Interfacial phenomena during drop coalescence in polymeric systems

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Interfacial Phenomena During Drop Coalescence in Polymeric Systems

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Copromotor:
dr.ir. G.W.M. Peters
In memory of my father
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Summary

The effect of mutual diffusion between two polymers on drop interaction is established. This is achieved by a detailed interfacial characterization of the polymer combinations involved and a detailed investigation of the film drainage for these material combinations. From the former a critical initial interfacial tension of approximately 4 mN/m was found, below which diffusion leads to a decreasing interfacial tension in time, respectively an increasing interfacial thickness, and above which diffusion leads to an increasing interfacial tension in time, respectively a decreasing interfacial thickness. The film drainage experiments show that in the case of thick diffuse interfaces the film thinning rate is in the order of 100 times faster than the model predictions, while in the case of thin diffuse interfaces a reduced film thinning rate is observed after a period of time where the experimental and predicted results are in close agreement. Oscillatory dilatational interfacial measurements on the diffuse interfaces show that they can be considered as diffuse layers with a viscoelastic response to deformations. Furthermore, a novel approach for drop coalescence is used in which flow effects can be separated from specific effects related to the material properties. By using this approach for systems with a large length scale of diffusion (tens of microns), an attraction between two drops is observed when the diffuse layers around the drops overlap. In contrast, for systems with a small length scale of diffusion (less than a micron), a repulsion between two drops is observed when the diffuse layers around the drops do not overlap even after a close contact between the drops. These phenomena and the film drainage results are explained by interfacial tension gradients (inducing Marangoni convection, i.e. interfacial flow), caused by the inhomogeneous thickness of the diffuse interfaces due to the interaction between the drops. Results from numerical calculations based on the diffuse interface method support this explanation. From a practical point of view, this work shows the importance of a critical length scale of diffusion, related to the thickness of film formation between two interacting drops, above which drop coalescence is facilitated and faster coarsening of a blend can be expected, and below which drop coalescence is suppressed and a finer morphology can be obtained.

In addition, by using a non-diffusive system with surfactants, the current theoretical models are validated in the limiting cases of immobile and partially-mobile film drainage, for a constant and a slightly rising interaction force between the drops, respectively. The increased film drainage rate in the case of rising interaction force, i.e. increasing contact area between the drops, is attributed to the redistribution of the surfactants due the changing boundary conditions.
For most of the systems investigated the film thickness at rupture was determined using the intensity changes of the light reflected from the film interfaces. The results show that with increasing molecular weight of the dispersed phase, the critical thickness at rupture also increases. The experimental results are compared with the model predictions based on van der Waals forces.

Based on the results of this work some concepts for structure development in polymeric systems can be critically reviewed. For example, the often reported anomalously low viscosity of immiscible polymer blends is usually attributed to apparent slip at the polymer-polymer interfaces, while our study suggests that the low viscosity can be attributed to the access of small molecules at the interfacial zone which leads to a local reduction of the viscosity and, in this way, modifies the blend viscosity. Another contribution to this low viscosity effect that emerges from our work is that due to the diffuse layers around the drops, especially in the case of thick diffuse layers (tens of microns), the interfacial response to deformation is weaker than in the case of sharp interfaces, which are usually assumed in the models. The concept of apparent slip at the polymer-polymer interfaces is also used to explain an enhanced coalescence rate in experiments with a single coalescence events while the mutual diffusion has been neglected. In contrary, our results show that mutual diffusion, through the mechanism of interfacial tension gradients, has an overruling effect on drop coalescence. A considerable amount of studies on shear-induced coalescence in polymer-polymer systems indicate a high tendency of drop coalescence, which is attributed to an extremely large film thickness at rupture, determined by fitting experimental coalescence times with coalescence models. Diffusion was neglected, while our study shows that in this polymer-polymer interactions diffusion can play a major role.
Chapter 1

Introduction

1.1 Blend morphology formation during processing

The increased demand for new products with specific properties such as increased stiffness, impact strength, permeability, special optical properties and low materials cost requires efficient ways of production that can only be obtained through deep understanding of the physics involved. Blending is a flexible and a cost-effective way of obtaining new (e.g. polymer) tailor-made materials. The properties of the resulting materials largely depend on the size and the distribution of the dispersed phase, i.e. the blend morphology. Depending on the initial materials and the processing conditions, quite different morphologies can be obtained [1]. For a given mixing flow (fixed mixing conditions), the interfacial and bulk properties of the constituents determine the final morphology of the blend. During mixing the structure develops and the final morphology is obtained through two processes: break-up and coalescence of drops. While break-up is a single drop event, coalescence is a clearly more complex process that results from interaction between two or more drops during flow. Although drop coalescence has been a subject of extensive experimental and theoretical investigation for more than a century (for reviews see, e.g. Reynolds [2], Mason and coworkers [3; 4] and Chesters [5]), due to the complexity of the processes involved, still not all aspects are fully understood.

In this work some unexplained results from structure development in polymeric systems are clarified by directed experiments on a set of well defined material combinations. It is shown that diffuse interfaces can play a dominant role in drop coalescence through the mechanism of Marangoni convection.

1.2 Drop coalescence mechanism

The initial stage (1) of the process of drop coalescence is when liquid drops, immersed in another liquid, approach and collide due to an external bulk flow. Subsequent stages are (2) drainage of the intervening liquid, trapped between their interfaces and, if the time for drainage is sufficient, (3) drop confluence. During this process different interconnected phenomena can occur simultaneously. For drops with deformable interfaces a flattening (parallel interfaces) in the contact zone occurs,
known as a film formation, usually considered as the initial part of the second stage (see Fig. 1.1). The liquid in the film drains out due to the pressure difference that exists between the capillary pressure, $P_c$, in the flattened region and the ambient pressure, $P_0$. This goes on until film rupture occurs or the drops separate again due to the external flow. Film rupture is usually considered as the final part of the second stage and as the initiation of the third stage. In combination with the external bulk flow that determines the duration and radius of the drop contact, $a$, the film drainage is the rate-determining stage of drop coalescence. The flow in the film depends, apart from the contact radius, drop radius, and matrix viscosity, on the mobility of the interfaces of the drops. The interface mobility, in the case of drops with pure sharp interfaces (without excess material, e.g. surfactants), is determined by the dispersed to continuous phase viscosity ratio $\lambda = \mu_d / \mu_c$ \cite{5}. In systems with a large ratio ($\lambda > 10^2$, typically) the drainage is in the immobile regime. When $\lambda$ is between $10^{-2}$ and $10^2$, film drainage is in the partially-mobile regime. Finally, when the drop viscosity is very low compared to the viscosity of the continuous phase ($\lambda < 10^{-2}$) the drainage is in the fully-mobile regime.

1.3 Theoretical models and assumptions for film drainage and rupture

For film drainage the Navier-Stokes equation \cite{6, 7} can be simplified using the lubrication approximation, since the Reynolds number is low and the film thickness, $h$, is much smaller than the radius of the film, $a$. Both assumptions are justified in the
case of viscous systems (typical for polymers) and not too small drops \( (R > 1 \, \mu m) \) and not too high interfacial tensions \( (\gamma \text{ between } 1-4 \, mN/m, \text{ typical for polymer-polymer interactions}) \), the latter two allow for flattening and film formation. Further simplification can be introduced to facilitate the theoretical analysis if the radius of contact, \( a \), is much smaller than radius of the drop, \( R \). The latter is a reasonable assumption, since only gentle collisions lead to substantial probability of coalescence \([5]\). Summarizing, a reasonable assumption for drop coalescence for most of the polymeric systems is:

\[
h \ll a \ll R
\]

The early asymptotic models introduced by Reynolds \([2]\), and Mason and Mackay \([4]\) assume immobile interfaces and approximate the drops in the contact region as parallel disks. It is known from such simple analysis that the drop deformation (film formation) leads to a slower rate of coalescence. A later asymptotic model proposed by Chesters \([5]\) deals with partially-mobile interfaces and assumes plug flow in the film and creeping flow in the drop. According to this model, film thickness, \( h \), decreases as \( t^{-1} \). During the last 10-15 years, numerical models are used for studying film drainage \([5; 8; 9; 10; 11]\). These models describe the film drainage that is coupled with the flow in the drops in a more detailed way and even can predict the experimentally observed slight deformation of the film, known as a dimple (Fig. 1.1). As a result of such computations it was found by Yiantsios ans Davis \([8]\) that for the case of constant force, i.e. constant film radius, and for the limiting cases of immobile and partially-mobile film drainage that the film thickness at the periphery (minimum \( h \)) decreases as \( t^{-1/2} \) and \( t^{-2/3} \), respectively. Their work was extended by Bazhlekov et al. \([12]\) to cover the entire viscosity ratio range. The different length scales involved, drop sizes typically from 1 \( \mu m \) to a few \( mm \), film thicknesses from few dozens \( nm \) to 1 \( \mu m \) and interface thicknesses from few \( nm \) to tens of \( \mu m \) require extremely high accuracy of the numerical methods. To the best of our knowledge, at present, there is no numerical method without restriction for drop deformation that can resolve film thickness smaller then 0.1\% of the drop size \([13]\).

Most of the models for film rupture for systems with pure interfaces (i.e. no surfactants or charged molecules) are based on analyses that include van der Waals molecular forces \([14]\). They show (see e.g. Chesters \([5]\)) that the critical film thickness depends, apart on the Hamaker constant, which is material property, on the radius of the drops \( \sim R^{1/3} \) and on the interfacial tension \( \sim \gamma^{-1/3} \). While the former is responsible for initiation of the film instability through the steep gradient of the film thickness at the film periphery, the latter is acting as to damp the film instabilities. The competitive role of these two parameters determines the film rupture thickness. It is known that the presence of surfactants at the film interfaces does not have an effect on film thickness at rupture \([11]\). Diffuse interfaces are not incorporated in these models.

### 1.4 Experimental investigations

There are no quantitative experimental data for the film drainage rate and for the film rupture thickness for polymer blends, so far. However, there are many
morphological studies which show tendencies of drop coalescence in polymeric systems. Fortelny and Kovar [15] found that the available models predict substantially slower rates of coalescence than those determined from experiments in a polypropylene/EPDM elastomer system. Lyu [16] determined that for a polystyrene (PS)/high density polyethylene (HDPE) system the coalescence rate does not monotonically decrease with an increasing viscosity ratio, as predicted by all current theories. Instead, with an increase in the viscosity ratio, the coalescence rate first increases and then decreases. The high values of the dispersed and continuous phase viscosities are expected to result in long drainage times for the film between the interacting drops. However, Elmendorp and van der Vegt [17] found experimentally that polymer combinations with PE and PS as a drop phase and polydimethylsiloxane (PDMS) as a continuous phase, despite their high viscosities, have a high coalescence probability and they concluded that these polymers have much more mobile interfaces than expected. A considerable amount of studies (for a review see [18]) have shown an anomalously low viscosity of immiscible polymer blends. Zhao et al. [18] attributed this phenomena to an apparent slip at the polymer-polymer interfaces. Recently, several in situ studies of shear-induced coalescence has been reported (for a review see [19]) for blends of polyisobutylene (PIB) and PDMS. Rusu and Peuvrel-Diedier [19] attributed the high tendency of drop coalescence in this system to an extremely large film thickness (150-200 nm) at rupture, determined by fitting experimental coalescence times with coalescence models [5].

Only a few attempts of more detailed investigation of single events of drop coalescence are available in the literature. Leal and coworkers [20] investigated flow-induced drop coalescence of Polybutadiene (PBD)/PDMS systems and found an increase in the rate of coalescence with increasing the molecular weight of the matrix. The authors attributed this effect to apparent slip at the polymer-polymer interface. Guido and Simone [21] and Verdier and Brizard [22] reported shear induced coalescence in PIB/PDMS systems. The first authors found that after coalescence of two PIB drops in PDMS matrix, a new trial, after breaking the resulting drop, did not lead to coalescence. Verdier and Brizard, using a particle image velocimetry technique, detected very rapid motions around the neck of two interacting PDMS drops in a PIB matrix. This phenomenon remains unexplained. Schoenberg et al. [23] investigated drop coalescence in the commercial system PS/LDPE by using a spinning drop apparatus. The shorter coalescence times detected were attributed to existence of a low molecular weight material at the interface acting as a lubricant.

Most of these researchers used similar methods, coalescence was monitored under shear or elongation flow. However, these methods do not provide information on the film thickness during drainage and thus a quantitative comparison with coalescence models was not possible. It is clear that more detailed experiments are necessary, in order to measure the film drainage rate and film rupture thickness and to separate the effects of the flow from the effects of the material properties on film drainage and thus on drop coalescence.
1.5 Interfacial tension gradients and interfacial viscoelasticity

Interfacial tension gradients are a fairly well studied for low viscous systems in the case of adsorbed species (surfactants) on the drop interfaces [24; 25; 26]. From these studies it is known that only a small amount of surfactant is sufficient to immobilized the interfaces of the drops in the film. As the liquid flows out of the film, it causes an inhomogeneous distribution of the surfactant molecules along the drop interfaces, accumulating molecules outside of the periphery of the film, which leads to interfacial concentration gradients. These give rise to interfacial tension gradients, which in turn induce tangential (Marangoni) stresses [27] that produce interfacial flow in the direction opposite to the film flow. In the case of a constant film radius, there is a balance at the interface between the hydrodynamic and Marangoni stresses, resulting in immobilization of the interface [25].

In the case of polymeric systems, due to the relatively low interfacial tension, typically from 1 to 4 mN/m, the interfacial properties will be governed by diffusion effects rather than by effects from adsorption of surface-active species. In other words, for polymeric systems the interface is not sharp but diffuse and can be represented like a diffuse interfacial layer with finite thickness [28]. Nevertheless, the rheological behavior of such diffuse layers in the film is expected to be similar to systems with soluble surfactants, the difference being that a new length scale should be introduced. Depending on the time and length scales of the processes involved during film drainage, one may expect mass transfer from the bulk toward the interface, initiated in order to restore the equilibrium interface properties disturbed by the film flow, lateral diffusion and interface flow due to interfacial tension gradients, to play a role. The competitive contribution of these processes can determine to a large extend the interface mobility and thus drop coalescence.

