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Coalescence and interfacial tension measurements for polymer melts: experiments on a PS–PE model system

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A novel technique to measure coalescence phenomena in polymer blends was developed using a spinning drop apparatus. To date, coalescence experiments on polymers were performed by the slow process of gravity driven collisions. In comparison, the spinning drop method is more rapid and more versatile in its control of the contact radius and coalescent force. The governing parameters of the coalescence process, notably interfacial mobility and matrix film rupture thickness, can be assessed by testing a range of droplets of varying size. The relatively high mobility of the interface demonstrated by the experiments explains the dominant role played by coalescence in controlling the dispersion size in polymer melt blending. Estimates of the matrix film rupture thickness are in the order of 20–40 nm for the purified systems. This suggests that in the final stages of film drainage and rupture, entropic effects of the macromolecules play only a minor part.

Commercial polymers were shown to coalesce considerably faster than a purified system. Here, impurities may lead to premature coalescence through lubrication of the interface (increasing its mobility) or by third-phase particles destabilising the matrix film. © 1997 Elsevier Science Ltd.

(Keywords: spinning drop technique; coalescence; polystyrene–polyethylene system)

INTRODUCTION

The mechanical properties of heterogeneous polymer blends strongly depend on the size of the dispersed particles (see, for example, Refs. [1,2]). The microrheological processes that take place during blending and determine particle size, therefore, are subject to intensive study (see, for example, Refs. [3–7]). In addition to the break-up of dispersed phase droplets, coalescence is an important phenomenon. Coalescence occurs when two droplets moving in an externally applied flow field collide and the duration of the collision is sufficient to allow completion of the coalescence process. The extent to which coalescence will occur therefore depends upon the time of contact (t_c) needed for two colliding droplets to actually coalesce.

The rate-determining step in the coalescence process (*Figure 1*) is usually the drainage up to the critical thickness (h_{crit}) of the matrix film separating the two droplets. At h_{crit} the film ruptures and coalescence rapidly follows.

The coalescence time decreases with decreasing contact radius (R_f) because of the shorter distance over which the matrix needs to be drained. Contact radii will decrease in size with decreasing droplet size (R), force of the collision (depending on the shear rate γ) and increasing interfacial tension (σ). As a result, similarly to droplet break-up, the regime where coalescence is dominant can be characterised by the capillary number which is given by

$$\mathrm{Ca} = \frac{\eta_m \dot{\gamma} R}{\sigma} \qquad (1)$$

where η_m is the matrix viscosity, $\dot{\gamma}$ is the shear rate, R is the droplet radius and σ is the interfacial tension.

Coalescence will dominate at roughly $\mathrm{Ca} \leq 10^{-1}$–10^{-2}, whereas droplet break-up is dominant at $\mathrm{Ca} \geq 1$–10^{-1} [4,5].

This indicates that for blends where the dispersed phase is broken up into sufficiently small particles (below 5–10 mm, as in common extrusion melt blends or in reactor blends), coalescence will be an important factor in the further development of the dispersion.

Apart from the contact radius, the main parameters determining the rate of drainage are the mobility of the interface[8], and obviously the rupture thickness h_{crit}. *Figure 2* shows the cases of a fully mobile, partially mobile, and immobile interface. With higher interfacial mobility, the velocity of the flow in the matrix film increases and thereby also the drainage rate increases.

At high mobility and large h_{crit}, the capillary number at which coalescence becomes important will increase.

Direct measurements of interfacial mobility and rupture thickness in polymer blends have not been performed so far. In this paper we describe a study of the coalescence behaviour using a spinning drop apparatus. Experimental data allow us to assess whether it is worthwhile to actively influence the interfacial mobility and/or rupture thickness, *e.g.* through compatibilisation with block copolymers in polymer blend systems.

LITERATURE

Polymer morphology studies frequently show that in situations where polymer dispersions are much coarser than are desirable for good end-use properties e.g. $R \approx 10^{-5}$ m[5,6,9], conditions are, in theory, fulfilled for yielding sufficiently fine dispersions through particle break-up ($\mathrm{Ca}/R \geq 10^5$, $R \leq 10^{-6}$ m). This remains valid when the

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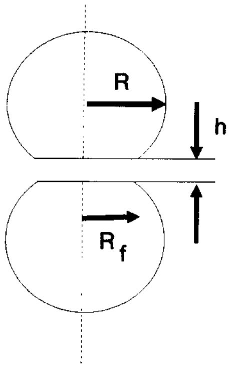

Figure 1 Relevant dimensions in the coalescence process. R, droplet radius; R_f, flattened or contact radius; h_{crit}, critical film thickness

