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ORIGINAL CONTRIBUTION

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Diffusion effects on the interfacial tension of immiscible polymer blends

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Abstract Most methods of measuring the interfacial tension between two immiscible polymers are based on the analysis of the shape that a drop of one polymer immersed in the other one exhibits under the action of flow or gravity. In such a situation, the small, yet nonzero mutual solubility between the two polymers acts toward mass transfer between the drop and the surrounding fluid. In this work, diffusion effects on the interfacial tension of the pair polyisobutylene/polydimethylsiloxane have been investigated by drop deformation under shear flow. When the drop was made of polyisobutylene, drop size decreased with time due to diffusion. Drop shrinkage was associated with a significant increase in interfacial tension, until an apparent plateau value was reached. The effect was attributed to a selective migration of molecular weights, which would act to enrich the drop with higher molar mass material. To support such an interpretation, drop viscosity was evaluated by drop shape analysis and it was actually found to increase with time. In some cases, the ratio between drop and continuous phase viscosity became higher than the critical value for drop breakup in shear flow. Upon inverting the phases (i.e., when the drop was made of polydimethylsiloxane), no significant transient effects were observed. In the light of these results, the problem of what are the correct values of interfacial tension and viscosity ratio for a polymer blend of a certain composition will also be discussed.

Key words Interfacial tension · Immiscible polymer blends · Drop deformation · Shear flow · Diffusion

Introduction

It is well known that interfacial tension is a key parameter in the characterization of the structural properties of polymer blends, such as morphology and stability of the dispersed phase (Utracki 1989). An extensive body of knowledge is available in the literature on well-developed experimental techniques for measuring the interfacial tension of polymer pairs, as reviewed long ago by Wu (1974). Most methods are based on the analysis of the shape assumed by an isolated drop of one polymer immersed in the other one, under the action of gravity or flow. The results provided by drop-based methods are usually taken as representative of the interfacial tension of blends of the two polymers, independent of blend composition.

Even though most polymers are considered immiscible for practical purposes, some mutual solubility, however small, is always present and it will give rise to some mass transfer during the measurements. The effect might be especially relevant in drop-based methods, where, because the drop is usually small compared to the surrounding volume of fluid, interdiffusion of the two polymers will not lead to a phase equilibrium and eventually the drop should disappear by dissolving in the continuous phase. On the other hand, the kinetics of polymer–polymer diffusion is expected to be quite slow and mass transfer might be negligible on the time scale of the experiment. In any event, one is faced by the problem of finding the extent of the influence of diffusion on interfacial tension.

Few results of diffusion effects on the interfacial tension have been reported in the literature, and these were mostly obtained by classical techniques, such as the Wilhelmy plate and the du Nuoy ring (Wu 1974). A decrease in interfacial tension with time was observed by Smith et al. (1961) for a pair of miscible silicone oils of different viscosities. The effect was attributed to diffusion between the two mutually soluble liquids. The Wilhelmy plate technique used in the measurements allowed the authors to determine only the trend and not the actual values of interfacial tension. Grace (1982) used a du Nuoy ring tensiometer to measure the interfacial tension of the system Vorite/Si 1000. A decrease in interfacial tension with time was observed and it was attributed to slow diffusion in the highly viscous system under study, due to the very small, yet nonzero mutual solubility between the two components. The interfacial tension of the same system was also independently measured by Grace from the stationary deformation of an isolated drop in shear flow. The results determined by the du Nuoy ring technique were extrapolated to zero contact time (i.e., before the onset of diffusion), thus obtaining the interfacial tension between the pure components. The extrapolated value was in good agreement with the interfacial tension measured by drop deformation under shear flow. The explanation proposed by Grace for such agreement was that, since under shear the interface between drop and continuous phase is dynamic, fresh components are in contact and the interfacial tension acting is that between the pure components for an extended period. A way of testing such an explanation would be to exploit the drop deformation method to monitor interfacial tension as a function of time, but this has not yet been done. More recently, Varanasi et al. (1994) measured the interfacial tension of several Newtonian systems using the sessile drop technique. It was found that interfacial tension decreased with time, in agreement with Grace's results, and an extrapolation procedure was used to estimate a dynamic value of interfacial tension.