There is a lack of literature concerning the influence of the interfacial viscoelasticity on film drainage. Ivanov et al. [29], Barber and Hartland [30], and Ivanov and Dimitrov [31] investigated the effect of the interfacial viscosity on film drainage for low viscous systems with surfactants. However, in these studies the interface was assumed to be Newtonian. Callaghan et al. [32] and Eley et al. [33] performing experiments of crude oil/brine system, and Tambe and Sharma [34], performing numerical simulations of film drainage between viscoelastic interfaces, have shown that the dilatational modulus (the measured viscoelastic parameters) have an essential effect on the emulsion and foam stability. Little experimental work is done on the effect of viscoelastic interfaces on film drainage for pure polymer-polymer interfaces (for a recent review see Puyvelde et al. [35]). Most of the work involves polymer blends compatibilized with some surfactant and subjected to oscillatory shear flow, so the viscoelastic interfacial properties could be estimated by using the Paliere model [36]. Nevertheless, one may expect that the polymer-polymer interface due to its ‘non-pure’ nature (polydispersity will lead to mutual diffusion) will have a viscoelastic behavior that, in combination with the film flow, will play a role during film drainage. While the interface viscosity is expected to have a minor effect on film drainage, the additional interfacial elastic stress (Marangoni elasticity, i.e. interfacial tension gradients) is known to have a large influence on interface mobility and thus on film drainage.
1.6 Experimental techniques for film formation

The methods for forming liquid films can be divided into two groups. In the first group, "supported films" are formed into capillaries, frames, etc. In the second group, two captive drops are formed at the end of two capillaries and can be forced to approach.

A typical representative of the first group is a device for formation of liquid film in a circular capillary, invented by Scheludko and Ezerova [37]. When in the circular capillary a liquid drop from the film phase is introduced and the liquid is sucked out by a side capillary, the meniscus surfaces are deformed and either dimpled or planar film appears. If the capillary is embedded in another immiscible liquid an emulsion film (between two drops) can be formed. Since the meniscus capillary pressure depends on the film radius, both can be controlled by the sucking pressure. Limitations of the method are the very narrow range of pressures (when the film becomes large the meniscus is usually sucked in the side capillary) and liquid viscosities (in the case of high liquid viscosity of the film phase, it is difficult to handle the withdraw procedure) that can be used. By using light interferometry one can measure film thickness, thinning rate, film lifetime and contact angle. A representative of the second group is an experimental apparatus developed by Abid [38]. The principle scheme of the apparatus is shown in Chapter 2. Two drops are formed at the ends of tubes, incorporated in a chamber that is filled with another immiscible liquid (matrix phase). The bottom tube can move with respect to the upper one with a controlled velocity. When the drops are close enough, film drainage starts and observation of this process by means of interferometric techniques is possible. The advantage of this cell is the wide range of liquid viscosities that can be handled. One can determine the film drainage rate, absolute film thickness, film deformation and film thickness at rupture.

1.7 Lay-out of the thesis

The main part of this thesis is dedicated to an experimental investigation of the effects of surfactants and mutual diffusion in polymeric systems on film drainage and thus on drop coalescence.

The main goal is to elucidate and explain the mechanism of film drainage in complex polymeric systems. This is achieved by a detailed characterization of the interfacial and bulk properties of the polymer pairs involved and a detailed investigation of the film drainage rate and film rupture thickness by using an interferometric technique. In Chapter 2 the interferometric technique is introduced and validation of the existing film drainage models is presented for systems with apolar-apolar interfaces with surfactants for the cases of immobile and partially-mobile film drainage. In Chapter 3 special attention is paid to the interfacial properties of systems with apolar-apolar interfaces when mutual diffusion plays an important role. It is shown that the interface in such systems has to be considered as a diffuse layer with viscoelastic behavior. Next, in Chapter 4, using interferometric visualization of the films, it is demonstrated that the film drainage in such diffusive systems can become unstable and non-axisymmetric. By comparing with the available film drainage
models a good estimate about the polymer-polymer interface mobility in these systems can be obtained. In Chapter 5 phenomena of drop attraction and repulsion in polymeric systems with diffusion are studied and related to interfacial tension gradients. In addition to that computational results, based on the diffuse interface model, are used to explain the observed phenomena. Finally in Chapter 6 conclusions and recommendations are given.
Chapter 1
Chapter 2

Film Drainage between Two Captive Drops: PEO-Water in Silicon Oil

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Film Drainage between Two Captive Drops: PEO-Water in Silicon Oil

An experimental study on the deformation and the drainage of a Newtonian liquid film trapped between two viscoelastic drops is performed for the cases of constant and slightly rising interaction-force. The aim is to validate the film drainage models in the cases of the immobile and the partially-mobile film drainage and as well to understand the film drainage for systems with surfactants and changing boundary conditions, i.e. film radius. Series of polyethylene oxide (PEO) water solutions are used for the dispersed and polydimethylsiloxane (PDMS) for the continuous phase. The film evolution is observed by an interferometric technique. Experimental data for the film thinning rate and for the film profile allow for quantitative comparison with the available drainage models.

2.1 Introduction

Coalescence and breakup of viscous drops in a viscous matrix control the drop size distribution in processes such as phase separation, emulsification and polymer blending. Compared to break up, where the interaction is only between the bulk flow and a single drop, coalescence is a more complex process, that involves the interaction between the bulk flow and at least two (usually unequal) drops. The different length scales involved (drop sizes typically in the range of μm to mm and film thicknesses in the range of nm to μm) make this process even more difficult to study. The
coalescence process can be split into three coupled, but individually manageable sub-processes [5]:

1. Particle approach in an external flow field
2. Film formation and drainage
3. Film rupture and drop confluence

In combination with the first sub-process that governs the frequency, strength and duration of the collision, the drainage up to the critical film thickness is considered to be the rate-determining sub-process in drop coalescence. Different conventions for regimes of film drainage can be found in the literature. The one proposed by Chesters [5], based on the mobility of the drop interfaces, is used hereafter. In systems with a high value of dispersed to continuous phase viscosity ratio ($\lambda > 10^2$, typically) or in most of the cases when surfactants are present in the system, the drainage is in the immobile regime. When $\lambda$ is between $10^{-2}$ and $10^0$, and no surfactants are present, film drainage is in the partially-mobile regime. Finally, when the drop viscosity is very low compared to the viscosity of the continuous phase ($\lambda < 10^{-2}$) and no surfactants are present, the drainage is in the fully-mobile regime. Analyses of these regimes are available in the literature. The earlier models approximate the film as parallel-sided [2; 3], while the later ones use a numerical approach for the fully coupled problem of interface deformation and film flow [8; 9; 10; 11]. Most of the models suppose simple boundary conditions: a constant interaction-force or a constant approach velocity, while in reality both will vary during a collision. In order to validate these models, experimental data for film thickness and film drainage rate are needed. So far, many experimental studies of coalescence have been performed, but most of them are in situ [39; 40; 41] so they do not provide information for the film thinning behavior. More detailed experiments on close approach of two biconcave menisci or of a drop towards a rigid plane, a deformable interface or another drop have often been reported [42; 43; 44: 45: 46: 47], but most of these studies consider parallel-sided thin liquid films. Klaseboer et al. [48] have studied film drainage between two colliding viscous drops at constant approach velocity, but the authors reported values of the film thickness ($\approx 1.5\mu m$) that are far from the critical ones ($\approx 50\, \mu m$).

To verify the existing theoretical drainage models, a well characterized model system is needed. In particular, a system that provides possibility of varying the viscosity while the interfacial properties are kept unchanged. Polyethylene oxide (PEO) is a nonionic water-soluble polymer, which is used for a wide range of applications including coatings and drag reduction. The bulk and surface properties of aqueous PEO solutions are well studied. Kawaguchi et al. [49] have investigated the solubility of PEO in water and the properties of an aqueous PEO solution by using static light scattering and intrinsic viscosity measurements. Schurz et al. [50] have characterized PEO water solutions rheologically on the basis of the shear viscosity and its dependence on the shear rate. One outcome of their work is that for shear rates higher than $1\, s^{-1}$ the solutions have a non-Newtonian behavior. The influence of the molecular weight polydispersity of PEO on the bulk properties of water solutions has been studied by Kulicke et al. [51], who have established that with the
increase of the polydispersity the viscoelasticity of the solutions increases as well. The surface activity and properties of PEO in water have been investigated by Kim 
[52] and Kawaguchi et al. [53]. The authors have found out that the $CH_2CH_2$ component of PEO is sufficiently hydrophobic to form an adsorbed layer at the air/water 
interface. Moreover, Kim [52] has investigated the influence of the molecular weight 
on the adsorption using surface light scattering measurements and has concluded that for molecular weights higher than $1 \times 10^6$ PEO molecules do not form a thick 
and dense adsorbed layer. Glass [54] has studied the adsorption kinetics of the PEO 
molecules with different molecular weights and he has shown that for high molecular 
weight PEO ($2.4 \times 10^6$) the time required to reach an equilibrium at the interface 
is of the order of a few hours. At present, there are no results available in the literature 
for adsorption of PEO molecules at water/PDMS interface. However, due to the polar/apolar nature of this interaction, the interfacial tension will be relatively high (20-30 mN/m), which, one may expect, to result in adsorption of the PEO 
molecules at the water/PDMS interface as well.

We report experimental results on film deformation and film drainage rate in the 
case of constant and of slightly changing interaction-force between two PEO-water 
drops in a PDMS matrix. Measurements of the absolute thickness of the draining 
films are performed and a quantitative comparison with the available drainage 
models is made.

2.2 Experimental materials and methods

2.2.1 Materials

The polymers used in the experiments were polydimethylsiloxane (PDMS) and 
opolyethylene oxide (PEO, with molecular weight $M_w = 8 \times 10^6$). PDMS was supplied 
by United Chemical (Amchro, Germany) and used in all experiments as a continuous phase. PEO was supplied by Aklich and used without further purification. 
PEO water solutions with different concentrations $c$ were used as a dispersed phase 
(Table 2.1).

<table>
<thead>
<tr>
<th>liqud phase</th>
<th>c [wt%]</th>
<th>$\mu_c$ [Pa.s]</th>
<th>$\mu_d$ [Pa.s]</th>
<th>$\tau_{rel}$ [s]</th>
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<tbody>
<tr>
<td>PDMS phase</td>
<td>continuous</td>
<td>-</td>
<td>1 and 10</td>
<td>-</td>
</tr>
<tr>
<td>PEO-0.40 dispersed</td>
<td>0.40</td>
<td>3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>PEO-0.65 dispersed</td>
<td>0.65</td>
<td>30</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>PEO-1.00 dispersed</td>
<td>1.00</td>
<td>100</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

All PEO water solutions were prepared by pouring the polymer in a bottle filled 
with deionized (Millipore) water, which was then left, without shaking, for 2-3 days. 
After that the bottle was gently rolled until the polymer was fully dissolved. The 
zero shear viscosity ($\mu_d$ for the dispersed phase and $\mu_c$ for the continuous phase)
and the characteristic relaxation time $\tau_{rel}$ of the solutions were measured on a plate-plate configuration in steady shear (Rheometrics, ARES) and their values are listed in Table 2.1. According to Kawaguchi [49] for PEO water solution with molecular weight $M_w$ higher than $6 \times 10^5$, the expression for the intrinsic viscosity, $[\eta]$, is:

$$[\eta] = 4.33 \times 10^{-4} M_w^{0.670}, d \ell g^{-1},$$

which in our case gives $[\eta] = 21 \ d \ell g^{-1}$. Following de Gennes [55] and coworkers for the formulation of concentration regimes in a good solvent:

$$1 < c[\eta] < 10, \quad \text{semidilute};$$

$$c[\eta] \geq 10, \quad \text{concentrated},$$

one can determine that the PEO-0.40 solution is in the semidilute (coil overlap) regime, and PEO-0.65 and PEO-1 are in concentrated (entanglement) regime. The interfacial tension, $\gamma$, of all PEO/PDMS systems was measured with a Pendant drop apparatus (PAT-1, Sinterface, Germany) and was in the range of 25 to 27 mN/m. The interfacial tension of pure water/PDMS system, $\gamma_w$, was measured with the same apparatus and was $41.0 \pm 0.1$ mN/m. As discussed in the introduction, PEO molecules adsorb from the PEO water solution and according to Kim [52] for molecular weights higher than $4 \times 10^5$ and concentrations higher than $1 \times 10^{-3}$ wt% the interfacial properties of all solutions are the same. In this respect, the molecular weights and the concentrations that were used in the present study are assumed to be high enough to ensure equal properties at the interface for all solutions used.

### 2.2.2 Film drainage cell

The experiments were performed in a film drainage cell in which two captive drops with equivalent radius $R_{eq} \approx 750 \ \mu m \ (R_{eq}^{-1} = 0.5 (R^{-1}_1 + R^{-1}_2))$ were formed on the tops of two conical tubes incorporated in a chamber filled with the continuous phase (Fig. 2.1). The bottom (movable) tube can be forced to approach the top (fixed) one with a constant velocity by means of a motor (Maxon). The chamber is supplied with optical glass windows, that allow observation of the drops from aside and interferometric visualization of the liquid film from above. All parts of the cell were made from stainless steel allowing to be thoroughly cleaned with an alcohol based cleaning solution in combination with an ultrasonic bath. A detailed description of the film drainage cell is available elsewhere [48]. To the best of our knowledge, the technique of investigating film drainage between two captive drops (bubbles) was first applied by Cain and Lee [56]. A similar technique is also applied by Wilde and Clark [46] and Dell’Aversana et al. [57].

### 2.2.3 Experimental protocol and technique

The films were formed by forcing the drops to approach each other with a constant velocity ($v = 1 - 3 \mu m/s$) until a certain film radius was reached ($a = 80 - 85 \ \mu m$, Fig. 2.2). The latter is measured from the middle of the extreme outer Newton ring (see e.g. Fig. 2.1, the wider outer bright ring). After that, the approach was stopped and the film was left to thin under the pressure difference that exists between the capillary pressure in the film and the reference pressure in the chamber.
The film was observed with reflected laser light ($\lambda_0 = 632.8 \text{ nm}$, Uniphase 1105P) using a microscope (Zeiss, Stemi SV11), a CCD camera and a monitor. The images were recorded by means a video recorder. The film thickness difference between two neighboring interferometric rings of the same intensity is $\lambda_0/2n$, where $n$ is the refractive index of the continuous phase. In our case this gives a thickness difference of 226 nm. The recorded images were processed to obtain the evolution of the film thickness and of the film profile. Two well distinguished stages of the film thinning were observed during each experiment: fast thinning, during the dimple formation, accompanied with the appearance of numerous rings from the center of the film (pictures a–e in Fig. 2.2), and slow, representing an asymptotic film thinning behavior accompanied with the appearance of few rings at the rim of the film (pictures e and f in Fig. 2.2). The two stages are also shown by means of the film profile in Fig. 2.3. An experiment was stopped either when rupture of the film occurred, or when it was observed that the process of drainage was well in the asymptotic part (see next section). When the last bright Newton ring at the periphery started to appear the process of film drainage was so slow that the changes in the film thickness can be detected only by changes in the intensity of the light reflected from a small spot at the rim (the size and position of the spot can be adjusted). By using the intensity of the reflected light one can determine the film thickness at this spot at any moment [42]:

$$h = \frac{\lambda_0}{2\pi n} (m\pi \pm \arcsin \sqrt{\Delta}), \quad m = 0, 1, 2, 3, 4, \ldots$$ \hspace{1cm} (2.4)$$

$$\Delta = \frac{I - I_{\text{min}}}{I_{\text{max}} - I_{\text{min}}},$$ \hspace{1cm} (2.5)
Figure 2.2: Six subsequent interference pictures of a Newtonian film formed between two PEO-0.40 drops. The observation was carried out in reflected laser light ($\lambda_0 = 632.8\text{nm}$). Black and white rings correspond to film thicknesses in multiples of $\lambda_0/4\pi$. The reference bar shown in picture $f$ is equal to 50 $\mu\text{m}$. A particle trapped in the film is visible in pictures $d$ and $f$. 
Figure 2.3: Film profile evolution for PEO-0.65/PDMS system.

where $I$ is the instantaneous value of the intensity of the reflected light, and $I_{\text{min}}$ and $I_{\text{max}}$ are the minimum and maximum values of $I$, respectively. When film rupture occurred or when the experiment was stopped, the film thickness at this moment was determined using Eq. (2.4) and the film thickness at any instant and any place in the film can be reproduced by counting the Newton rings backwards in time (Fig. 2.3).