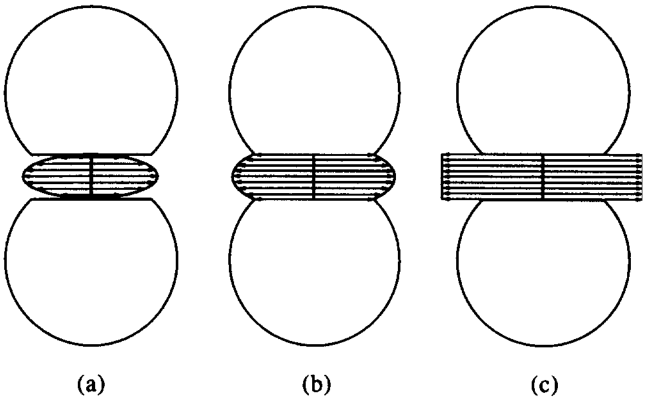

Figure 2 Flow velocity patterns in the matrix film with (a) fully immobile, (b) partially mobile, and (c) fully mobile interface

viscoelastic behaviour of polymers is taken into account, as was recently demonstrated by Sundararaj and Macosko[6].

The reasons for this may be several, *e.g.* the residence time during processing may be too short or the effective shear rate may be lower than that assumed. However, by varying the dispersed phase concentration (see, for example, Refs. [6,9]), it is easily demonstrated that smaller particles can be obtained at smaller volume fractions. Therefore, the coarsening at larger volume fractions is ascribed to coalescence.

Very few attempts to investigate experimentally the coalescence behaviour of molten polymer droplets have been described. Janssen[4] reported that experiments performed in an opposing jets device remained irreproducible. A limited number of data gathered by Elmendorp[5] qualitatively indicate that the interface is relatively mobile. This has been ascribed to the high viscosity of the polymers, which prevents surface-active contaminants — which readily immobilise interfaces in low viscosity systems — from migrating to the interface rapidly. There is no known quantitative experimental information on interfacial mobility or matrix film rupture thickness for polymer blends.

Based on the morphological studies in combination with the coalescence results of Elmendorp[5] mentioned earlier, it is generally accepted that polymer interfaces are relatively mobile and therefore coalescence is relatively fast[4–7].

Thus immobilisation of the interface to prevent coalescence should be useful. Moreover, it was recently stated[6] that the importance of coalescence is mainly due to the mobility of the interface and that compatibilisers work more effectively through immobilisation of the interface than through reduction of the interfacial tension.

There is ample literature on the coalescence of droplets in fluid/fluid dispersions with low viscosity, mostly Newtonian fluids. Reviews were recently published by Chesters[8] and Ivanov[10]. Since the drainage step during which the matrix thins to its critical thickness is the most time-consuming, this step will determine whether in a given flow field the contact time between the two droplets is sufficiently long to allow coalescence. The time involved will depend upon the thinning rate and the rupture thickness.

Thinning rate: interfacial mobility

Analytical models. In this paper we are concerned with deformable droplets where the interface is flattened in the region of excess pressure (*Figure 1*). The mobility (*Figure 2*) of the interface determines the velocity with which matrix liquid can be drained from the thin matrix film between the flattened interfaces, *i.e.* the thinning rate of the film. For an immobile interface, the velocity in the matrix film is zero at the interface. This will obviously limit the rate of transport of fluid in the matrix film most efficiently. In a fully mobile interface, the velocity in the matrix film is not limited by the interface at all and the overall velocity of drainage will be larger. The partially mobile case is the intermediate situation.

Theoretical models usually describe the velocity profile of the matrix film. Once this is obtained, assuming that the matrix film is perfectly flat and there is no tangential flow, the thinning rate can be calculated. Depending on other assumptions and simplifications, various results may arise.

In this paper, we will analyse the data with three models from the literature. The classical model by MacKay and Mason[11] assumes a completely immobile interface, as shown in *Figure 2a*.

A model by Chesters[8] describes the partially mobile situation of *Figure 2b*. This model assumes that when the matrix viscosity is not too different from that of the dispersed phase, the rate of drainage is determined by the internal flow in the droplet, which is hydrodynamically coupled to that in the matrix film. Furthermore, the model assumes that the velocity gradient in the matrix can be neglected and that a creeping flow regime dominates in the droplet phase. This model leads to the following equation for drainage rate, where h is the film thickness, R is the droplet radius, σ is the interfacial tension, F is the coalescent force and η_d is the dispersed phase viscosity

$$-\frac{dh}{dt} \approx \frac{2(2\pi\sigma/R)^{3/2}h^2}{\pi\eta_d F^2} \qquad (2)$$

which is independent of the matrix viscosity.

Finally, in one particular case, the model of Barber and Hartland[12] was used to describe a situation where surface-active species are present. This model assumes that the interfacial mobility can be regarded as an interfacial viscosity, comprising both shear and dilatational viscosity. It applies to systems containing surfactants.

The models mentioned above predict a specific dependence of coalescence time on droplet radius. In this paper, we analyse the results from a range of experiments where droplet sizes varied from 0.1 to 1 mm in order to judge in which regime of interfacial mobility fall non-compatibilised polymer interfaces.