In this work, the influence of diffusion on the interfacial tension of immiscible polymer blends has been investigated. The experiments were carried out on the pair polyisobutylene/polydimethylsiloxane (PIB/PDMS). Interfacial tension was measured by analyzing drop deformation under shear flow in a parallel plate apparatus. The analysis of the drop shape was based on small deformation theories by Taylor (1932, 1934) and Chaffey and Brenner (1967). Drop size was monitored over the course of the experiment to evaluate the extent of diffusion. The measurements of interfacial tension were also carried out as a function of time to investigate the effects of diffusion.

Experimental

The polymers used in the experiments are polyisobutylene (PIB) and polydimethylsiloxane (PDMS). The former was supplied by Exxon under the trade name of Parapol 1300; the molecular weight M_W was 2200, with $M_W/M_n = 1.7$ (C.K. Chai, personal communication). The latter was supplied by Rhone-Poulenc under the trade name of Rhodorsil 47V200,000. The molecular weight of the PDMS sample was estimated as 173,000 from the Newtonian plateau viscosity at 25 °C using data from Rhone-Poulenc and several authors, reported by Longin et al. (1998). Both PIB and PDMS are transparent liquids at room temperature. The small density difference between the two polymers (around 0.08 g/cm^3) and the high viscosity (81 Pa·s for PIB and 190 Pa·s for PDMS, both at 25 °C) ensure that buoyancy effects are negligible. For both PIB and PDMS under shear rates of up to around 1 s^{-1}, viscosity is constant with shear rate and the first normal stress difference is so small that it can hardly be measured with common instruments (at 23 °C and $\dot{\gamma} = 1$ s^{-1}, $N_1 \approx 1.8$ Pa for PDMS and the extrapolated value of N_1 is 0.13 Pa for PIB; Minale et al. 1997). In all the experiments care was taken to keep the shear rate below 1 s^{-1}, thus ensuring Newtonian behavior for the two polymers. The interfacial tension of the PIB/PDMS system used in this work was measured by Sigillo et al. (1995) and Guido and Villone (1998) using several methods, and an average value of 2.5 ± 0.5 mN/m was obtained.

Simple shear flow was generated by a parallel plate apparatus, which has been described in detail elsewhere (Guido and Simeone 1998; Guido and Villone 1998). Briefly, each plate was glued onto a glass slide, which fits into a window cut on a rigid mount. A motorized stage was used to displace one of the mounts to apply the shear. Parallelism between the two plates was adjusted through a set of tilting, rotating and translating micrometric stages. To load the polymer selected as the continuous phase, the moving plate was first driven apart from the fixed one. The sample was then loaded between the two plates using a syringe and the moving plate was moved toward the fixed one until the desired gap was reached. A drop of the other polymer was injected into the sample between the glass plates using a tiny glass capillary, which was introduced into the gap by means of a homemade micromanipulator. Drop deformation under shear flow was observed along the vorticity direction of shear flow by looking through the glass slides with a transmitted light microscope. Images of the sample were captured by a CCD video camera and recorded on tape for later analysis. Images were digitized by a frame grabber installed on a PC and data analysis was performed in an automated way using image processing techniques (Guido and Villone 1998). The projected drop shape was described as an ellipse with the same first and second moments of area as the image of the drop in the plane of shear. It has been shown that such a description provides a good representation of the drop projection up to rather high deformations (Guido and Villone 1998), even though the exact shape deviates somewhat from an ellipse (Guido et al. 1999). The two axes of the equivalent ellipse and the angle between the major axis and the velocity gradient were calculated from the moments of area (Guido and Villone 1998).

Drop deformation was expressed in terms of the deformation parameter $D = (a - b)/(a + b)$, where a and b are, respectively, the major and the minor axis of the drop in the shear plane. Two nondimensional quantities, first introduced by Taylor (1932, 1934), were used in the analysis of drop shape: the capillary number Ca, defined as $\mu_c R\dot{\gamma}/\sigma$, where μ_c is the viscosity of the continuous phase,

R is the radius of the underformed drop, $\dot{\gamma}$ is the shear rate and σ is the interfacial tension; and the viscosity ratio λ, defined as μ_d/μ_c, μ_d being the viscosity of the drop.