2.3 Results and Discussion

2.3.1 Asymptotic laws of film drainage

As mentioned in the Introduction, Yiantsios and Davis [8] have tackled numerically the fully coupled problem of interface deformation and flow in the film. Their work has been reviewed by Chesters [5] and extended to cover the entire viscosity ratio range by Bazhlekov et al. [12]. In the present work, two long time asymptotic laws for the evolution of the film thickness, $h$, in the limiting cases of the immobile and the partially-mobile film drainage were used [12]:

$$h = \left( \frac{0.36\mu_c}{\gamma} \right)^{1/2} \frac{R_{c0}^{1/2} a}{t^{1/2}}, \quad \lambda \to \infty$$  \hspace{1cm} (2.6)$$

$$h = \left( \frac{0.32\mu_d}{\gamma} \right)^{2/3} \frac{R_{c0}^{1/3} a^{4/3}}{t^{2/3}}, \quad \lambda \to 0$$  \hspace{1cm} (2.7)$$

where $t$ denotes the time.
2.3.2 Immobile film drainage in case of constant film radius

Most of the measurements were done with drops with an equivalent radius \( R_{eq} = 750 \pm 20 \, \mu m \) and a constant film radius, \( a = 85 \pm 5 \, \mu m \) i.e. a constant interaction-force. As mentioned in the materials section, the interfacial tension of all systems under investigation was between 25 and 27 \( mN/m \) and was chosen to be \( 26 \pm 1 \, mN/m \) for all of them. The results for the minimum film thickness (the thickness at the rim of the film, see Fig. 2.1) versus time are presented in Fig. 2.4 (starting at the moment when flattening between the two drops occurred, picture a in Fig. 2.2). The data presented in this plot are for two aqueous PEO solutions with different concentrations, i.e. different viscosities. All other properties and parameters for the two experiments were kept the same. The good overlap of the experimental data (triangles and circles) illustrates that the bulk properties of the dispersed phase in the case of a constant film radius did not play a role during the film drainage and hence, the drainage is expected to be in the immobile regime. Indeed, the asymptote for immobile film drainage matches the experimental data well. The asymptote was obtained by taking all required parameters in Eq. 4.1 from the experiments (\( \mu_s = 1 \, Pa.s, \gamma = 26 \, mN/m, a = 85 \, \mu m \) and \( R_{eq} = 750 \, \mu m \)). Further support of the statement that in the case of a constant film radius the film drainage is in the immobile regime is given in Fig. 2.5. In the experiments shown in this plot all parameters were kept fixed, only the film viscosity was increased 10 times. The results illustrate that with an increase of the viscosity of the continuous phase 10 times the time of drainage is also increased 10 times, as predicted by the models (i.e. Eq. (4.1)). The last part of the minimum film thickness curves is again well described by the immobile asymptote. The results presented here are in agreement with some previous
Figure 2.5: Evolution of the minimum film thickness for two experiments with different continuous phase viscosity $\mu_c$, 1 Pa.s (squares) and 10 Pa.s (circles). All other material properties and experimental parameters were kept fixed.

studies [24; 26], which show that only a small amount of surfactant is necessary to immobilized the interface. The effect of immobilization is usually attributed to the so-called Marangoni effect. As the liquid flows out of the film, it causes an inhomogeneous distribution of the surfactant molecules along the interface, accumulating molecules outside of the periphery of the film, which leads to interfacial concentration gradients. These give rise to interfacial tension gradients, which in turn induce tangential (Marangoni) stresses [27] that produce interfacial flow in the direction opposite to the film flow. In the case of a constant film radius, there is a balance at the interface, in the region of the minimum film thickness, between the film flow and the interfacial flow, resulting in immobilization of the interface [25]. Considering the bulk viscoelasticity, as the film drainage is of the immobile type, the flow in the dispersed phase will be negligible and, therefore, viscoelasticity will not play a role.

2.3.3 Effect of the initial approach velocity (at constant film radius)

The evolution of the minimum film thickness for two experiments with the same material properties ($\mu_d = 30 \text{ Pa.s}$ and $\mu_c = 1 \text{ Pa.s}$) but different initial approach velocity, $v$, is presented in Fig. 2.6. In the case of a higher initial approach velocity (triangles), the film is formed at a higher drop separation and reaches the immobile asymptote later. Fig. 2.7 illustrates the results from the same experiments but in terms of the film profile. The film profile curves are compared at the same minimum film thickness. In the case of a higher approach velocity (curves on the right), the dimple is more pronounced at the beginning but when the film drainage reaches the asymptotic part (Fig. 2.6), the dimple is as much pronounced as in the lower approach velocity (curves on the left). The results presented in Figs. 2.6 and 2.7 show that in the case of a constant film radius the initial approach velocity and the
Figure 2.6: Minimum film thickness versus time for two experiments with different initial approach velocity \( v \). In the case of a higher initial approach velocity (triangles) the film is formed at a larger separation and reaches the immobile asymptote later.

Figure 2.7: Comparison of the film profile for two different initial approach velocities \( v \), at given minimum film thickness.

dimple shape are not of critical importance for the drainage time.

2.3.4 Effect of the film radius increase

It was not always possible during the film drainage experiments to keep the radius of the film constant. In approximately half of the experiments the film was either
decreasing or increasing in size and this phenomenon was attributed to a thermo-compression or thermo-expansion of the liquid in the tubes, respectively. We used this phenomenon to study the effect of small changes in the interacting force on the film drainage process. In the case of a decreasing film radius, no single coalescence event was observed and, therefore, only films with a slow increase in the film radius will be considered hereafter. Fig. 2.8 gives the minimum film thickness versus time

![Graph](image)

Figure 2.8: Evolution of the minimum film thickness for a constant (circles) and for a slightly increasing film radius (triangles and squares). In the case of an increasing film radius the thickness curves deviate from the immobile asymptote.

for three experiments with the same material properties but different experimental conditions: one with a constant film radius (circles) and two others with an increasing film radius (triangles and squares). It is observed that the expansion of the film leads to a faster drainage and, depending on the speed of the expansion, the minimum film thickness curves can deviate quite strongly from the immobile asymptote. In this case, the film thickness curves approach the partially-mobile asymptote but in the time scale of the experiments it is never reached. Further support for this statement is given in Fig. 2.9. In this plot a comparison between two experiments with a constant film radius (triangles and circles) and one with an increasing film radius (squares) is made. The latter experiment was performed with a dispersed phase viscosity of 100 Pa.s and it is in a good agreement with the partially-mobile asymptote obtained for a constant film radius of 100 μm, which is close to the final experimental value of the film radius. For a long time asymptote the film radius at the late stages of the experiment should be taken into account rather than the one at the early stages. Within a film radius range of 95-105 μm a good match with experimental data is observed. One reasonable explanation for the observed phenomenon is that, due to a gradual increase in the film radius, depletion of the interfaces, in the minimum thickness region, from adsorbed polymer molecules takes place, leading to a partially-mobile film drainage. Depletion is likely to occur as the
Figure 2.9: Comparison between two experiments with a constant film radius (triangles and circles) and one with an increasing film radius (squares). The film thickness evolution curves in the case of a constant film radius is in a good agreement with the immobile asymptote, while the film thickness evolution curve in the case of an expanding film matches well with the partially-mobile asymptote.

time scale of the film drainage experiments in the present work is typically in the order of $10^2 - 10^3$ s, while for reaching the equilibrium adsorption of high molecular PEO molecules at the interface it takes typically $10^4 - 10^5$ s [54]. As discussed in the introduction, according to Kim [52] the adsorption of high molecular weight PEO molecules at the air/water surface is relatively weak. Unfortunately, results for the dynamics of PEO molecules at oil/water interface are, to the best of our knowledge, not available at the moment, but one can assume that for oil/water interface the adsorption must be even weaker because the interfacial tension is smaller than the surface tension. This assumption is in a good agreement with the results presented in this section, which show that a small additional interacting force turns the film drainage from immobile to partially-mobile type. Another possible explanation is that, due to the film radius increase, the minimum film thickness is moved to a region with excess material (surfactants) at the drop interfaces, which is accumulated at the interfaces outside the film, initially immobilizing the interfaces, that leads to redistribution of the surfactants at the interfaces in the film. The latter, trough interfacial flow, this time promoting film drainage, can lead to a faster thinning rate in the minimum film thickness region. However, dealing with changing boundary conditions (film radius), lateral diffusion and adsorption-desorption of surfactants all influencing the film drainage process, is a challenging problem that represents an interesting topic for further theoretical investigation of these factors.

It should be mentioned at this point that during all experiments film rupture occurred (see Figs. 2.8 and 2.9) at drop separations much higher than ones predicted by the models (20-30 nm, [11] and [14]). This phenomenon was usually attributed to
particles trapped in the film (Fig. 2.2). Also it should be pointed out that according to Glass [54] parts of the PEO molecules are oriented out of the interfacial region, which is not taken into account in [11] and [14].

2.4 Conclusions

In this work, the drainage of a Newtonian film formed between two captive drops was investigated by an interferometric technique. The goal was to validate the existing asymptotic film drainage models in the case of dimpled films. For this purpose, series of aqueous PEO solutions with different concentrations were used as a dispersed phase. In the case of a constant interaction force between the drops (constant film radius) the film thickness evolution curves for drops with different bulk properties overlapped and matched very well with the immobile film drainage asymptote. In contrast with this, in the case of a slow increase of the film radius (i.e. a non-constant interaction force) the film drainage tended to be of a partially-mobile type. From the experiments performed, there was no clear evidence of the influence of the additional viscoelastic stresses of the drop phase on the film drainage as all data were well described by Newtonian asymptotic laws. Considering the characteristic time of the experiments (from half hour to few hours) and the characteristic relaxation times of the solutions (seconds), and taking into account that the process of drainage was very slow it was not very likely that viscoelastic effects will influence the film drainage. Moreover, if there was any effect of the viscoelasticity, it should be expected to appear during the first stage of the film drainage when the drainage rate is higher. However, the experiments with different approach velocities showed that the initial conditions do not matter, as at some moment either the immobile or partially-mobile asymptote was reached. The main contribution of this work is the validation of the existing theoretical models in the limiting cases of immobile and of partially-mobile film drainage. For the PEO/PDMS systems investigated, it was found that the drainage is very sensitive to the film radius increase and the effect was attributed to a depletion of the adsorbed polymer molecules from the drop interfaces in the film.
Chapter 3

Transient Interfacial Tension and Dilatational Rheology of Diffuse Polymer-Polymer Interfaces


We have measured the interfacial tension as a function of time of polymer combinations for a broad range of interfacial properties in a sessile drop apparatus. The interfacial properties were obtained by varying the asymmetry in molecular weight across the interface. These results show that neglecting mutual solubility, assumed to be a reasonable approximation in many cases, very often does not sustain. Instead, a diffuse interface layer develops in time with a corresponding transient interfacial tension. Depending on whether the initial interfacial tension is above or below some critical value ($\approx 4 mN/m$), the transient interfacial tension is found to increase or decrease in time, respectively. Using oscillatory dilatational interfacial experiments the viscoelastic behavior of such diffusive interfaces is demonstrated. The dilatational elasticity and the dilatational viscosity show a frequency dependency that is qualitatively described by a simple Fickian diffusion model and more quantitatively by a Maxwell model. Also, the interfacial tension and the dilatational elasticity as functions of time show the same trend as predicted by the theory of diffuse interfaces, supporting the idea that the polymer combinations under consideration indeed form diffuse interfaces.
### 3.1 Introduction

Interfacial properties of immiscible and partially-miscible polymer blends are of importance for processes related to structure development during mixing. Understanding polymer-polymer interface dynamic behavior is a key issue for controlling processes like drop break-up and coalescence. The mutual diffusion between two polymers that are not fully miscible is, at long times, restricted to a finite width [58; 59; 60]. The response of such diffusion layers to deformations, caused by interaction between the bulk flow and the drops or by interaction between two or more drops, is one of the main factors determining the final morphology of a polymer blend.

The main reason for the discrepancies between theoretical predictions on structure development and experimental results [15; 16; 17; 21; 61; 62] is, most likely, due to the complex interfacial properties of, and the mutual interaction between the polymers. In many cases mutual solubility is considered to be negligible for practical purposes [15; 16; 17; 19; 22; 63]. This seems reasonable as the polymers consist of long molecules and mixing of long molecules is thermodynamically unfavorable [64]. Moreover, polymers possess a high (macroscopic) viscosity (typically from a few up to thousands of Pa.s) and therefore mutual diffusion, if present, is expected to be slow (the mutual diffusion coefficient is of the order of $10^{-15}$ cm$^2$/s and smaller, [65]). However, the picture is different when there is a large asymmetry in molecular weight across the interface and the two polymers can interchange molecules for entropic reasons. The small molecules start the diffusion process as they move faster than the slow, entangled, large molecules and creating in this way an increase in the density in the interfacial zone that quickly settles down by the relaxation of the large chains, resembling osmotic pressure effects [65]. Despite the fundamental and practical importance of the mutual diffusion effects of immiscible and partially-miscible blends on the interfacial properties, only a limited number of experimental studies on these effects have been reported in the literature. LeGrand and Gaines [66] were first to report on mutual solubility of homologous series of polyisobutenes (PIB) and polydimethylsiloxanes (PDMS) and on the molecular dependence of interfacial tension of these pairs. For the liquid pair Vorte 125/Si 1000 (polymerized Castor oil/Silicon oil), a decrease in the interfacial tension with time was observed and attributed to a slow mutual diffusion in the highly viscous system [67]. More recently, confirming these results, a decrease of the dynamic interfacial tension with time was found for several Newtonian systems [68]. A fast decrease, followed by an increase of the interfacial tension was reported [69] for a surfactant that is diffusing from the drop (limited, small volume) to the continuous phase (unlimited, large volume). The increase of the interfacial tension was found to be due to the transfer of the surfactant into the continuous phase resulting in a depletion of the drop and the interfacial area. An increase of the interfacial tension with time was reported [61] for a PIB/PDMS combination and this was attributed to depletion of the PIB drop from small molecules through the dynamic interface subjected to steady shear. Little experimental work has been done on the viscoelastic properties of a pure polymer-polymer interface. Most of the work involves polymer blends compatibilized with some surfactant and subjected to oscillatory shear flow.
so the viscoelastic interfacial properties could be estimated by using the Palierne model (for a review see [36]). None of these studies have included diffusion effects on the viscoelastic interfacial behavior. To the best of our knowledge experimental results of the non-Newtonian behavior of a diffuse polymer-polymer interface have not been reported so far.

