. (2)). The asymptote is obtained by using the parameters from Table 1 and the corresponding experimental conditions (the radius of the film \( a \) is given for every experiment in the legend of the figures). For these two experiments the film radius was constant from the beginning of the measurement. The high rate of drainage in A3 system can be attributed to the Marangoni flow acting in the direction of the drainage (see previous section, Fig. 4b). For the area with minimum film thickness the mechanism depicted in Fig. 4b has a similar effect as a fully mobile interface, i.e., an enhanced removal of matrix material from this region. If this is correct then the film drainage is driven by the film interfaces and it seems reasonable to compare this result with the fully mobile asymptote for film drainage (Eq. (4), solid line, Fig. 5). Indeed, the asymptote describes the experimental data rather well, confirming the idea of Marangoni flow driven film drainage. It should be pointed out here that the parameter \( h_0 \) (the initial film thickness in Eq. (4)) is chosen in such a way that the asymptote and the measurements begin at the same moment.

Fig. 6 shows results for the A5 combination. The ‘fresh’ system (a few minutes residence time) shows a stable film drainage with drainage rate that is a few times slower compared to the ‘older’ (half an hour residence time) and ‘old’ system (1 h residence time), both showing unstable drainage. Fig. 6 shows another interesting feature; while the ‘fresh’ system shows unstable film drainage and \( a \) is loosing its relevance. For example, although in the ‘older’ experiment the film radius is smaller than in the ‘old’ experiment the film drainage is slower. Moreover, Fig. 6 illustrates again that the film drainage is approximately 100 times faster than predicted by the partially mobile model (dashed line, Eq. (2)), stressing the dominating effect of the local interface flow on the film drainage, at least in the first steep part of the experimental curves. The two different parts of the experimental curves are related to two types of film drainage; the first part with increasing film radius (where the Marangoni flow is dominating) and second part with constant radius (where the Marangoni flow contribution is less pronounced). The first part fits well with the fully mobile asymptote (solid line, Fig. 6) while the second part fits well with the parallel-film model (dashed–dotted line, Fig. 6). The latter is understandable since the experimental observations revealed that the films for system A5, at the later stages of the film drainage, are parallel sided (see Fig. 3d). The good fit of the second part of the experimental curves with a model that assumes sharp interface is an indication that for this system, at that stage, the Marangoni flow does not contribute much to the film drainage. The difference between the results for A3 and A5 system is that for A3 system the Marangoni driven film drainage is dominating during the entire drainage process while for A5 system only for the first part. This is most likely related to the low viscosity of the matrix for system A3.

One more set of experiments was performed with the even less diffusive A6 system. Here the effect of repeated experiments for a fresh system was studied (every next experiment was done immediately after the previous by breaking the coalesced drops into two new ones). A behavior similar to A5 system is observed and again the film drainage is approximately 100 times faster than the film drainage predicted by the partially mobile model, see Fig. 7. Again two different slopes in the film thickness evolution curves are seen which again are fitted well with the fully mobile asymptote (solid line, Fig. 7) and with the parallel-film model (dashed–dotted line, Fig. 7). The difference between the first experimental curve (circles) and the other two (square and stars) as seen in Figs. 6 and 7 is attributed to the continuously increasing film radius, \( a \), and the fresher inter-
faces in the first experiments. It should be mentioned here that the film radius for systems A5 and A6 is not so controllable parameter because they consist of relatively small interfacial tension and high viscosities. This results in a prior deformation of the drops, followed by drop shape relaxation after the approach is stopped. Moreover, the Marangoni convection in the contact region also leads to increasing film radius [42]. It should be pointed out here that the fully mobile asymptote and the parallel-film model curve are fitted to the experimental results by means of adjustable parameters, $h_0$ and $k_1$, respectively, while for the partially mobile asymptote no adjustable parameters are used. This is indicating that for systems with thick diffuse layers (thickness in order of tens of micrometers) the film formation takes place at closer drop–drop separations. This can be ascribed to the attraction between the drop interfaces which is larger at the apexes of the drops [42].

The film thickness at rupture, $h_{cr}$, was measured for systems A5 and A6 using the change in intensity of the reflected light from the film interfaces [36]. The last points in the film drainage curves in Figs. 6 and 7 represent the values of the critical thickness at rupture. For system A5 a value of $67 \pm 5$ nm for $h_{cr}$ was determined, which is close to the calculated value of 53 nm using the available models for film rupture [43]. The critical thickness at rupture was found to be independent of the aging of the system. For the system A6, $h_{cr}$ was determined to be $93 \pm 5$ nm while the predicted value is close to 50 nm. This indicates that with increasing molecular weight, $M_n$, of the drop phase, $h_{cr}$ also increases, which is not taken into account in the models [43].