Numerical descriptions. Apart from analytical models, more recently numerical descriptions of coalescence behaviour have been published based on similar assumptions as in the Chesters model[13–15]. These have shown that the contact area is not exactly flat, but has a slight dimple in the centre. The analyses published to date are for a case of constant coalescence force[13] and constant approach velocity[14,15]. The ratio of the film thickness in the centre (h_0) to that at the periphery (h_{min}) depends on the stage of thinning of the film. Yiantsios and Davis[13] have shown that for a specific case (constant force), the thickness in the centre decreases as $t^{-1/3}$ and at the periphery as $t^{-2/3}$ whereas for the constant velocity case, Abid[14] found $t^{-0.8}$ and $t^{-1.6}$ respectively. For intermediate drainage times, the thickness ratio h_{min}/h_0 is in the order of 0.1 in both cases.

Despite the much more detailed nature of these models, a comparison of the prediction of h as a function of time in Chesters model did not yield large differences from that for h_{min} in the numerical models[8].

Rupture thickness

The film rupture thickness for low molecular mass liquids has been studied by various authors. Experimentally, rupture thickness in the order of 1–10 nm is usually observed. The approach to film rupture most frequently referred to is one where the thermodynamic stability of a film against perturbations of a certain amplitude are considered[16,17]. The free energy of the film may diminish as perturbations grow, under the action of London van der Waals interactions between the droplets. This approach was postulated by Scheludko[16] and further developed by Vrij and Overbeek[17]. For small droplets (R around 10^{-6} m) the rupture thickness will be round 5 nm, assuming a typical Hamaker constant A of around 10^{-20} according to this model. For larger droplets, as studied in this work, the rupture thickness may increase to 40 nm according to this approach.

Polymers in thin films

During the major part of the coalescence event, the matrix polymer extends biaxially and is confined to a thin film. There have been several publications containing both theoretical and experimental evidence that confining polymer molecules into a film may alter their viscosity and/or cause a long-range interaction between the interfaces[18–23].

Burton *et al.*[18] have shown that the viscosity decreases in shear flow of PS films at a thickness of several microns, probably due to molecular orientation. On the other hand, it is well known that biaxial elongational flow will lead to an increase in viscosity with a factor of 6 up to very large values at high flow rates. However, in our experiments, the flow rates were expected to be very slow and these effects would be mild.

The rupture thickness has not been investigated for polymers to the best of our knowledge. Usually h_{crit} is assumed to be in the same order of magnitude as for low molecular mass liquids, *i.e.* 5–15 nm (see, for example, Ref. [4]). However, a consideration that we would like to put forward here is that the radius of gyration of commercial polymers is usually larger than this; for example, common polymers in the matrix film used in this research have radii of gyration (R_g) in the order of 10–20 nm.

Israelachvili and co-workers[20–22], and Montfort and Hadziioannou[23] have shown experimentally that an increase in viscosity is observed for liquid polymers confined between two rigid plates, accompanied by a long-range repulsive force that begins to be felt at around 4–10 times the radius of gyration. In fact, these forces are so large that it is questionable whether they could be overcome by the relatively small forces exerted by drops colliding in a flow field. Thus, they would probably inhibit coalescence.

The reasons for this repulsion have been a matter of some debate. Monte Carlo simulations (see, for example, Refs. [24,25]) have confirmed earlier predictions by De Gennes[26] that in the case where the plates are neutral, no long-range repulsive forces between the walls should exist, whereas in the case of adsorbed molecules at constant coverage they would be strong. There appears to be general agreement that the experimental observations of Israelachvili and Hadziioannou and their respective co-workers[20–23] must be explained by the fact that some of the molecules are pinned to the rigid wall by adsorption[23–26].

One of the issues that we will address in this contribution is whether controlled coalescence experiments can yield information about the extent to which film viscosity increases and/or repulsive interactions occur in the case of coalescing droplets with uncompatibilised interfaces. In their absence, it is clear that introducing them through compatibilisation with block copolymers would be a very efficient route to stabilise a blend against coalescence.

EXPERIMENTAL

Coalescent force

The experimental set-up and procedure have been discussed in a previous contribution[3]. In short, a matrix polymer (polystyrene (PS)) and two equally sized droplets of a dispersed phase (polyethylene (PE) and polypropylene (PP)) are inserted in the spin chamber of a spinning drop apparatus. Upon rotation of the apparatus, the droplets deform and elongate towards an equilibrium shape with droplet diameter R_e. This is illustrated in *Figure 3*. Because the size of the droplets has been chosen such that this shape cannot be achieved without an encounter between the droplets, a collision takes place. The droplets exert a coalescent force upon one another, the size of which can be calculated.