In this work, we report on the transient behavior of the interfacial properties of polymer combinations with small but still not zero mutual solubility. The goal is to estimate the time and length scale of the diffusion around a drop and to investigate the response of the diffuse layer to small deformations of the drop area. All measurement are done on a pendant/sessile drop apparatus. The results are interpreted in terms of a diffuse interface with a thickness $\xi(t)$ and for two simple rheological models it is examined if they can described the oscillatory results.

### 3.2 Dilatational interfacial rheology of diffuse interfaces

In the following we will focus on a rheological description, rather than an "adsorption-desorption" description, of a diffuse interface subjected to oscillatory dilatational/compressional deformation. The reason is that it is not possible to consider a diffuse interface layer as a discrete 2-D layer where specific species (i.e. molecules) set. Moreover, because the polydispersity causes different concentration profiles for different fractions of the molecular weight distribution, it is also not possible to define one specific concentration but rather think in terms of an averaged concentration.

Interfacial rheology [70] is based on the well known bulk rheology [71] and has been developed to describe the kinetics of adsorption/desorption of surfactants and the rheological behavior of adsorbed interface layers. The main differences between the 2-D interfacial and 3-D bulk rheology is that the former deals with open systems that are, in general, compressible. During dilatation/compression of a soluble adsorption layers adsorption/desorption can take place. Analogous, during dilatation/compression of a diffuse polymer-polymer interface a compression/expansion of the concentration profile in the direction perpendicular to the interface takes place. In addition, during this deformation a flux of molecules into or out of the diffuse layer can be initiated to restore the equilibrium thickness of deformed layer. The overall evolution of the concentration profile is a superposition of these two opposing processes [72]. The deformation of a diffuse interface gives rise to excess elastic and viscous stresses, related to the response of the changing interfacial tension $\gamma$. Both the elastic and the viscous contributions can be affected by the diffusion, depending on the ratio of the characteristic deformation and diffusion times.

#### 3.2.1 Principles of the radial oscillatory expansion/contraction of a sessile/pendant drop

The pendant/sessile drop technique [73] allows for nearly isotropic area changes by changing the volume of a drop hanging or sitting at the tip of a capillary. The advantage of this method is that no flow perpendicular to the interface has to be taken into account. During the area oscillations the drop shape is recorded and analyzed as a function of time using an image analyzing system. From the data the interfacial tension response function is calculated by using Fourier analysis [73].
The dilatational interfacial viscoelastic modulus, $E$, is defined as the change of the interfacial tension, $\gamma$, as a function of the interfacial area, $A$, which is subjected to a dilatation or a compression:

$$E = \frac{d\gamma}{dnA/A_0} \quad (3.1)$$

For oscillatory area change (for convenience in complex notation):

$$\Delta A(t) = A(t) - A_0 = \Delta A_0 e^{i\omega t}, \quad (3.2)$$

where $A_0$ is the initial or the equilibrium area, $\Delta A_0$ and $\omega$ are the amplitude and frequency of the area oscillations, respectively. In this complex form of the oscillatory area change the physical meaning is kept by the imaginary part. In the case of a linear response of the interfacial tension to the oscillatory area change, the frequency is the same and $\gamma(t)$ can be written as:

$$\Delta \gamma(t) = \gamma(t) - \gamma_0 = \Delta \gamma_0 e^{i\omega t + i\phi}, \quad (3.3)$$

where $\gamma_0$ is the initial or equilibrium interfacial tension, $\Delta \gamma_0(\omega)$ is the amplitude of the interfacial tension and $\phi(\omega)$ the phase angle between the area oscillations and the interfacial tension oscillations. Then the dilatational modulus $E$ can be conveniently written as:

$$E = E'(\omega) + i\eta_d(\omega)\omega = E'(\omega) + iE''(\omega) = E_0 e^{i\phi}, \quad (3.4)$$

with

$$E_0 = [E'^2 + E''^2]^{1/2}, \quad \tan \phi = \frac{E''}{E'}. \quad (3.5)$$

$E'$ is the dilatational elasticity or (in phase) dilatational modulus, $E''$ the (out phase) dilatational loss modulus (in analogy with the terminology in bulk rheology). The dilatational loss modulus is related to the dilatational viscosity by $E'' = \eta_d\omega$. The dilatational viscosity contains all relaxation processes, i.e. intrinsic viscosity and, in this case, diffusion effects. The intrinsic elastic and viscosity can, in principle, be separated from the apparent ones (due to diffusion) by applying an oscillatory interface deformation with $\omega^{-1}$ (much) higher than the characteristic relaxation time determined by the diffusion.

Combining Eqs. 3.1, 3.2, 3.3 and 3.4, after simple transformations the following relationship between $\Delta \gamma(t)$, $E'$ and $\eta_d$ can be defined:

$$\Delta \gamma(t) = E' \alpha(t) + \eta_d \dot{\alpha}(t), \quad (3.6)$$

where $\alpha(t) = ln(A(t)/A_0)$ is the deformation and $\dot{\alpha}(t) = \dot{A}(t)/A$ is the rate of deformation. From the periodic signals $A(t)$ and $\gamma(t)$, provided by pendant/sessile drop apparatus, the in phase, and out of phase contributions, $E'$ and $\eta_d$, respectively, can be calculated. The range of oscillations that can be applied is limited to relatively small frequency, $\omega \sim 0 - 0.3$s$^{-1}$ and small amplitudes, $\alpha \sim 0.0 - 0.05$. The former is determined by the bulk viscosity of the materials while the latter is necessary in order to stay in the linear regime.
3.2.2 Apparent dilatational elasticity and viscosity

The dependency of the dilatational elastic modulus and the dilatational loss modulus on the oscillatory deformation frequency is not known for systems with a diffuse interface layer. For diffusive systems with surfactants, the approach based on a Fickian diffusion does give such a relation and, hereafter, it will be investigated to what extend this relation (qualitatively) describes the diffuse interface results. For a diffusion model with one characteristic time constant the in phase and out of phase dilatational moduli are given by

\[ E'(\omega) = E_0 \frac{1 + \sqrt{\omega_0/\omega}}{1 + 2\sqrt{\omega_0/\omega} + 2\omega_0/\omega}, \]  

(3.7)

and

\[ E''(\omega) = E_0 \frac{\sqrt{\omega_0/\omega}}{1 + 2\sqrt{\omega_0/\omega} + 2\omega_0/\omega}. \]  

(3.8)

respectively [74, 75], where \( \omega_0 \) is a specific material parameter related to the characteristic diffusion relaxation time of the system under consideration.

For fast deformations, i.e. a time period much shorter then a specific diffusion time (\( \omega \gg \omega_0 \)), diffusion doesn't change the composition of the diffuse layer and a Kelvin model with a constant elastic modulus (equivalent to the Marangoni Elasticity) and a constant, intrinsic viscosity (if present) applies (Eq. 3.6). For slow deformations, i.e. a period of time much longer then a specific diffusion time (\( \omega \ll \omega_0 \)), the changes in the surface tension should be pure viscous if diffusion is the only acting process, i.e. no Gibbs Elasticity is present, and, if no intrinsic viscosity is present, these changes should go to zero for a decreasing deformation frequency.

Notice that \( E'' \) according to Eq. 3.8 has a maximum, \( E'' = 0.21E_0 \), for \( \omega = 2\omega_0 \). So if this one mode model applies and the experimental results for \( E'' \) show this maximum it is easy to determine the parameters, \( E_0 \) and \( \omega_0 \).

Another approach that can be taken is to adopt the basic model for stress relaxation process in bulk rheology, the Maxwell model. In this case the one mode version model reads:

\[ E' = E_0 \frac{\omega/\omega_0}{1 + (\omega/\omega_0)^2}, \]  

(3.9)

and

\[ E'' = E_0 \frac{(\omega/\omega_0)^2}{1 + (\omega/\omega_0)^2}. \]  

(3.10)

Again, for a one mode model, \( E'' \) has a maximum, and in this case for \( \omega = \omega_0 \) and \( E'' = 0.5E_0 \).

The results in this work will be interpreted in terms of an effective diffuse layer thickness \( \xi \) as defined in the theory of diffuse interfaces [28, 76]. Within this approach the interfacial tension is inversely proportional to this thickness, i.e. \( \gamma \sim 1/\xi \). When
the diffusion does not play a role, i.e. when deformations are fast, the layer thickness is related to the surface area by conservation of the volume, $\xi_0 A_0 = \xi A$, and thus, the dilatational elasticity too (see Eq. 3.6). This implies that the long term behavior of the dilatational elastic modulus, when measured with a high enough frequency, should follow the long term behavior of the interfacial tension. In next section results will be presented that come close to these cases.

3.3 Methods and Materials

The polymers used in this work as a drop phase were polybutene (PB, BP Chemicals, UK), polyisobutylene (PIB, Infineum, UK) and polybutadiene (PBD, Aldrich). For the bulk phase polydimethylsiloxane (PDMS, United Chemical, USA) was used. The polymers were chosen such that a broad range of interfacial properties was covered by varying the asymmetry in molecular weight across the interface. Their number average molecular weight, $M_n$, and molecular weights polydispersity, $\frac{M_w}{M_n}$, are given in Table 3.1. All materials were used as supplied.

<table>
<thead>
<tr>
<th>Polym.</th>
<th>dispersed phase/ matrix phase</th>
<th>$\mu_d/\mu_e$</th>
<th>$M_n$ [Pa.s/Pa.s]</th>
<th>$\frac{M_w}{M_n}$</th>
</tr>
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<td>635/28000</td>
<td>2.1/1.8</td>
</tr>
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<td>950/6000</td>
<td>2.5/1.6</td>
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<td>2.5/1.8</td>
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<td>950/62700</td>
<td>2.5/1.8</td>
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<tr>
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<td>1300/62700</td>
<td>2.2/1.8</td>
</tr>
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</tr>
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<td>2.2/1.8</td>
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<td>1.1/1.6</td>
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<td>12/10</td>
<td>8000/62700</td>
<td>1.1/1.8</td>
</tr>
</tbody>
</table>

*Provided by supplier.

Light scattering.

GPC based on polystyrene standards.
Table 3.2: Polymer pairs interfacial properties

<table>
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<th>Polym. comb.</th>
<th>$\gamma_0$ [mN/m]</th>
<th>$\gamma_{1/2,h}$ [mN/m]</th>
<th>$\gamma_{4h}$ [mN/m]</th>
<th>$\Delta R_{4h}$ [µm]</th>
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<td>A2</td>
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<td>55</td>
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<td>A5</td>
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<td>3</td>
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<tr>
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<tr>
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<td>$4.4^\circ$</td>
<td>$4.5^\circ$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

spectroscopy [77].

3.4 Results and discussion

3.4.1 Transient interfacial tension and drop size reduction

As it is not our goal, at this stage of our work, to give a full characterization of an extensive set of polymer combinations, but rather to demonstrate how far effects on the transient and oscillatory behavior of diffuse interfaces are similar as those found with surfactants, we limit ourselves to give a complete set of transient results, an extended set of oscillatory results for one specific polymer combination, and, finally, show some the general trends in oscillatory deformations for some of the other combinations. It is important to notice that some of the limitations were put forward by, for example, the high viscosities of the polymer combinations which restricted the frequency range that could be applied by the experimental system.

The mean values of the interfacial tension $\gamma$ (with accuracy $\pm 0.1$ mN/m) at three successive moments are given in Table 3.2. The arrows in Table 3.2 indicate the tendency of the change in time. In Fig. 3.1 the long term behavior of the interfacial tension for a special set of polymer combinations is shown; the matrix phase is kept the same ($M_n = 62700$) while the drop phase is changed by increasing $M_n$ from 635 to 8000. It is observed that with increasing $M_n$ and decreasing asymmetry in molecular weight of the components the interfacial tension increases.

Although, in the literature, most of the polymers under consideration are assumed as immiscible, the decay and the increase of the transient interfacial tension as seen in Fig. 3.1 and in Table 3.2 (indicated with arrows), can be explained by mutual diffusion. For apolar/apolar interaction between polymers, the interfacial properties mainly depend on the asymmetry across the interface (i.e. the molecular weight difference), the average molecular weight and the polydispersity of both phases. The polydispersity of the materials contributes to the interface formation since the mutual solubility is enhanced. First, because the asymmetry across the
interface is enlarged and, secondly, because the small molecules diffuse faster than the large ones. However, the polymer combinations were chosen in such way that they have similar polydispersity. Therefore, the effect from the polydispersity will not be discussed extensively hereafter.

The change of the drop size after 4 hours (ΔR4h, Table 3.2) due to mutual diffusion was used as an estimate for the length scale of the diffusion. The accuracy of measuring ΔR is ±0.5 μm and that is why one of the material combinations shows zero diffusion. The thickness of the diffusion layer around a drop can be estimated to be at least of the order of magnitude of ΔR. In reality it should be few times larger than ΔR, at least for the first hour for the A combinations, where γ is a decreasing function in time. To validate this statement we performed confocal Raman spectroscopy [77]. The two liquids were sampled in a standard microscope glass in such way that the denser one (PDMS) is lying beneath the lighter one (PIB or PBD). The two samples were scanned in confocal way for the concentration of the double bonds in ± 50 μm range perpendicular to the interface. The double bonds, which demonstrate strong Raman absorptions, are only present in one of the samples (PIB or PBD but not in PDMS). For combination A5 the thickness of the diffuse interface was measured to be 35 ± 3μm after 3-4 hours, while for the same combination ΔR4h is 14 μm. Using the same technique for combination B4, no diffusion was detected, at least within the accuracy of the technique (±3 μm), for 2-3 days. This result is also in agreement with the ΔR4h measurement. The diffusion process is clearly demonstrated by the change of the drop size, see Table 3.2. In all cases the molecular weight of the drop phase is smaller than for the matrix and thus the drops reduce in size. It is observed that the changes are larger for lower molecular weight drop material and for a larger asymmetry in the

![Figure 3.1: Transient interfacial tension for a drop phase with different molecular weights. The matrix phase is kept the same (PDMS60k).](image-url)
molecular weights. Moreover, the larger changes in drop size correlate with lower interfacial tensions which, in turn, indicates thicker diffuse interfaces (see Fig 3.2). Finally, small changes in drop size also correlate with small changes in time of the interfacial tension, see Fig. 3.1.