The results of the experiments with the A combinations are in agreement with our experimental observations on the attraction of two droplets that were put in an overall quiescent matrix at a mutual distance that ensured overlap of their diffuse layers [42]. These results show the important role of diffusive effects that facilitate coalescence by increasing the length scale at which drops ‘notice’ each other. Additional evidence for such effects comes from results on shear induced coalescence in a blend of type A [5]. The authors observed a higher, then expected from theoretical predictions, rate of drop coalescence and very good reproducibility of the experiments. The authors did not consider diffusion as a cause for their results but attributed the high tendency of coalescence to a large film rupture thickness ($h_{cr} = 150–200$ nm).

In addition, one more conclusion can be drawn from the film drainage experiments regarding the process of mutual diffusion for the A systems. The results for the fresh systems (Figs. 5–7) show that only a few minutes after the two phases were brought into contact, the diffusion is well in progress (with a length scale of a few micrometers and larger) since the deviation from the predicted drainage results is already a factor 100. This fast response is contributed to the small molecules that initiate the diffusion process as they move much faster than the large, relatively entangled molecules. Small molecules determine the initial interface thickness and profile while the final profile is determined by the diffusion of larger molecules [9]. Therefore, the presence of small molecules (i.e., a broad molecular weight distribution) in at least one of the phases will have a substantial influence on structure development during mixing.

### 3.3.2. Film drainage for systems with thin diffuse layers

A relatively stable and axisymmetric film drainage was observed for system B3 that consists of closely matched molecular weights, i.e., with little diffusion (see $\Delta R$ in Table 1). The results are presented in Fig. 8 for a ‘fresh’ (15 min residence time) and an ‘old’ (1 h residence time) system. These experimental results are much closer to the model predictions than for the A systems. Moreover, it is seen that aging of the system leads to deviations from the asymptotic behavior. The results for the ‘fresh’ system are in good agreement with the partially mobile asymptote (dashed line, Eq. (2)), at least for the first 10 min (at that moment an early rupture of the film occurred). The ‘old’ system shows at some moment film drainage faster than the model predictions, although the deviation is not that large, after which the drainage slows down again and even reverses (Fig. 8, last part of curve B3—old). Based on the schematic mechanism similar to that presented in Fig. 4a an explanation can be given for the observed reverse behavior. The film drainage rate decreases with the decreasing thickness of the film while the induced Marangoni stresses do not depend on the thickness. Hence, at some thickness the opposite acting Marangoni convection can overtake the film drainage and the overall effect is film thickening.

The results on the B combinations can help to explain some of the phenomena and problems on film drainage and related processes reported in literature [31,32,42]. For example, we observed for B systems a repulsion between two drops brought into close contact and left to interact in an overall quiescent fluid matrix [42]. The reverse thinning behavior, as is seen in Fig. 8, is the same process but a separation of the drops is not possible since they are captive. In Ref. [32] a B type system was subjected to simple shear and it was found that drop coalescence was almost absent and thus had little effect on the drop size evolution. This observation is in agreement with the results presented in Fig. 8. Finally, it was reported [31] that

![Fig. 8. Film thickness evolution curves for system B3. The aging of the system leads to deviation from the model predictions.](image-url)
flow-induced coalescence in B type systems is enhanced when the $M_n$ of the matrix phase is taken large enough. This finding is in agreement with our results that with increasing the $M_n$ of the matrix phase the asymmetry across the interface becomes, for some $M_n$, large enough to make the diffusion more pronounced (see Table 1). The mechanism (Fig. 4b) that promotes the film drainage is switched on and the overall result is faster coalescence. In contrast, for closely matched across the interface $M_n$ the diffusion is restricted below the length scale of the film thickness and the Marangoni convection opposing the film drainage has a large contribution (Figs. 4a and 8).

This work points out the importance of the Marangoni flow for systems with mutual diffusion and in this way opens room for more experimental and theoretical investigations. The main lines that should be taken into account in future research are that for more diffuse systems (systems A in this work) the film formation is taking place at closer drop-drop separations and the Marangoni flow has significant contribution in the initial part of the drainage period while for less diffusive systems (systems B in this work) Marangoni flow has significant contribution in the final part of the film drainage period.

4. Conclusions

The effect of mutual diffusion between polymer combinations on film drainage, and thus on drop coalescence, was studied experimentally. Two groups of fluid combinations with different interfacial properties were used: A systems, which are polymer combinations with thick diffuse layers (from a few to tens of micrometers), and B systems, which are polymer combinations with relatively thin diffuse layers (from a sub-micrometer to a few micrometers). It was found that film drainage is unstable and non-axisymmetric when the total diffusion length scale is of the order of the thickness of the film. The evolution of these instabilities was shown to depend on the age of the system. The film drainage results for the more diffusive A systems show an approximately 100 times faster drainage rate than the one predicted by using a partially mobile asymptote, while the less diffusive B systems gave results close to the partially mobile model predictions. However, in the latter case a reversal in the film thinning rate was observed. For both material combinations the aging was found to lead to larger deviations from the theoretical predictions. The results are explained on the basis of a simple schematic mechanism, representing Marangoni convection that promotes the film drainage when the diffuse layers are overlapping and reduces the film drainage when the two layers are not overlapping. These findings stress that the often used assumption, that the solubility in polymer systems is negligible for practical purposes, often can not be sustained.

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