Taylor derived the following equation for the steady state value of D:

$$D = \frac{19\lambda + 16}{16\lambda + 16}\mathrm{Ca} \qquad (1)$$

which is valid at small deformations and for Newtonian fluids. Equation (1), which predicts a linear relation between D and Ca, can be used in a straightforward way to determine the interfacial tension between the two fluids. Indeed, by fitting Eq. (1) to experimental data of D versus shear rate, σ can be directly calculated as the only fitting parameter. The application of Eq. (1) to the evaluation of interfacial tension is well documented in the literature and good agreement was found with results obtained by other techniques (Rumscheidt and Mason 1961; Torza et al. 1972; Sigillo et al. 1995; Guido and Villone 1998).

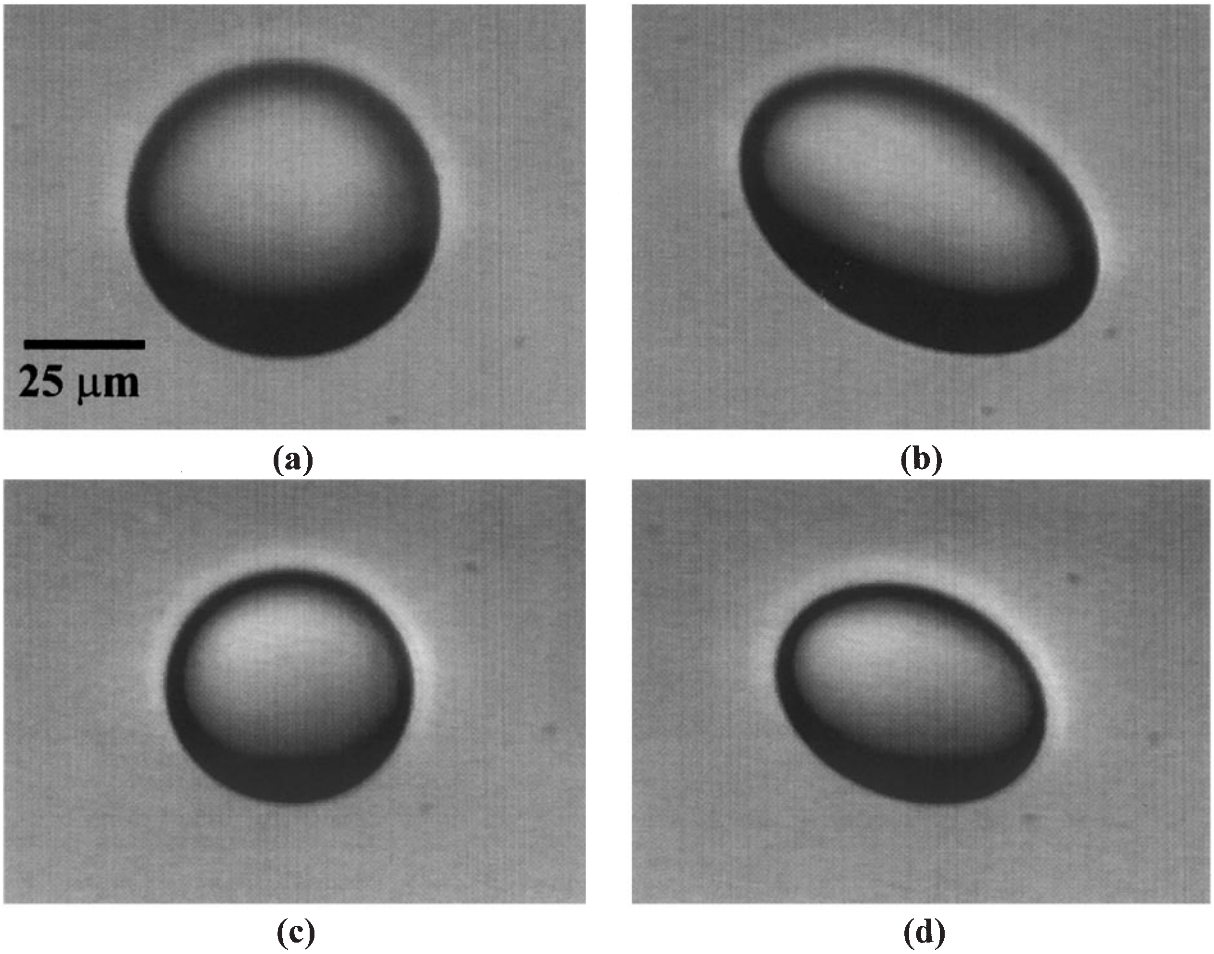
Results

The experimental results are presented in the following four subsections. In the first and second one, the case of a PIB drop injected into a PDMS sample in the parallel plate apparatus is considered. In the third subsection, results obtained for a PDMS drop injected into PIB are shown. Finally, experiments of diffusion in PIB/PDMS blends are presented in the fourth subsection.

Drop of PIB in PDMS sheared at a fixed $\dot{\gamma}$ at different times

In the first set of experiments a drop of PIB was injected into a PDMS sample between the glass plates. The sample was sheared at a fixed shear rate for enough strain units to ensure that the drop reached a steady-state shape. The flow was then stopped and the drop allowed to relax back to the spherical, undeformed shape. The sample was sheared again at the same value of shear rate and for the same number of strain units, but in the opposite direction, in order to test reproduc-

Fig. 1 Images of a PIB drop injected into PDMS in the shear apparatus: at rest (**a**) and at steady state under shear flow (**b**) in the beginning of the experiment (~30 min), and at rest (**c**) and at steady state under shear flow (**d**) at the end of the experiment (~140 h)



ibility. The whole procedure was repeated several times (at a fixed interval) for a few days, keeping both the shear rate and the number of strain units constant. Since, as pointed out in the Experimental section, buoyancy effects are very small for the PIB/PDMS system under investigation, vertical displacement of the drop was negligible throughout the experiment.