Relating the interfacial tension to the interfacial thickness, it follows that for the time period used thick interfaces become initially thicker, see Fig. 3.1 and Table 3.2, and than for some combinations (A1-A3) thinner, while the thin interfaces only become thinner. Moreover, the effects are much stronger for the thick interfaces (low interfacial tension) than for the thin interfaces (high interfacial tension). So the combination of the (transient) interfacial tensions and the evolution of the change in the drop sizes gives us a clear picture of the evolution of the diffuse interface layers for the different material combinations. Due to the polydispersity the diffusion kinetics at or close to the interface can be rather complex, as shown by the transient behavior of the interfacial tension (see Fig. 3.1, A2 system). Therefore, in the sequel, the long term change of the drop radius is taken as a characteristic value for the (mixed) diffusion time.

The observation from Fig. 3.1 that below $\gamma \approx 4 \text{mN/m}$ the diffusion leads to a decay followed by an increase of the interfacial tension (for example the A2 curve), while above this value the diffusion leads to an increase in the interfacial tension can be explained by considering the interface to have a selective permeability that is determined by the initial interfacial tension. With a relatively high initial $\gamma$, respectively average $M_n$, the permeability of polymer-polymer interface is restricted to the small molecules. The decay and the increase of $\gamma(t)$ for the "A" combinations can be explained by accumulation and depletion at and from the interface layer of the small molecules with a relatively broad molecular weight distribution (A1, A2 and A3). Accumulation when the initial diffusion builds the diffusion layer and depletion when the finite amount of these small molecules in the drop spreads out in
the matrix. The increase of the interfacial tension for the "B" combinations is then explained by the diffusion of a much smaller amount of molecules with similar size as those that diffuse in "A" combination, which move through the interface without reaching a high enough concentration (also due to a short residence time) to enrich the interfacial zone. In other words, one can say that the diffusion in "B" pairs is restricted to a smaller fraction of the molecules and is faster, preventing thickening of the interfacial zone. Hence, the interfacial width for "B" combinations is expected to be much smaller than for "A" combinations where the diffusion causes a reduction of the interfacial tension, at least in time range of the first hours. The equilibrium γ for "B" pairs which is reached much faster than for "A" pairs confirms this. For example, for the B4 combination the equilibrium value γ = 4.6 mN/m is reached after 4-5 hours while for the A5 pair the equilibrium value γ = 3.2 mN/m is reached after, at least 24 hours.

With increasing the average molecular weight of both phases, the value of the dynamic interfacial tension also increases and, moreover, slows down the diffusion substantially as is observed from the change of γ with time (Table 3.2 and Fig. 3.1). This is understood from the fact that mixing of long molecules is less favorable [64], a well known phenomenon that was reported also by others [78; 79]. The results also show that the effect of the low molecular weight phase (here this is always the drop phase except for the B3 combination) on the value of the interfacial tension (the A combinations versus the B combinations) is more pronounced than the ratio of the molecular weight. For example, the systems B4 and A3 have the same order of asymmetry but a large difference in the interfacial tension γ while the systems B3 and B4 have a big difference in asymmetry but relatively small difference in γ.

3.4.2 Oscillatory experiments
The oscillatory experiments were performed on the pendant/sessile drop apparatus as well. From these experiments the dilatational elasticity $E''$ and dilatational viscosity $\eta_d$ were determined. Table 3.3 gives an overview of all oscillatory experiments.

<table>
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<tr>
<th>Experiment number</th>
<th>$T$ [s]</th>
<th>$\omega$ [s$^{-1}$]</th>
<th>$E'$ [mN/m]</th>
<th>$E''$ [mN/m]</th>
<th>$\eta_d$ [s.mN/m]</th>
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</thead>
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<td>0.34</td>
<td>1.60</td>
</tr>
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<td>0.47</td>
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</tr>
<tr>
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<td>-0.40</td>
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</tr>
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<td>60.5</td>
</tr>
<tr>
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<td>85.9</td>
</tr>
<tr>
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<tr>
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<td>2.55</td>
<td>8.50</td>
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</table>

Table 3.3: Interface characteristics and parameters obtained by oscillatory experiments.
done. The table shows that the "B" pairs that have thinner interfaces, i.e., higher interfacial tensions, have a higher dilatational modulus compared to the "A" pairs that have thicker interfaces, i.e., lower interfacial tensions. This is rather important as $E'$ plays a significant role during structure development in emulsions and polymer blends with respect to the interfacial mobility [80].

![Graph showing interfacial tension vs. interface deformation](image)

Figure 3.3: Typical interfacial tension versus interface deformation curves for three experiments with different polymer combinations and frequencies of oscillations (A2-1, A6-1, B2-1).

Fig. 3.3 gives three typical examples of the different viscoelastic responses that can be found depending on the material combination and the frequency. The plot shows the response of the interfacial tension due to oscillatory interface deformation for several periods. The experimental conditions are specified in Table 3.3. Combination A2-1 is a typical example of a mainly elastic response, combination A6-1 a fully viscous response (the slight negative average slope of the curve is considered as an experimental artifact) and, finally, combination B2-1 shows clearly both aspects, resulting in a large hysteresis loop.

For the material combination B4 the viscoelastic response was measured over a range of frequencies. The (apparent) dilatational elastic and the (apparent) dilatational viscous moduli as a function of the radial frequency are shown in Fig. 3.4. For all results presented here the deformation amplitude was in the linear range. Some of the measurements were repeated to demonstrate the reproducibility. The results show the expected trends for a diffusion controlled interfacial response. This is, in a qualitative sense, confirmed by Eq. 3.7 and Eq. 3.8 for which the parameters values $\omega_0 = 0.05$ and $E_0 = 25$ were used (see Fig. 3.5). Notice that the experimental curves cross, a feature that is not described by the Fickian diffusion model (Eq. 3.7 and Eq. 3.8). The Maxwell model (Eq. 3.9 and Eq. 3.10) does give a much better description (see Fig. 3.6, $\omega_0 = 0.1$ and $E_0 = 14$, based on the maximum of $E''$),
Figure 3.4: Frequency dependence of the dilatational interface moduli $E'$ and $E''$ for system B4. The solid lines are drawn to guide the eye.

Figure 3.5: $E'$ and $E''$ dependence from $\omega$ for system B4 (solid lines). Comparison with the Fickian model predictions (dash lines), Eqs. 3.7 and 3.8.

and does capture the crossover of $E'$ and $E''$. From $\omega_0$ a characteristic relaxation time $\tau_d = 2\pi/\omega_0$ of the interface due to diffusion can be determined, $\tau_d \approx 63$s. An even better description is obtained with a two mode model ($\omega = (0.125, 0.167)$, $E_0 = (8, 6)$) see Fig. 3.7. For clearness Fig. 3.8 shows the experimental and fitted (two modes Maxwell model) $\eta_d$ as a function of $\omega$. 
Figure 3.6: $E'$ and $E''$ dependence from $\omega$ for system B4 (solid lines). Comparison with the predictions of an one mode Maxwell model (dash lines), Eqs. 3.9 and 3.10.

Figure 3.7: $E'$ and $E''$ dependence from $\omega$ for system B4 (solid lines). Comparison with the predictions of a two mode Maxwell model (dash lines).

Next, we measured the long term (for $10^4$s) dilatational modulus behavior for system A2 (Fig. 3.9). This system showed the most particular transient behavior for the interfacial tension (see Fig. 3.1) and, therefore, is considered as a good test of the posed correlation between interfacial tension and dilatational modulus. The frequency was $\omega = 0.2$ for which the interface response was mainly elastic
Chapter 3

Figure 3.8: $\omega$ dependence of dilatational viscosity $\eta_d$ for system B4. Comparison with two mode Maxwell model prediction (solid line).

Figure 3.9: Comparison between the transient behavior of $\gamma$, $E'$ and $\eta_d$ for system A2.

(see Table 3.3). As explained before, for fast enough deformations, the dilatational modulus should follow the same trend as the interfacial tension. In Fig. 3.9 the time evolutions of the interfacial tension, the dilatational modulus and the dilatational viscosity are plotted. It is observed that, indeed, this expected coupling between the interfacial tension and the dilatational elastic modulus is present for this system. Notice that the long term behavior of the dilatational viscosity is opposite to that of the dilatational modulus. Similar measurements were done for system B2, but now
for the same frequency $\omega = 0.2$ the oscillations has to be considered as a slow, i.e. the (fast) diffusion processes govern the interfacial behavior (Fig. 3.10). It is seen that the correlation between interfacial tension and dilatational elastic modulus is lost.

### 3.5 Conclusions

In summary, we have determined that diffusion can lead to either decreasing or increasing transient interfacial tension, depending whether the initial $\gamma$ is above or below some critical value (in our case around $4\text{mN/m}$). In the first case thick diffuse interfaces are formed on a time scale of a few hours while in the second case thin interfaces are formed. These properties were obtained by varying the asymmetry in molecular weight across the interface of polymer combinations. Oscillatory experiments show that the rheologically behavior of both type of systems ("A" and "B") is frequency dependent, qualitatively described by a simple diffusion model but quantitatively described by a Maxwell model (2 mode model). For system B4 the dilatational elastic and loss moduli showed a crossover from which the relaxation time of the diffuse interface can be determined. Moreover, the transient interfacial tension and dilatational elasticity show the same trend as predicted by the theory of diffuse interface, supporting the idea that the polymer combinations indeed form diffuse interfaces. It is expected that the "B" combinations will give more predictable results during structure development experiments as their interfacial thickness is much closer to a sharp interface, usually assumed in the models. However, the larger values for the elasticity $E'$ for these polymer pairs will give rise to stresses opposing interfacial deformation (i.e. Marangoni stresses). The same holds for "A" polymer combinations but there the interfacial response will be weaker due to the lower values of $E'$. In Chapters 4 and 5 we show that the diffusion length scale has
a large effect on film drainage between two interacting drops.

We conclude that neglecting mutual solubility, assumed to be a reasonable approximation in many cases, is very often not allowed. The results show that a diffuse interface, especially for systems with small diffusion, has a viscoelastic behavior which has to be considered during a structure development experiments.
Chapter 4

Diffusion Controlled Film Drainage and Instabilities in Polymer-Polymer Systems

We report an experimental investigation of the effect of mutual diffusion between two polymers on film drainage, and thus on drop coalescence. The goal is to show the influence of diffuse interfaces on film drainage. This is demonstrated by using two different material combinations with different interfacial properties. Interferometric visualization of the film between two interacting drops shows that for a diffuse system film drainage is, in contrast to immiscible systems, non-axisymmetric and unstable already at thicknesses of the film formation (1-2 μm). Depending on whether the total thickness of the diffusion layers in the film is smaller or bigger than the thickness of the film, Marangoni convection was found to enhance or delay film drainage. Enhanced film drainage is estimated to be in order of 100 times faster than predicted by the current models, while reduced drainage is observed after a time period where experimental and predicted results are in close agreement.

4.1 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 in polymer blends is, apart from its importance for the production of new tailored materials, of fundamental interest as well, 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 up to the critical film thickness is considered to be the rate-determining step in drop coalescence [3].

In this paper we will focus on polymer blends. Mutual diffusion in polymer blends is mostly considered negligible for practical purposes [15; 16; 17; 19; 22; 63] and this assumption seems reasonable due to high macroscopic viscosities and because mixing of long molecules is thermodynamically unfavorable [64; 65]. However, the molecular weight polydispersity of most (commercial) polymers will enhance mutual solubility, since short molecules have a higher entropy of mixing than long ones [81].

The discrepancies between predicted and experimentally determined drop coalescence rates (in particular in the film drainage step) as reported in the literature [62; 15; 16; 17; 21; 61] are, most likely, due to a small but still non-zero mutual solubility in polymer systems. Even a small solubility can, in analogy to the effect of a small amount of surfactant, substantially alter the interface response to a deformation [24; 26]. The effect of mutual diffusion becomes even more important during the film drainage step where small length-scales are involved; film thicknesses of the order of 1 μm and less. It is known that for systems with pure interfaces 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 [5; 10; 12]. However, in systems with surfactants and/or diffuse interfaces, they can loose their importance 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 two interfaces in the film region, which leads to inhomogeneous surfactant distribution or inhomogeneous thickness of the diffuse layer along the drops interfaces. This produces interfacial tension gradients that induce (Marangoni) stresses [82]. They can overrule film drainage and even stop drop coalescence. While these effects are well investigated for systems with surfactants and for thermally induced gradients [24; 26; 25; 83; 84; 85], they are hardly studied for diffuse systems. MacKey and Mason [4] were the first to point out the importance of diffusion effects of a third component (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 [86; 87] when again a third component was diffusing from the drop to the matrix phase. On the contrary, thick and very stable aqueous films between oil phases were observed in systems where a surfactant diffuses across the interface towards the film [88]. This phenomenon was related to an osmotic pressure difference that exists between the film and the surrounding area, caused by the increase of the surfactant micelles concentration in the film.

In this paper we present experimental film drainage results for polymer-polymer combinations with varying interfacial properties (interfacial tension and diffuse interface length scale), using direct observations of the film drainage process and of the film thickness evolution. The aim is to understand the film drainage in complex polymeric systems with polydisperse molecular weights of the two phases, ensuring
asymmetry of the molecular weights across the interface and thus mutual diffusion.