Clearly, in the flattened contact area there is no component of the interfacial tension in the x-direction and we may state that

$$F_c = F_p \text{ for } 0 < y < R_c \tag{3}$$

where R_c is the radius of the contact area. The pressure difference across any point of the droplet is

$$p(y) = p_0 - \frac{\omega^2 y^2 \rho}{2} \tag{4}$$

The x-component of the force caused by the pressure difference is obtained by integration, yielding as the coalescent force

$$F_x = \int_0^R p(y)\,\mathrm{d}A = \int_0^{R_c} p(y) 2\pi y\,\mathrm{d}y \tag{5}$$

R_c can be obtained[3] from

$$C = \sqrt{\frac{2D^3 + 1 - \sqrt{(8D^3+1)}}{2D}}$$

(Eq. (1) in Ref. [3]) since $D = R_d/R_e$ and $C = R_c/R_e$. This leads to a coalescent force of

$$F_c = \pi \Delta\rho\omega^2 \left(\frac{R_d^2 R_c^2}{2} - \frac{R_c^4}{4} + \frac{R_e^3 R_c^2}{4R_d} \right) = \pi\sigma R_e D(D^3 - 1) \tag{6}$$

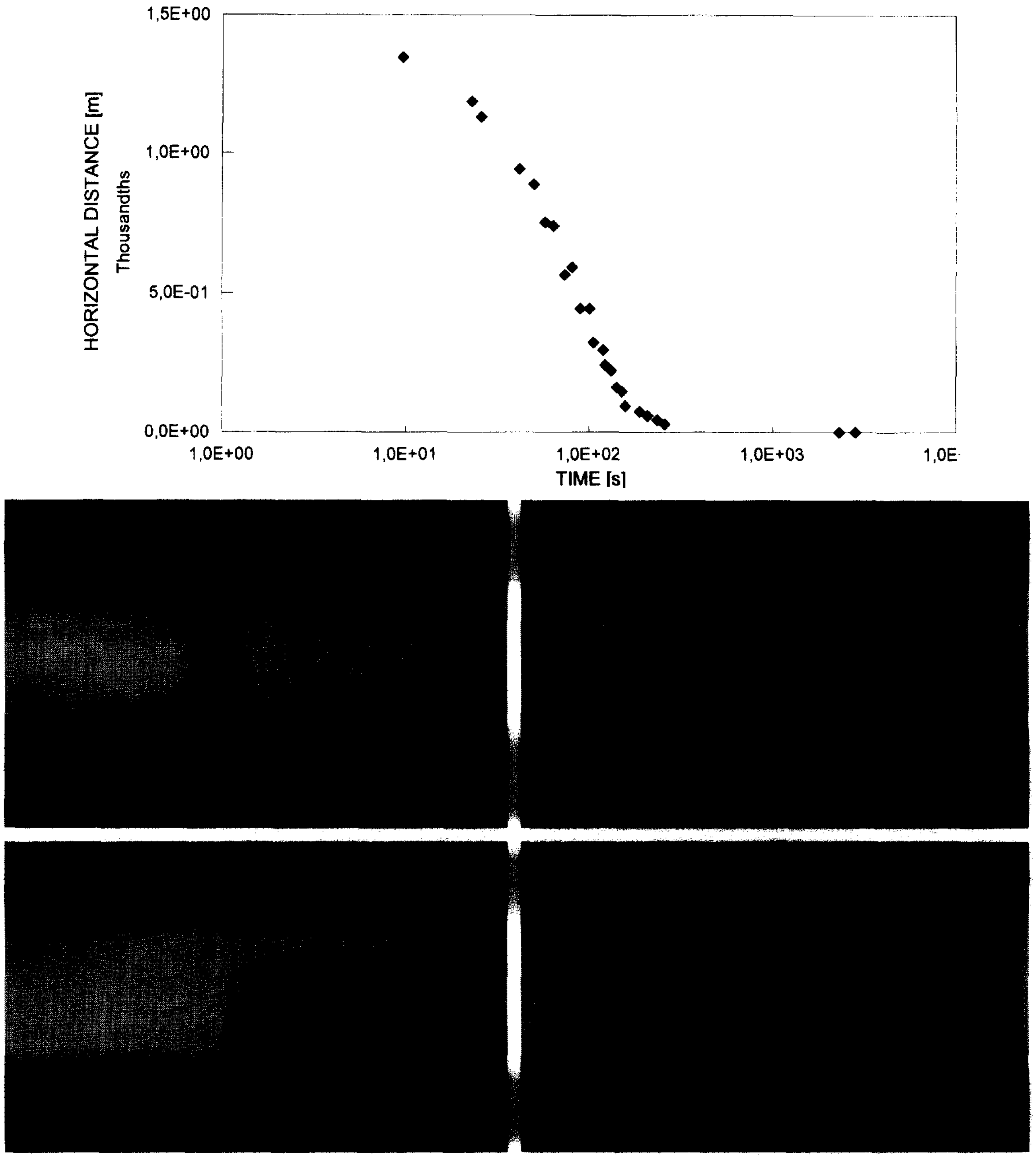

Figure 3 Distance between two coalescing droplets in the spinning drop apparatus: (a) approach; (b) quasistatic shape, drainage; (3) during rupture; (4) after coalescence