4.2 Materials and methods

The polymers used in this work are polybutene (PB, BP Chemicals, UK), polyisobutylene (PIB, Infinum, UK) and polybutadiene (PBD, Aldrich) as the dispersed phase and polydimethylsiloxane (PDMS, United Chemical, USA) for the matrix phase. These materials have been frequently used in experiments on structure development [19; 20; 21; 61; 63; 89], mainly because they are considered to be ideal model systems, concerning their viscosity at room temperature, while their mutual solubility is considered negligible. In Chapter 3 we reported a detailed bulk and interfacial characterization of these polymer combinations and in Table 4.1 the relevant properties are summarized. The coding of the combinations is kept the same as in Chapter 3. The number molecular weight, $M_n$, is given after each of the polymer abbreviations. The zero shear viscosities ($\mu_d$ for the dispersed phase and $\mu_c$ for the continuous phase), were measured using a rotational viscometer (Rheometrics, ARES) using a plate-plate configuration and applying steady shear. At shear rates below 30 s$^{-1}$ and at 25°C, all polymers show Newtonian behavior, i.e., no shear rate dependency of the viscosity was found. In all coalescence experiments performed, slow collision rates (with approach velocities of the order of 1-3 $\mu$m/s) were used to ensure Newtonian behavior of the materials. 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 $\gamma_{dd}$, 4 hours later) are also given in Table 4.1. The arrows in Table 4.1 indicate the tendency of the change in time of $\gamma$. The change of the size of a sessile drop after 4 hours ($\Delta R_{4h}$, Table 4.1), due to mutual diffusion, was used as an estimate for the length scale of the diffusion. The accuracy of the method is ±0.5 $\mu$m and that is why one of the material combinations shows zero diffusion. The thickness of the diffusion layer around a drop can be estimated to be at least of the order of magnitude of $\Delta R$. In reality it should be few times larger than $\Delta R$, at least for the first hour for

<table>
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<th>Polym. comb.</th>
<th>disp. phase/</th>
<th>$\mu_d/\mu_c$ [Pa.s/Pa.s]</th>
<th>$\gamma_{fresh}^*$ [mN/m]</th>
<th>$\gamma_{dd}^*$ [mN/m]</th>
<th>$\Delta R_{4h}$ [µm]</th>
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<td>2.5</td>
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<td>B1</td>
<td>PBD1800/PDMS28k</td>
<td>0.7/1.0</td>
<td>4.0</td>
<td>4.0</td>
<td>1.5</td>
</tr>
<tr>
<td>B3</td>
<td>PBD8k/PDMS66k</td>
<td>12/0.1</td>
<td>4.2</td>
<td>4.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*a few minutes after the drop is formed.

*b hours after the drop is formed.
the A combinations, where $\gamma$ is a decreasing function in time. For the combinations A5 and B1, the evolution of the thickness of the diffusion zone was measured by means of confocal Raman spectroscopy [77]. For A5 the thickness of the diffuse layer was, after 3-4 hours, determined to be $35 \pm 3\mu m$. For B3, within the accuracy of the technique, for 2-3 days, no diffusion was detected. For more detailed results on these materials combinations, the reader is referred to Chapter 3.

Film drainage experiments were performed with two captive drops of radius $R_d \approx 750 \mu m$, formed at the ends of two tubes that are incorporated in a stainless steel box filled with the continuous phase. The bottom tube can be moved towards the upper one by means of a motor (for a detailed description of the set-up see Chapter 2, and [48; 83]). A film is formed during the approach with a constant velocity (1-3 $\mu m/s$) and when flattening between the drops is observed, the approaching is stopped. The films are interferometrically visualized with reflected laser light ($\lambda = 632.8nm$) and the images are recorded by means of a CCD camera and a video recorder (Fig. 4.1). 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 evolution of the film thickness and of the film profile, Chapter 2. For some of the experiments, the thickness at rupture is determined by using the changes in intensity of the reflected light [42].

4.3 Results and discussion

4.3.1 Film drainage: observations

Fig. 4.1 shows the film evolution for two fresh systems, i.e. results obtained a few minutes after the drops are formed: the A1 pair (pictures: a-c) and the B1 pair (pictures: d-f). The A1 pair is representative for a system with a thick diffuse layer and the B1 pair for a system with a relatively thin diffuse layer. 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 $\mu m$. For system A1 many peristaltic instabilities are observed during the drainage, which grow until, after 20 s, film rupture occurs. In contrast, the instabilities in the B1 system are more restricted; they grow to some extend and reverse, leading to much longer film drainage times. The parameters $\gamma$ and $\mu_d$, that are known to influence the film drainage [12], have values that favor faster drainage of system B1. However, the drainage for system A1 is at least 10 times faster. The discrepancy arises from the fact that all drainage theories [5; 10; 12] assume sharp interfaces, while in reality a small solubility substantially changes film drainage. In diffuse systems, parameters like the film radius and the drop radius loose their importance. For system B1, it should be stressed that although $\gamma$ is constant during the first 4 hours (within the accuracy $\pm 0.1 mN/m$, see Table 4.1) the film drainage is unstable. Therefore, it is the thickness of the diffusion layer (in our case the relevant parameter is $\Delta R_{4h}$), rather than the tendency of the interfacial tension to change in time that should be taken into account.

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 and more developed than for the B1 systems (see $\Delta R_{4h}$.
in Table 4.1). Two drops were formed and left in the matrix for different times before being brought into contact. In Fig. 4.2 a comparison is made between a fresh system, with only a few minutes of drop residence time before starting the experiments, pictures: a-d, and an old system, with a few hours of drop residence time before starting the measurements, pictures: e-h. These results illustrate that film drainage in the fresh system is stable and axisymmetric. The time of drainage is approximately 30 minutes 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 diffusion layers plays an important role and is in favor of the film drainage. An interesting feature can be observed; the film rupture event is much
Figure 4.2: Comparison between the film drainage behavior of a fresh A5 system (pictures: a-d) and an old A5 system (pictures: e-h). The reference bar in picture a is equal to 100 μm. Note the difference in time, at the bottom of the pictures.
slower compared to systems with apolar/polar interactions and can be followed for several seconds (Fig. 4.2, d and h). 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 4.1).

### 4.3.2 Mechanism of film drainage in systems with diffuse layers

When diffuse layers of two drops overlap during a collision, the concentration in this zone becomes higher, resulting in a lower interfacial tension relative to the interfacial tension of those parts of the drops that are not in contact. Moreover, film drainage also enhances the uneven thickness 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. Depending on the distribution of the thickness of the interfacial layer they can promote or reduce film drainage [4; 82]. Fig. 4.3a schematically shows 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 than the minimal film thickness. This mechanism is thought to be responsible for a stabilization of the film by opposing the film drainage.

![Figure 4.3: A schematic representation of a half film region with a hydrodynamic dimple: (a) without overlap of the diffuse layers where Marangoni convection (dashed arrows) is opposing the film drainage, and (b) with overlap of the diffusion layers where Marangoni convection is locally promoting the film drainage.](image)

When there is an overlap in the diffuse layers, see Fig. 4.3b, the Marangoni convection promotes local film drainage. The unstable and non-axisymmetric film drainage observed in Figs. 4.1 and 4.2 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. It should be mentioned that in this rather simple description of how gradients in diffuse interfaces cause Marangoni convection, the ongoing process of diffusion is neglected during the film drainage process. Only the age of the interface, giving some interfacial thickness, and film formation effects are mentioned. In reality, depending on the time scales of the different processes, ongoing diffusion might also contribute to the film drainage process.
4.3.3 Film drainage for systems with thick diffuse layers: a 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. Here we will use two asymptotic laws for the evolution of the film thickness, $h$, for the limiting cases of immobile and partially-mobile drainage [12]:

$$h = \left( \frac{0.36 \mu_c}{\gamma} \right)^{1/2} \frac{R_d^{1/2} a}{t^{1/2}}, \quad \lambda \to \infty \quad (4.1)$$

$$h = \left( \frac{0.32 \mu_d}{\gamma} \right)^{2/3} \frac{R_d^{1/3} a^{4/3}}{t^{2/3}}, \quad \lambda \to 0 \quad (4.2)$$

where $t$ denotes the time and $a$ the film radius. In the experiments where the film radius is changing during the initial stage of film drainage the comparison is made only for the final one when the film radius is fixed. First we consider systems A, which have a relatively thick diffuse interface (see materials section). The minimum film thickness versus time for the system A3 is presented in Fig. 4.4. Results from two

![Diagram](image_url)

Figure 4.4: Film thickness evolution curves for the system A3. The aging of the system leads to approximately 3 times faster film drainage. The theoretical predictions (dash line, Eq.4.2) under estimate the film drainage around 100 times.

experiments are given with the same experimental conditions but different system age. The relatively 'fresh' system (10-15 minutes after the two phases were loaded) shows a stable film drainage and 2-3 times slower rate of drainage compared to the 'old' system (> 1 hour) that shows unstable drainage. Moreover, Fig. 4.4 illustrates
that the film drainage is approximately 100 times faster than what the partially-mobile model predicts (dash line, Eq. 4.2). The predicted asymptote is obtained by using the parameters from Table 4.1 and the relevant experimental conditions. Fig. 4.5 shows similar results for the A5 combination, which has a 100 times higher matrix viscosity (10 times higher Mn). A 'fresh' (few minutes residence time), an 'older' (half an hour) and 'old' (> 1 hour) system were used. Again the fresh system

![Graph showing film thickness evolution curves for combination A5.](image)

Figure 4.5: Film thickness evolution curves for combination A5. The aging of the system leads to a few times faster film drainage. The theoretical predictions (dash line, Eq.4.2) under estimate the film drainage around 100 times.

is slower and the deviation from the model predictions is again approximately 100 times, stressing that in such systems other phenomena than those incorporated in current models on film drainage are governing the coalescence process. Fig. 4.5 shows another interesting feature; while the 'fresh' system shows stable film drainage (Fig. 4.2 a-d), and thus the film radius, \( a \), is still a relevant parameter, the other two experiments show unstable film drainage and \( a \) is loosing its importance. For example, although in the 'older' experiment the film radius is smaller than in the 'old' experiment the film drainage is slower.

One more set of experiments was performed with the A6 system which has a two and half times higher viscosity (1.4 times higher Mn) compared to the A5 system. Here the effect of aging of the system was not studied (all experiments were performed one after the other). No big differences are observed in comparison with the previous experiments and, again, film drainage is approximately 100 times faster than what the model predicts, see Fig. 4.6. The difference in the slopes between the first experimental curve and next two can be attributed to the continuously increasing film radius, \( a \), in the first one. In the same way, the two parts with different slopes in the film thickness evolution curves in Figs. 4.5 and 4.6 can be explained. The first, steep part can be consider as drop interaction with increasing force (increasing film radius \( a \)), while the second part as drop interaction with constant force.
(constant \( a \)). This is the main reason why the asymptotes are compared with the second part. The film radius is not that controllable parameter because the A systems have relatively small interfacial tension but high viscosities, which results in a prior deformation of the drops, followed by drop shape relaxation after the approach is stop.

The film thickness at rupture, \( h_{cr} \), was measured for the experiments presented in Figs. 4.5 and 4.6 using the change in intensity of the reflected light from the film interfaces [42]. The last points in the film drainage curves in these plots represent the values of the critical thickness at rupture. For system A5 a value of 67±5 nm for \( h_{cr} \) was determined, which is very close to the calculated value of 53 nm using the available models for film rupture [11]. 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±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. This is not taken into account in the models [11].

The results of the experiments with the A combinations are in agreement with other experimental observations we made on the attraction between two droplets that were put in an overall quiescent matrix at a mutual distance that ensured overlap of their diffuse layers, see Chapter 5. Attraction between immiscible droplets is normally not observed. However, here the results show the important role of the diffusive effects that facilitate coalescence by increasing the length scale at which drops 'notice' each other. Additional evidence for these effects comes from results on shear induced coalescence in a blend of an A type system [19]. The authors observed a rate of drop coalescence that was higher than expected from theory, while the reproducibility of their experiments was very good. They did not consider
diffusion as a cause for their results but attributed the high tendency of coalescence to a large film rupture thickness (150-200 nm).

In addition, one more rather interesting conclusion can be drawn from the film drainage experiments regarding the process of mutual diffusion in the A combinations. The results for the fresh systems (in Figs. 4.4, 4.5 and 4.6) show that only a few minutes after the two phases were brought into contact, the diffusion is well in progress (with length scale of a few μm and larger) since the deviation from the predicted drainage results is already a factor of 100 times. This fast response is contributed to the small molecules that initiate the diffusion process as they move much faster than the slow, entangled, large molecules. The small molecules thus determine the initial interface thickness and profile while the final profile is determined by the diffusion of the large molecules [65]. 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.

4.3.4 Film drainage for systems with thin diffuse layers: a comparison with available film drainage models

A relatively stable and axisymmetric film drainage was observed for the B3 system that consists of closely matched molecular weights (Table 4.1). The results from these experiments are presented in Fig. 4.7 for a ‘fresh’ (15 minutes drops residence time) and an ‘old’ (> 1 hour) system. These experimental results are much closer to the model predictions than was the case for the A systems. Moreover, it is seen that aging of the system leads to deviations from the asymptotic behavior. The results for

![Figure 4.7: Film thickness evolution curves for system B3. The aging of the system leads to deviation from the model predictions.](image)

the 'fresh' system are in good agreement with the partially-mobile asymptote (dash line, Eq. 4.2), at least for the first 10 minutes (at that moment an early rupture of the film occurred). The results for the 'old' system show that at some moment
film drainage faster than the model predictions is observed, although the deviation is not that large, after which the drainage slows down again and even reverses (Fig. 4.7, last part of curve B3 - old).

An explanation based on a mechanism similar to that presented in Fig. 4.3a can be given to understand the observed reversing 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 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, Chapter 5 and [89; 20]. For example, for B systems we observed a repulsion between two drops brought into close contact and left to interact in an overall quiescent fluid matrix, see Chapter 5. The reversing of the film drainage, as is seen in Fig. 4.7, is the same process but a separation of the drops is not possible since they are captive. In [89] a B type system was subjected to simple shear and it was found that drop coalescence had little effect on the drop size evolution. This observation is in agreement with the results presented in Fig. 4.7. Finally, in [20] it was reported that 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 4.1). The mechanism (Fig. 4.3b) that promotes the film drainage is switched on and the overall result is faster coalescence. In contrast, for smaller $M_n$ 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. 4.3a and 4.7).

### 4.4 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 $\mu$m), and B systems, which are polymer combinations with relatively thin diffuse layers (from a submicrometer to a few $\mu$m). 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 (for system A5). The film drainage results for the more diffusive A systems show an approximately 100 times faster drainage rate than predicted by the current models, while the less diffusive B systems gave results close to the 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 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.
Chapter 5

Diffusion Controlled Drop Coalescence in Polymer-Polymer Systems

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Diffusion Controlled Drop Coalescence in Polymer-Polymer Systems

We report an attraction between two drops with thick diffuse interfacial layers (tens of \(\mu m\)) when the layers overlap. In contrast, a repulsion between two drops with relatively thin diffuse layers (within 1\(\mu m\)) is observed when the drops are brought into close contact. This is achieved by using a novel experimental approach in which the flow effects on drop interaction are avoided. A mechanism, based on Marangoni type of convection is used to explain the observed phenomena. Results from numerical simulations, based on the diffuse interface method, support this explanation.

5.1 Introduction

Theoretical and computational modeling [2; 3; 5; 8; 9; 10; 11; 90; 91] of coalescence processes is well advanced but experimental work is still limited. The latter is usually performed by monitoring flow-induced drop coalescence [21; 61; 63; 19; 89; 20], which does not allow the flow effects to be separated from specific effects related to material properties. In this paper, we report diffusion controlled drop coalescence. The bulk flow is used only either to bring the drops in close proximity or into contact. The importance of material interfacial properties such as a dynamic interfacial tension and the thickness of a diffuse interface layer around the drops on drop coalescence is demonstrated. Depending on whether the length scale of diffusion is larger or smaller than 1-2 \(\mu m\) (the length scale related to the thickness of
Table 5.1: Materials and materials characteristics

<table>
<thead>
<tr>
<th>Polym. comb.</th>
<th>disp. phase/ matr. phase</th>
<th>$\mu_d/\mu_c$ [Pa.s/Pa.s]</th>
<th>$\gamma_0$ [$\text{mN/m}$]</th>
<th>$\gamma_1^{1/2h}$ [$\text{mN/m}$]</th>
<th>$\Delta R_{1/2h}$ [$\mu m$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2</td>
<td>PB635/PDMS60k</td>
<td>3/10</td>
<td>2.4</td>
<td>1.8</td>
<td>43</td>
</tr>
<tr>
<td>A5</td>
<td>PIB950/PDMS60k</td>
<td>30/10</td>
<td>2.8</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>B2</td>
<td>PBD1800/PDMS60k</td>
<td>0.7/10</td>
<td>4.0</td>
<td>4.1</td>
<td>0.7</td>
</tr>
<tr>
<td>B4</td>
<td>PBD8k/PDMS60k</td>
<td>12/10</td>
<td>4.1</td>
<td>4.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*a few minutes after the drop is formed.

*b half an hour after the drop is formed.

the film formation Chapter 4) the diffusion is found to facilitate or suppress drop coalescence. Both phenomena are attributed to interfacial tension gradients (inducing Marangoni stresses) due to thickness variations of the diffuse layers around the interacting drops. The mechanism proposed is supported by results from numerical simulations based on the diffuse interface method [28; 76]. The results show that solubility in polymer systems can not be neglected, as it is usually done [19; 20; 63; 89], since it can have an overruling effect on drop coalescence.

5.2 Materials and Methods

The polymers used as the drop phase were polybutene (PB, BP Chemicals, UK), polyisobutylene (PIB, Infineum, UK) and polybutadiene (PBD, Aldrich). For the bulk phase polydimethylsiloxane (PDMS, United Chemical, USA) was used. The polymers were chosen such that a broad range of interfacial properties was covered by varying the asymmetry in molecular weight across the interface. All materials were used as supplied and their characteristics are listed in Table 5.1. The coding of the combinations (A2, A5 etc.) is kept the same as in Chapter 3. The number molecular weight, $M_n$, is given after each of the polymer abbreviations. 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 25°C, all polymers show Newtonian behavior, i.e., no shear rate dependency of the viscosity. In all coalescence experiments we performed, slow approach velocities (of the order of 0.1 mm/s) were used to ensure Newtonian behavior of the materials. 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 (with an accuracy of ±0.1 mN/m) at two successive moments are also given in Table 5.1, the arrows indicate the tendency of change of $\gamma$ in time. The change of the size of a sessile drop after 1/2 hour ($\Delta R_{1/2h}$, Table 5.1), due to mutual diffusion, was used as an estimate for the length scale of the diffusion. The accuracy of the method is ±0.5 μm and that is why one of the material combinations shows zero diffusion. The thickness of the diffusion layer around a drop can be estimated to be at least of the order of magnitude of $\Delta R$. In reality it should be few times larger than $\Delta R$. 
at least for the first hours for the A combinations, where \( \gamma \) is a decreasing function in time. For the polymer combinations A5 and B4 the evolution of the thickness of the diffusion zone was measured by means of confocal Raman spectroscopy [77]. For combination A5 the thickness of the diffuse layer was, after 4 hours, determined to be \( 35 \pm 3 \mu m \). For the combination B4 no diffusion was detected within the accuracy of the technique for 2-3 days, indicating that the diffusion for the B pairs is much more restricted in length than for the A pairs. For more detailed information on these material combinations the reader is referred to Chapter 3.

The coalescence experiments were performed in a cross-slot flow set-up [92; 93], (Fig. 5.1). The set-up produces a two dimensional hyperbolic extensional flow and was used to monitor drop interaction for almost quiescent conditions (density difference around 0.08 g/cm\(^3\)). The drops were formed at the stagnation point of the flow cell by initially introducing one drop, which was broken into two by applying a flow above the critical capillary number (\( Ca = \mu \epsilon R/\gamma \), where \( \epsilon \) denote the deformation rate for elongational flow) for the current fluid combination (Fig.
5.1a). The two drops were subsequently forced to approach by applying a reverse flow in a stepwise manner (the flow can be stopped suddenly), controlling the distance between them (Fig. 5.1b). The advantage of this approach is that flow history effects on drop coalescence can be avoided.

5.3 Results and Discussion

5.3.1 Experimental observations and results

The effect of diffusion on drop coalescence

In Fig. 5.2 drop coalescence for two systems, A2 (pictures: a–f) and B2 (pictures: g–l) is shown. The drops were forced to approach until a certain separation between them was obtained (Fig. 5.2a and Fig. 5.2g). Then the flow was stopped and the two drops were left to come into contact by relaxation of their shapes from elongated to spherical. All coalescence experiments were performed almost immediately (within few minutes) after the two drops were formed. Both experiments shown in Fig. 5.2 were repeated several times and a very good reproducibility of the coalescence times (± few seconds), was obtained. This was unexpected considering the complexity of the phenomena. Fig. 5.2 shows that despite the fact that all material characteristics (γ and μ, Table 5.1) and process parameters (drop radius and contact zone, i.e. film radius, Fig. 5.2) are, according to the known models [12], in favor of system B2, the coalescence there is approximately 3 times slower than in system A2. This is pointing to an additional effect in the system A2 that is overruling the known factors involved in drop coalescence. The effect that can play this role and it is not included in the models, is related to the diffuse layers around the drops. The experiments shown in Fig. 5.2 indicate that in the more diffusive system A2 the coalescence is faster than in the less diffusive system B2, although the models, based on a sharp interface, predict the opposite. This suggests that the diffusion plays an important role in drop coalescence.

Mutual attraction between two drops in systems with a thick diffuse layer: system A5

In Fig. 5.3 attraction between two drops in a system with a relatively large diffusion length scale is shown (system A5). The drops were forced to approach each other very slowly in a stepwise manner, controlling in this way the distance between them and avoiding any a priory drop deformation (as seen in Figs. 5.2a and 5.2g). Then they were left in almost quiescent conditions (density difference of 0.085g/cm³) at a distance of 45-50 µm. Fig. 5.3 shows that the attraction between the interfaces of the drops is still active even after a contact between them is established (Fig. 5.3c–d) and until a very wide contact area is formed (Fig. 5.3f). The experiment was repeated several times to ensure that this is not a random phenomenon. Again good reproducibility of the coalescence times was obtained (± few seconds). In general, due to the complexity of the phenomenon, such reproducibility is not expected (see for example [21]). To investigate the effect of the aging in this system, the two drops were left in the matrix longer (15-20 minutes) instead of being immediately brought into a close vicinity (45-50 µm). In this experiment, the coalescence of the drops was approximately three times faster than for a fresh system, showing the
Figure 5.2: Comparison between drop coalescence in system A2 (pictures: a–f) and system B2 (pictures: g–l). The process is followed from the moment when the flow is stopped (pictures a and g). The reference bar shown in picture a is equal to 100 μm. Note the difference in time (hrs, minutes, sec) on the right-hand bottom of the picture.
Figure 5.3: An mutual attraction between two drops, system A5. The initial separation between the drops was set to be 40-50 μm. The reference bar shown in picture a is equal to 100 μm.

time dependence of the phenomenon. In the cases where the distance between the drops was larger than 200 μm no attraction was observed, indicating that the length scale of the diffusion, in the time scale of 10-15 minutes, is around 100 μm. When the experiment presented in Fig. 5.3, was performed with a less diffusive system (system B4, see materials section), no attraction between the drops was observed at any distance between them in the time range of the experiment (half an hour).
The attraction between two drops in the system A5 is in good agreement with the results reported elsewhere, see Chapter 4 and [19]. In [19] the authors report results on shear-induced coalescence in a blend that consist of a combination of polymers similar to the A5 system. A high rate of drop coalescence and very good reproducibility of the experimental results was observed. Diffusion was neglected and the high tendency of coalescence was attributed to a large thickness of film rupture (150-200 nm). The results presented here suggest that diffusion effects do have an overruling effect that leads to a good experimental reproducibility. In Chapter 4, we reported that the film drainage rate between two captive drops in system A5 is approximately 100 times faster than the model predictions, which is in accordance with the results presented here.

**Repulsion between two drops in systems with a thin diffuse layer: system B4**

In Fig. 5.4 a repulsion between two drops in system with very restricted length scale of diffusion (within 1 µm, system B4, see materials section) is shown. The drops were initially brought into a firm contact by applying a flow in a stepwise manner, avoiding in this way any a priori drop deformation. Fig. 5.4 shows that in the beginning the contact between the drops is stable (Figs. 5.4a and 5.4b) and the effect of repulsion appears at later stages (Figs. 5.4c and 5.4d). The experiment was performed several times to ensure that it is not a random phenomena. In some of the experiments drops with different sizes were used. It was found that the effect of repulsion is more pronounced for small drops (30-60 µm in diameter) where the film drainage rate is higher [12].

The results on drop repulsion in the system B4 are in agreement with other studies reported elsewhere, see Chapter 4 and [89]. In [89] the authors determined that shear-induced drop coalescence in a blend similar to the B4 system has only little effect on drop size evolution. This conclusion is in agreement with the results presented here. In Chapter 4 we presented film drainage results between two captive drops in similar to the B4 system. Although the experimental results were close to the model predictions, during the final stage of the film drainage a reversal in the film thinning rate was observed. The same process is seen in Fig. 5.4.

**A mechanism for drop coalescence in systems with and without overlap of the diffuse layers**

Fig. 5.5 shows a schematic representation of two drops in contact, with (Fig. 5.5a) and without overlap (Fig. 5.5b) of their diffuse layers. When the layers around the two drops overlap (Fig. 5.5a), the concentration in this zone becomes higher, resulting in lower interfacial tension there. The induced gradient in the interfacial tension produces tangential stresses (Marangoni stresses) along the drop interface that result in convection from the areas with low to the areas with high interfacial tension, promoting drop coalescence [82; 4]. When the two diffuse layers are thin enough so that they do not overlap in the contact zone, the film drainage process leads to an inhomogeneous layer thickness along the interfaces of the drops (Fig. 5.5b). This time the induced Marangoni stresses act in the direction opposite to the film drainage direction and even can reverse the thinning rate when the film drainage rate becomes slow enough (at the final stage when the thickness of the film...
Figure 5.4: Two drops going apart after being brought into contact, system B4. Notice the satellite drop between the two large drops that acts as a flow marker showing the reversed flow in the contact zone. The reference bar shown in picture a is equal to 100 μm.

Figure 5.5: Schematic drawing of two drops in contact, a with and b without overlap of their diffuse layers. The dashed arrows represent Marangoni convection that is responsible for a attraction and b repulsion between the drops. The solid arrows represent the film drainage direction. The effect of the film flow on the thickness of the diffuse layers is exaggerated.
is small, in the order of 100 nm, see Chapter 4).

5.3.2 Numerical results

Simulation of the process of drop attraction

A diffuse interface method [28] was employed to study numerically the effect of mutual attraction between two drops in a highly diffusive system (A5 for example). A detailed description of this method and the numerical implementation can be found in [76]. The different system parameters and dimensionless groups used in the model were calculated on the basis of the experiment shown in Fig. 5.3. The dimensionless groups used are:

$$\begin{align*}
Pe &= 10; \quad C = 0.02; \quad Ca = 0.848; \quad Bo = 1; \\
\frac{\mu_d}{\mu_c} &= 1; \quad \frac{\rho_d}{\rho_c} = 0.91
\end{align*}$$

(5.1)

(5.2)

where Pe denotes the Peclet number (ratio of convection over diffusion of concentration), C the Cahn number (the dimensionless interfacial thickness), Ca the Capillary number (ratio of shear stress over interfacial tension), Bo the Bond number (ratio of gravitational forces over interfacial tension forces) and $\rho_d$ and $\rho_c$ are the density of the drop and continuous phase, respectively. The initial and boundary conditions used for the computations are shown in Fig. 5.6. The outcome of the calculations is shown in Fig. 5.7. Two equal drops (1 mm in diameter) with thick diffuse layers (interfacial thickness of 20 μm each) were initially put into contact in the way that the distance between the drops was 10 μm. This ensures overlap of the layers, i.e. an inhomogeneous interface thickness along the interfaces of the drops. No external

![Image](image-url)
Figure 5.7: Four consequent plots ($t^*$ denotes dimensionless time) of the velocity field showing the mutual attraction between the interfaces of two drops, after overlap of their diffuse layers. Only the contact region is shown. The solid and dashed lines show zero and ±0.9 concentration contour lines, respectively.

Flow was involved. The velocity vector plots in Fig. 5.7 show that overlap of the diffuse layers leads to attraction between the drop interfaces and finally drop coalescence. The closer the interfaces are, the faster the liquid between them is squeezed out. In the diffuse interface model, interfacial tension is inversely proportional to the thickness of diffuse layer. Hence, the prescribed inhomogeneous thickness is equivalent to prescribing an interfacial tension gradient. These gradients lead to Marangoni stresses that are responsible for the attraction between the interfaces. When the two drops were initially placed at distances larger than 40 μm (no overlap) no attraction between the drops was detected. In the calculations only the Pe number was varied to test the effect of the diffusion kinetics on the rate of drainage. It was found that with an increase of Pe with a factor of 10 (i.e., 10 times slower diffusion), the time of drainage also increases with a factor of 10. This indicates that the Marangoni convection has a big contribution in systems with relatively slow diffusion. The results in Fig. 5.7 confirm qualitatively the process of drop attraction shown in Fig. 5.5a.

**Simulation of the process of drop repulsion**

In Fig. 5.8 numerical results using the following dimensionless set of values are presented:

$$Pe = 1 \times 10^5; \quad C = 0.06; \quad Ca = 1; \quad Bo = 0;$$  \hspace{1cm} (5.3)

$$\frac{\mu_d}{\mu_c} = 1; \quad \frac{\rho_d}{\rho_c} = 1.$$  \hspace{1cm} (5.4)
For the sake of simplicity, the calculations here were done for a single drop and the uneven thickness of the diffuse layer is introduced a priori. At the top edge of the computational domain symmetry boundary conditions are applied, mimicking in this way the effect of the opposite drop (Fig. 5.8, \( t^* = 0 \)). A similar configuration of the diffuse layer would be produced either by some external flow or by interaction of the drop with another drop or even a solid surface. The two subsequent plots shown in Fig. 5.8 illustrate the motion of a drop due to the presence of a prescribed inhomogeneous thickness of the diffuse layer, mimicking induced Marangoni convection. Since the diffusion in the system is small (as characterized by large value of Pe) regularization of the thickness of the diffuse layer has to be due to convection with the consequence that the entire drop moves in the direction of low interfacial tension and away from the other drop (not shown in the Fig. 5.8). The result is a repulsion of the two drops. The numerical results presented here, at first glance confirm the model mechanism presented in Fig. 5.5b and, in this way, give an explanation of the process of drop repulsion presented in Fig. 5.4.