Table 1 Materials characteristics (PS, polystyrene; LLDPE, linear low density polyethylene; LDPE, low density polyethylene)

Material	η_0 at 220°C (Pa s)	M_n^a (kg mol^{-1})	M_w^a (kg mol^{-1})	σ with PS1 'pure' (mN m^{-2})	σ with PS2 (mN m^{-2})	σ withPS2 'pure' (mN m^{-2})	σ with PS3 (mN m^{-2})
PS1 'pure'	89	42	86				
PS2	800	77	184				
PS2 'pure'	1000	77	184				
PS3	9400	108	297				
LLDPE	307	15	52	4.5	4.6	4.4	4.7
LDPE 1	5600	17	94	4.1	3.1	4.4	4.1
LDPE 2	26000	19	108	4.5	3.4	4.3	4.3

[a] By g.p.c.

Table 2 Viscosity ratios η_d/η_m

	LLDPE	LDPE 1	LDPE2
PS1 'pure'	3.5	63.9	292
PS2	0.38	7.0	35
PS2 'pure'	0.31	5.6	26.0
PS3	0.03	0.60	2.77

Note that for $D = 1$, $F_c = 0$. This means that only if D is larger than 1 does a coalescent force build up as expected.

Materials and experiments

The materials used in the experiments are described in detail in Ref. [3]. In *Table 1* we summarise the most important experimental data only. The experiments were carried out at 220°C and a speed of rotation of 2100 rad s^{-1} and, in some cases, 1400 rad s^{-1}. The coalescence time t_c was registered as the time between reaching the quasistatic shape and rupturing of the matrix film. For the PS2/LDPE2 and the PS1/LLDPE (purified) systems, the droplet radius was varied between about 0.1 and 1 mm.

In the Chesters model, the mobility of the interface is considered to be related to the viscosity ratio η_d/η_m . To study the effect of the viscosity ratio, various combinations of PS and PE given in *Table 2* were tested at a fixed droplet radius of 0.5 mm. Because of the unexpected coalescence results for the commercial PS2 grade (which contains a plasticiser in the form of 5% of a white oil), this grade was also tested in its 'pure' state, i.e. with the same PS molecular characteristics but without additives.

RESULTS

Varying droplet size

Figure 4a and *Figure 4b* show the results of the coalescence times of the PS1/LLDPE (purified) and the PS2/LDPE1 systems. We analysed the data with three different models in order to establish which gives the best fit, *i.e.* which describes the drainage behaviour most realistically. From the poor fit to the MacKay and Mason model[11], it is clear that the immobile interface model does not apply. The Chesters model represents the data reasonably well. The rupture thickness for the PS2/LDPE1 system is in the order of 35 nm, which corresponds well to reports on low molecular mass liquids (see *Rupture thickness*).

Despite the much higher viscosity, coalescence times are not significantly increased in the PS2/LDPE1 system. Again the interface appears to be partially mobile. On the basis of the interfacial tension results, we expect this system to contain surface-active species[3] and it was therefore also treated with the Barber and Hartland model[12]. When both models are applied, the result is a much larger estimate of the rupture thickness than for the PS1/LLDPE system. The value calculated by the Chesters model here is 1.3 μm. The Barber model gives a value of around 11 μm, which appears to be very large. Observation with a microscope should allow the measurement of such a thickness. However, it is visually perceived as clearly smaller than this. Apparently neither model describes the data realistically. The possible explanation for this will be given later.

Varying speed of rotation

In contrast to the situation described in the literature so far, due to the centrifugal forces in the spinning drop apparatus, the pressure both inside and outside the droplet increases with radial distance. To investigate the effect this may possibly have on drainage behaviour, for several experiments on the PS2/LDPE1 system the speed of rotation was reduced to 1400 rad s^{-1}. Thus the centrifugal pressure component was reduced by one-third. However, in *Figure 4b* these data points cannot be discerned from the trend found at 2100 rad s^{-1}.

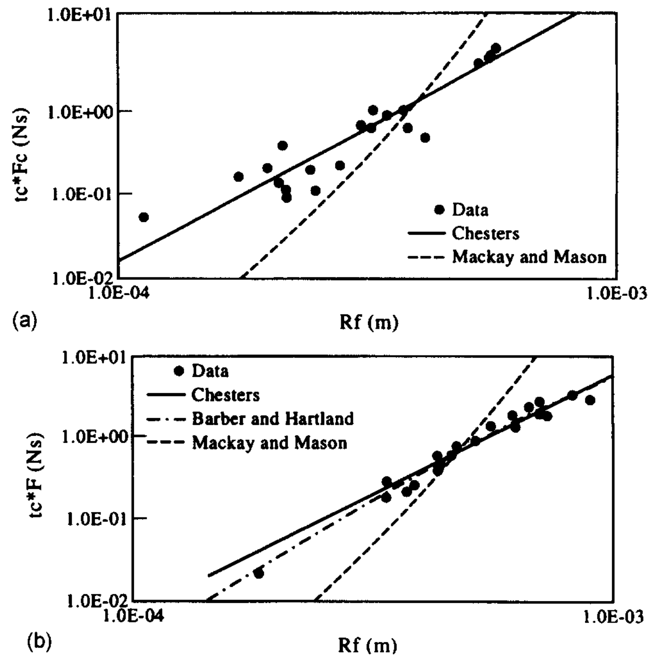

Figure 4 Product of coalescence time and force *versus* R_f. (a) Data for the PS1/LLDPE ('pure') system. Lines indicate best fits with the Chesters[8] and Mackay and Mason[11] models. (b) Data for the PS2/LDPE1 ('commercial') system. Lines indicate best fits with the Chesters[8] and Mackay and Mason[11] models and with the Barber and Hartland model[12]

Table 3 Average coalescence times (s) at R_d fixed at around 0.5 mm

	LLDPE	LDPE1	LDPE2
PS1 'pure'	**16500**	5000–26000	300–12000
PS2	2000	**9000**	20000
PS2 'pure'	30000	No coal.	No coal.
PS3	35000	No coal.	No coal.

This indicates that even with a considerable reduction of the centrifugal pressure component, the coalescence results are unaffected.

The centrifugal force field should reduce the tendency to form dimples. As discussed in the *literature* section, the difference between the analytical (no dimple assumed) and numerical (with dimple) models in their prediction of h (or h_{min}) as a function of time is only small. Therefore, we would also expect any effect that reduces dimple formation to have little effect on coalescence data. These considerations are supported by the results at lower speeds of rotation. Also, the fact that with increasing R_c, which also increases the centrifugal pressure component, there is no deviation of the predicted trends, in itself points in this direction. We conclude that for a first evaluation this centrifugal component can be neglected in the analysis.

Varying viscosity ratio

The Chesters model is intended to describe systems with a viscosity ratio between 0.01 and 100. Furthermore, in this model the drainage rate is independent of matrix viscosity.

Table 4 Rupture thickness h_{crit} (nm) predicted by the Chesters model

	LLDPE	LDPE1	LDPE2
PS1 'pure'	**35**	*Fully immmobile*	*Fully immobile*
PS2	250 (45)	**1300**	2600 (300)
PS2 'pure'	25 (7)	*< 100*	*< 1400*
PS3	15 (4)	*< 70*	*< 670*

Table 3 gives data at a fixed radius of 0.5 mm for the full set of viscosity combinations. In *Table 4*, the rupture thickness results as calculated with the Chesters model on the basis of the data are presented for all systems investigated. The data were corrected for small variations in interfacial tension and droplet size and are based on at least three experiments. Standard deviations are quoted between brackets. Data based on a broad range of droplet sizes are given in bold. In cases where coalescence did not occur within reasonable experimental times (in view of thermal degradation) the matrix film thickness theoretically achieved on termination of the experiments is given in italics.

The matrix and dispersed phase viscosity increase from the upper left to the lower right corner of *Table 3*. The viscosity ratio increases from the lower left corner (bordering the fully mobile regime) to the upper left (the fully immobile regime).

In the extreme of a very high viscosity ratio ($\eta_d/\eta_m = 292$) the immobile interface limit is surpassed. In addition, because of the high viscosity ratio, the experiment borders on the limit to 'undeformability' of the droplet. In the experiment, the flattening and coalescence processes cannot be clearly separated. This leads to fast coalescence and unacceptable scatter. The same applies, to a lesser degree, to the PS1/LDPE1 system with viscosity ratio 63.9.

In the lower right corner of the matrix, where both the dispersed and matrix phase viscosities increase, coalescence is not obtained because the drainage is too slow. Even after very long experimental times, where the sample starts to be seriously affected by degradation, the thickness theoretically achieved is still too large for rupture.

The behaviour of the commercial PS2 grade is remarkable in that it gives reproducible coalescence behaviour for short times. In *Table 4* this leads to a very large rupture thickness, as mentioned also in *the varying droplet size* section.

DISCUSSION

Interfacial mobility

As a first conclusion, the results in *Figure 4* provide direct evidence that the interface between two immmiscible polymers has partially mobile behaviour, as expected from the literature. This is one of the reasons why coalescence plays a relatively important role in morphology development during polymer blending.

The coalescence times increase with increasing dispersed phase viscosity, as predicted by the Chesters model. This leads to experimentally unacceptable coalescence times for systems which combine a high dispersed phase viscosity with a small rupture thickness.