5.4 conclusions

The effect of mutual diffusion in polymer systems on drop coalescence was investigated. Two groups of fluid combinations with different interfacial properties were used: polymer pairs with thick diffuse layers (tens of \( \mu m \), A systems) and polymer pairs with relatively thin diffuse layers (from a sub-micrometer to a \( \mu m \), B systems).
In system A2, approximately 3 times faster coalescence than in system B2 was observed, despite the fact that the current models predict the opposite. Moreover, in system A5 an interesting mutual attraction phenomenon between two drops was observed when they were placed at distance which ensure an overlap of their diffuse atmospheres. On the contrary, in system B4 a repulsion between two drops was monitored when the two drops were placed in firm contact, which did not ensure an overlap of their diffuse atmospheres. The results are explained on the basis of a model mechanism, that represents a Marangoni type of convection that promotes drop coalescence when the two diffusion layers overlap and suppresses coalescence when the two layers do not overlap in the contact zone. This mechanism was confirmed by some preliminary numerical simulations, based on the diffuse interface method. The findings in this work show that the solubility in polymer systems has an overruling effect on the process of drop coalescence.
Chapter 6

Conclusions and Recommendations

6.1 Conclusions

The focus of this thesis was on the experimental investigation of the effect of surfactants and mutual diffusion on drop coalescence for polymeric systems. The objective was to understand the mechanism of film drainage and thus drop coalescence in such systems. As drop coalescence is strongly determined by interfacial phenomena, special attention was paid to the interfacial properties of the material combinations, see Chapter 3. The materials in this work were polymer combinations with a wide range of molecular weight ratios between matrix and dispersed phase, introducing, in this way, different interfaces with a wide range in of properties. Due to the relatively low interfacial tension in polymeric systems, typically from 1 to 4 mN/m, the interfacial properties are determined by diffusion effects rather than by effects related to adsorbed surface-active species. Different experimental techniques were applied for characterization of the interfacial properties of the polymer pairs. The change of the interfacial tension in time and the interfacial rheological behavior of the polymer-polymer interfaces was measured with a sessile (pendant) drop technique while the length-scale of the diffusion was estimated using the reduction of a drop radius (sessile drop apparatus) and confocal Raman spectroscopy. To investigate drop coalescence, two set-ups were employed: a cross-slot flow cell and a film-drainage apparatus. The cross-slot produces a two dimensional hyperbolic flow that was used to monitor the approach and lifetime of drops, while the film-drainage set-up was used to observe in detail film drainage between two coalescing drops and to measure the film drainage rate, see Chapters 4 and 5. The measurements of the time evolution of the absolute thickness of the draining films allows for a comparison with the available film drainage models.

Three classes of polymeric systems were considered, defined by the interfacial properties:

1. Systems with a sharp interface: a few nm in thickness, with polar/apolar interactions, a high interfacial tension of 10-30 mN/m, negligible diffusion,
with surfactants, and an interfacial dilatational elasticity of \(\approx 12\) mN/m.

2. Systems with a slightly diffuse interface: a few hundred nm in thickness, with apolar/apolar interactions, a moderate interfacial tension of 4-5 mN/m, little diffusion, without surfactants, and an interfacial dilatational elasticity of \(\approx 16\) mN/m.

3. Systems with a highly diffuse interface: tens of \(\mu\)m, with apolar/apolar interactions, a small interfacial tension of 1-4 mN/m, large diffusion, without surfactants, and an interfacial dilatational elasticity of \(\approx 3\) mN/m.

As a representative for the first group, a system consisting of polyethylene oxide (PEO) water solution/polydimethylsiloxane (PDMS) was used, for the second group polybutadiene (PBD)/PDMS and for the third group polybutene (PB) or polyisobutylene (PIB)/PDMS. Experimental results on film deformation and on the film drainage rate for each of these three systems were reported, see Chapters 4.

To validate the existing theoretical models in the limiting cases of immobile and partially-mobile film drainage, a series of PEO-water solutions were used as the dispersed and PDMS as the matrix phase (system 1), see Chapter 2. To investigate the influence of the diffusion on drop coalescence, a series of PBD, PB and PIB with different molecular weights were used for the dispersed phase, and PDMS for the matrix phase (systems 2 and 3). Since the interaction between all these polymers is apolar/apolar, the mutual diffusion that was detected was attributed to the asymmetry across the interface, i.e. the molecular weight differences. Oscillatory rheological interfacial measurements demonstrated that the diffuse interface in these systems has a viscoelastic behavior which was found to correlate with the results from drop coalescence and film drainage experiments. System 3 shows an unexpected, much faster (at least 3 times) drop coalescence than system 2, although, according to the theory, all material bulk characteristics and experimental parameters were in favor for faster coalescence for the latter, see Fig. 5.2. Mutual-attraction phenomena between two drops in systems with well developed diffusion layers (35±3 \(\mu\)m in thickness) were observed when the layers overlap, see Fig. 5.3. In contrast, a repulsion between two drops with relatively thin diffuse layers (within 1\(\mu\)m) is observed when the drops are brought into close contact, see Fig. 5.4. For the case of high asymmetry in molecular weight across the interface, both systems, 2 and 3, show non-axisymmetric and unstable film drainage already at the thickness of film formation. For system 3 an approximately 100 times faster film drainage, compared to the theoretical predictions, was observed, while the less diffusive system 2 gave results close to the model predictions, see Chapter 4. However, for the latter system, at the final stage of film drainage, a reversal in the film thinning rate was measured. These phenomena were attributed to interfacial tension gradients (Marangoni convection) caused by an inhomogeneous thickness of the diffuse layers around the interacting drops. Depending on whether the total thickness of the diffusion layers in the film is smaller or bigger than the thickness of the film, Marangoni convection was found to enhance or delay film drainage. In addition to this experimental study, numerical simulations, based on a diffuse interface method, were presented and the results support the explanation that is given for the drop coalescence phenomena observed, see Chapter 5.
For most of the systems investigated the film thickness at rupture was determined using the intensity changes of the reflected light from the film interfaces. The results show that with increasing molecular weight of the dispersed phase materials, the critical thickness at rupture also increases. The experimental results are compared with the model predictions based on van der Waals forces, Chapter 4.

6.2 Recommendations

1. A specific property of polymeric systems is their bulk viscoelasticity. Since the first order effects (related to interfacial phenomena, e.g. Marangoni convection) on drop coalescence were determined, second order effects as additional elasticity in the drop and matrix phase can be added now. It is relatively easy to prepare a viscoelastic liquid, for example by adding a high molecular weight component to the low molecular component. By choosing different combinations and molecular weight fractions, liquids with the same zero-stress viscosity but different elastic behavior can be prepared and used to study in a systematic way the influence of the elasticity. However, although the viscosities are matched, the interfacial properties will be different if the amount of small molecules (the volume fraction of the low molecular weight) is different in the two tailor-made liquids. This will be the case in general and, therefore, a way to match the interfacial properties should be found as well.

2. One way to control the interfacial properties is to use surface-active block copolymers. They create a rigid “skin” at the interface and in this way can prevent mutual diffusion. As they immobilize the interface the effect of the drop bulk properties will be negligible, however, the influence of the bulk matrix properties, such as viscoelasticity, can be studied, for such systems, without influence of diffuse layer effects. To investigate drop coalescence in systems with such compatibilizers is a challenging task as they reduce the already low interfacial tension (typically between 1-4 mN/m), which, together with the immobile interfaces, can result in extremely long times of drop coalescence.

3. In this study, in most of the cases, the small molecules were in the drop phase. It will be interesting to study the case if the phases are reversed. Then, the small molecules will diffuse to saturate the small limited drop volume so the equilibrium state will be quickly reached. According to Masons and Mackey [4], who investigated diffusion of a third component from the film to the drop, the effect of diffusion on film drainage will be the opposite.

4. The fact that diffuse interfaces of polymeric systems can accelerate or decelerate the coalescence process is a crucial result as it has important practical implications for melt blending. Therefore, these effects should be studied, besides with detailed interface characterization techniques and with detailed film drainage technique, in concentrated blends using rheological and light scattering methods.

5. The results in this work, although new and limited, already show the complexity of the phenomena studied. In the small region of film formation and
film drainage, different distributive and transient processes take place and, depending on the large scale flow conditions and the material properties, they can have opposite effects. An experimental approach on its own, probably will never reveal all the details of these processes and, therefore, is not sufficient in future research. Numerical simulations should be used in close connection with the experiments in order to make further progress.
Bibliography

Bibliography


Samenvatting

De effecten ten gevolge van de onderlinge diffusie van twee polymeren op de eigenschappen en het gedrag van de grenslaag tussen die polymeren zijn bestudeerd. In het bijzonder zijn de gevolgen van diffuse grenslenagen op het coalescentie-gedrag van twee druppels onderzocht. Dit is uitgevoerd door middel van een experimentele karakterisering van grenslenagen, gevormd door middel van een verzameling van combinaties van telkens twee polymeren, en het in detail meten van de wijze van filmdrainage van de matrix-vloeistof tussen twee gedisperseerde druppels.

Het blijkt dat voor de bestudeerde materiëlcombinaties de grensvlakspanning niet constant is in de tijd. Beneden een initiele kritische waarde van ongeveer 4 mN/m neemt de grensvlakspanning af in de tijd ten gevolge van de diffusie; boven die waarde neemt grensvlakspanning toe in de tijd. Dit komt overeen met een in de tijd respectievelijk toenemende of een afnemende dikte van de van de diffuse grenslaag en een overeenkomstige kritische grenslaagdikte. De filmdrainage-experimenten laten zien dat voor relatief dikke diffuse grenslenagen, de snelheid waarmee de filmdikte tussen twee druppels afneemt een factor honderd groter is dan voorspeld met de huidige fysische modellen voor filmdrainage. Voor dunne grenslenagen wordt gevonden dat, na een periode waarin metingen en voorspellingen wel met elkaar overeen komen, de afnamesnelheid van de filmdikte zelfs wordt vertraagd.

Mechanische metingen aan de diffuse grenslenagen met behulp van oscillatorende dilatatie laten zien dat dergelijke lagen een viscoelastische respons vertonen op deformaties. Kennis van een dergelijke respons is van groot belang voor het begrijpen van coalescentie-gedrag in relevante processen waarbij botsingsfrequenties, contacttijden en deformaties van druppels worden bepaald door de macroscopisch opgelegde stromingscondities.

Er is verder een nieuwe experimentele methode toegewijkt voor het bestuderen van druppelcoalescentie, waarbij de effecten van stromingen en de materiaalspecifieke effecten kunnen worden gescheiden. Hiermee kan worden aangetoond dat voor materiaal-combinaties met een grenslaagdikte ver boven de kritische waarde, twee druppels in rust, en met overlappende grenslenagen, elkaar aantrekken. In tegenstelling daarmee werd waargenomen dat bij grenslaagdiktes beneden de kritische waarde, en niet overlappende grenslenagen, twee druppels, initieel in rust, elkaar afstoten; zelfs nadat ze weer in intiem contact zijn geweest.

Deze fenomenen, alsook het filmdrainage-gedrag, kunnen worden begrepen door gradinten in de grensvlakspanning te beschouwen, veroorzaakt door de gradinten in de grenslaagdiktes ten gevolg van druppeldeformatie. Deze gradinten induceren
Marangoni-convectie; dat wil zeggen stroming in de grenslagen zelf. Deze interpretatie wordt ondersteund door de resultaten van numerieke simulaties die gebaseerd zijn op de diffuse-grenslaag-methode.

Voor niet-diffuse materiaalcombinaties en met toevoeging van oppervlakte-actieve stoffen is aangetoond dat voor een nagenoeg constante interactierkracht tussen de druppels, de grensgewalten van immobile en gedeeltelijk mobiele grenslagen wel goed voorspeld worden door de huidige modellen. Wanneer de interactierkracht, en dus ook het contactoppervlak, aanzienlijk toeneemt in de tijd, neemt de drainagetijd aanzienlijk af. Dit verschijnsel, dat niet beschreven kan worden met de huidige modellen, wordt toegevoegd aan de herverdeling van de oppervlakte-actieve stoffen door de veranderende randvoorwaarden.

Voor bijna alle materiaalcombinaties is ook de minimale film dikte bij filmbreuk gemeten. De resultaten laten zien dat de kritische film dikte bij breuk toeneemt met het moleculair gewicht van de gedispergeerde fase. Deze experimentele resultaten zijn vergeleken met voorspellingen uit een model gebaseerd op de werking van Van der Waals krachten.

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Curriculum Vitae

November 6, 1971  Born in Kostenets, Bulgaria.


1997 - 1998  Department of Chemical Engineering, University of Patras, Greece. Five months research practice as a part of the educational plan of a Tempus project. Subject: Flow regimes and relative permeabilities during steady-state two-phase flow in porous media.

Stellingen
behorende bij het proefschrift

INTERFACIAL PHENOMENA DURING DROP COALESCEENCE
IN POLYMERIC SYSTEMS

door

Alexander Nikolov Zdravkov

1. The higher the initial interfacial tension between two polymers, the smaller the permeability of the polymer-polymer interface for higher molecular weight fractions, and vice versa.
   - This thesis, Chapter 3

2. Depending on whether the length scale of diffusion is larger or smaller than the thickness of film formation between two interacting drops, drop coalescence is facilitated or suppressed, respectively.
   - This thesis, Chapter 4

3. Attraction between drops in nonionic polymeric or emulsion systems without external field and at distances few times larger than the drop sizes has never been reported, until now.
   - This thesis, Chapter 5

4. In most of the studies on drop coalescence flow-induced coalescence is used which complicates the already complex process.
   - This thesis, Chapter 5

5. Often not fully understood phenomena in polymer science are attributed to apparent slip at polymer-polymer interfaces.
   - This thesis, Chapter 4
6. If some force or process in the world we live is not fully understood, this is, most likely, because it is examined from bulk instead from interfacial point of view.

7. Research requires a systematic approach (planning), however, most of the important inventions are done by chaotic persons, with a bit of luck.

8. The quest for knowledge and scientific understanding is related to the basic instinct of self-preservation.

9. “What makes one wizard great, is the imagination, since by it he can step over the boundary of the tradition and look beyond the conventional way of thinking in the true texture of the matter.” The same holds for a scientist.


10. “The traditions are not what they use to be”. However, in difficult times the old traditions revive again.

- A tv commercial of blend whiskey J&B.

11. The number of penalty goals scored by Dutch national soccer players is striking.

12. Although Bulgarian language is not that popular on Earth, it is believed in Bulgaria that it is one of the most popular among the inter-galaxy languages.