However, coalescence can be systematically studied with proper choice of experimental conditions. For higher-viscosity, dispersed phase polymers this would mean reducing the contact area, which could be done by reducing the velocity of rotation.

Correspondence to theoretical models

With regard to the calculated rupture thickness, the results are less unambiguous. *Table 4* contains values both smaller and considerably larger than the expected $h_{crit} \approx 40$ nm. This may have several causes which are related to the nature of the rupture mechanism, the presence of contaminants which affect the rupture thickness and/or the drainage rate, or the analytical model predicting the drainage rate being insufficiently accurate.

By comparing analytical and numerical results[4] Chesters has shown that the equations for h_{min} coincide remarkably well with those obtained analytically for the 'parallel film' model. For the constant force model of Yiantsios and Davis[13], which probably matches the spinning drop situation best, the analytical model appears to underestimate the thinning rate only slightly. Also, the Chesters model has not been shown to be inaccurate by recent developments in numerical analysis that take into account the centrifugal force[27] occurring in the spinning drop apparatus. Although thus far limited to much smaller contact radii than in our experiment, these calculations show only a slight deviation. The experiments with a varying speed of rotation also indicate that the centrifugal forces have only a slight effect. We therefore conclude that the inaccuracies of the Chesters model that are known so far do not indicate that the real h_{crit} values differ greatly from the estimates given in *Table 4*.

Implications for 'pure' systems

For the 'pure' PS grades with LLDPE, we calculated a rupture thickness of around 20–40 nm, which is in the order of magnitude expected by the rupture mechanism established for low molecular mass systems. At first sight, these results are surprising; it appears that despite the macromolecular character of the molecules, drainage and rupture are the same as for low molecular mass liquids. It is remarkable that this seems to hold even when the film reaches a thickness on the order of magnitude of R_g of the PS (10–20 nm). Because of the considerations given in Refs.[18–26], we might have expected drainage to be much delayed and consequently the calculated rupture thickness to be much smaller than 20–40 nm, because of an overestimation of the drainage rate in the later stages.

Our first concern was whether the viscosity of the matrix polymer in a thin film is the same as in the bulk. As mentioned in the *literature* section, this will depend mainly on the deformation rate. During drainage, the deformation rate proves to be very slow (strain rate 10^{-2}–10^{-5}); the time- scale is probably much larger than that of molecular relaxation. At this strain rate, the viscosity increase in biaxial extensional flow compared to the bulk is probably not greater than a factor of 6[19], which is negligible compared with the very large viscosity variation required to have a significant effect on the drainage rate in the partially mobile situation.

Secondly, the repulsive effects found earlier[20–23] would also lead to delayed drainage, *i.e.* much longer coalescence times, and possibly even coalescence inhibition. Apparently this does not occur, which might be explained as follows.

The thickness of the polymer–polymer interface studied is around 1.5 nm[28]. For simplicity, we consider this interface to act as a rigid wall, neglecting any effects on its thickness that might occur at increased pressure. The fact that we observe a partially mobile interface implies that there must be a number of molecules coupled to the interface. The reason for this may be interdiffusion[28] or interactions by their end-groups (either because of a surface-active effect[29] or for entropic reasons[25]).

As the interface is expanding, a new interface is formed which possibly leads to a mild surface elasticity effect, but new molecules will rapidly couple to the wall. On average, we assume the number of coupled molecules (*i.e.* the interfacial mobility) to be an approximately constant result of these two competing processes, sufficient for the kind of 'hydrodynamic coupling' described in the Chesters model.

However, compared to the case of a 'fully immobile' rigid wall with strongly adsorbing 'pinned' molecules, as in the above-mentioned experiments[20–23], the polymer–polymer interface is a laterally moving wall with loosely connected molecules. The effect of coupling in this situation, although it must exist, is expected to be much smaller. At present, we cannot judge the quantitative importance of the repulsive interaction this will cause. Both the fact that coalescence indeed takes place and at a calculated rupture thickness that agrees so well with predictions, is an indication that the effect is small, and the situation is probably closer to that of the 'neutral plates' described by De Gennes[26] where long-range interactions are absent.

An interesting point in this respect is that the rupture thickness decreases with increasing molecular mass of the matrix. Correcting for the effects of the matrix viscosity, which are neglected in the Chesters model, does not significantly alter this. A fortuitous explanation could be that the effect is an artefact caused by a (small) effect of long-range repulsive forces on the drainage rate at small film thickness, and is felt relatively more strongly for larger molecules.

Such effects can only be proven when the rupture thickness can be measured directly. We are currently developing a laser optical system which would allow such measurements.

Implications for commercial systems

The large rupture thickness of the commercial PS2 system is a striking feature of our results. Comparison with the much smaller value for PS2 'pure' suggests that the former is caused by additives/impurities in the system. The interfacial tension found for commercial PS2 is always significantly lower than for the other systems, which indicates that the internal lubricant added to this polymer (in fact, a low M_W polyolefin) acts as an interfacial agent. This could be explained by its low molecular mass compared to the (L)LDPE[25,28,29].

Another possible explanation is that such an additive forms micellar domains, which destabilise the film leading to premature rupture. However, the behaviour of the PS2/LDPE1 system is very systematic and reproducible at a calculated rupture thickness much larger than the expected size of these domains, which makes this explanation unlikely.

Normally the introduction of an interfacial agent should lead to a finite surface viscosity, both shear and dilatational (also named 'surface elasticity'), which is described by the type of model proposed by Barber and Hartland[12]. Including this component into the theoretical analysis leads to a decrease of the drainage rate, as is indeed confirmed by the larger rupture thickness calculated with this model. Since this rupture thickness is even more unreasonable, clearly this is not the effect in our situation.

At present, it appears more likely that the low M_W lubricant increases the drainage rate in a way that is not accounted for in either the Chesters or the Barber and Hartland model. Thus, for this particular system, these models underestimate the drainage, which expresses itself in an estimate for the rupture thickness that is too high.

An increase in the drainage rate can be accounted for if we consider that the lubricant might lubricate the interface and thus increases mobility. In the squeeze flow of polymers between rigid plates, it has been observed that a low-viscosity interfacial layer can lead to 'lubrication'[30]. Eventually the interfacial layer will be squeezed out, which should lead to a surface-elasticity effect. However, in our situation, where the additive is present in large quantities (5%) and is highly mobile, it could be readily replenished from the matrix film, suppressing such an effect. The drainage rate would then not so much depend on the viscosity of the dispersed phase as on the net, apparently positive effect of the 'lubricant' on interfacial mobility. This corresponds with the increasing underestimation of the drainage (increasing rupture thickness) with increasing dispersed phase viscosity by the Chesters model in our data.

Although we realise that such an explanation remains speculative without further experimental evidence, we would like to point out that this kind of mechanism would be unique to high molecular mass liquids such as polymer melts, where surface-active species with a viscosity much lower than the homophases can occur. In cases where the kind of additive referred to above is not intentionally introduced, such effects might also occur when low molecular homophase components segregate at the interface. If further evidenced this would provide an additional explanation as to why coalescence can play such an important role in commercial polymer blend systems.

Implication for 'real blends' and compatibilisation

In 'real blends', droplet sizes will be in the order of microns and the time-scale of the coalescence event will be much shorter (seconds rather than hours). With h_{crit} known, they can, in principle, be predicted with the Chesters model[4,8]. However, if the time-scale influences the viscosity or interfacial mobility, this prediction might fail.

At present, it appears reasonable to assume that on an increase in the interfacial expansion rate, the increase in interfacial mobility through the lower number of coupled chains (increased mobility) will be small and possibly counteracted by surface elasticity. Matrix viscosity effects will have to be quite large in the viscosity ratio regime of interest ($\eta_d/\eta_m \simeq 1$) to have a significant effect. Therefore, neglecting these time- scale effects should not lead to large errors. Given our results for the 'commercial' systems, the effects of additives in 'real blends' are expected to be much larger.

Finally, with respect to compatibilisation, effective inhibition of coalescence could be achieved by 'pinning' matrix film molecules to the wall. This can be done, for example, by introducing block copolymers with different tails that are compatible to either the matrix or the dispersed phase. Apart from reducing the interfacial mobility, such block copolymers could also inhibit coalescence through the introduction of a repulsive interaction, much like the stabilisation of colloids through steric hindrance[31]. It is clear, however, that the possible lubricating effect that we have found in the commercial system will have to be avoided.

CONCLUSIONS

It has been shown that using the spinning drop apparatus, reproducible coalescence experiments can be performed with polymer melts. Coalescence times increase with dispersed phase viscosity, as expected by the Chesters model[8] based on partially mobile interfaces.

The time-scale of the experiment is acceptable for low-viscosity dispersed phases. The operating window of the experiment can be enlarged to higher-viscosity dispersed phases by reducing the contact area through reducing the speed of rotation.

It was shown that in commercial polymers, the coalescence process can be considerably faster than for purified components. This appears to be related to the presence of low molecular mass interfacial active additives and/or impurities which also lower the interfacial tension and may represent an additional cause for coalescence problems in commercial systems.

For purified systems, the rupture thickness was found to be in the order of magnitude expected from what is known for low molecular mass systems. Given the macromolecular character of the matrix film, this raises questions as to the importance of repulsive interactions and/or the effects on the matrix viscosity due to entropic effects at very small film thickness. Apparently, these are negligible in our experiments, although there is some evidence that they become stronger on increasing the molecular mass of the matrix film.

Partial mobility is one reason why coalescence plays a relatively important role in morphology development during polymer blending. It therefore seems likely that compatibilising effects of block copolymers are partly based on reducing the interfacial mobility. However, the introduction of repulsive effects at close droplet approach might also add a significant contribution.

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