The results obtained from a one-week experiment are presented in Figs. 1–6. The shear rate was fixed at 0.09 s^{-1}. Images of the PIB drop taken at several times during the experiment are reported in Fig. 1a–d.

The time at which the first shear was applied was taken as the origin of the time scale (the exact time of drop injection was not recorded in this experiment, but it was about 1 h before the first shear). In Fig. 1 the drop is shown at rest in the beginning of the experiment (Fig. 1a) and in the deformed state in the subsequent shear flow once a stationary shape was attained (Fig. 1b. ~30 min). The same drop is shown at rest at the end of the experiment (Fig. 1c) and at steady state in the last shear flow (Fig. 1d, ~140 h). The decrease in the drop size from Fig. 1a to c is quite remarkable, and so is the change in drop deformation and orientation from Fig. 1b to d. The variation of drop diameter with time during the whole experiment is shown in Fig. 2 on a logarithmic time scale. The data are well represented by a linear fit, shown by the *solid line* in Fig. 2. Starting with a diameter of about 67 μm, the PIB drop shrunk gradually with time, reaching a diameter of 51 μm at the end of the experiment. Thus, the percent reduction of the diameter was about 24%, corresponding to a reduction in the volume of 56%.

The next step in the data analysis was to calculate the interfacial tension, in order to evaluate whether the measurements were somehow affected by the drop shrinkage. To this purpose, the deformation parameter D was measured from the steady-state shapes assumed by the deformed drop in the course of the experiment. The variation of D with time is shown in Fig. 3 on a logarithmic time scale (the solid line is again a linear fit to the data).

The difference between the two points plotted at each time (corresponding to two runs in opposite directions and at the same shear rate) gives an estimate of the experimental error involved in the measurements. It can be seen that D underwent a significant decrease with time, going from the initial value of 0.22 to 0.13 at the end of the experiment. Such a trend is not unexpected, since Eq. (1) shows that a reduction in drop size should be followed by a proportional decrease in D, if all the other quantities stay constant. However, when the interfacial tension was calculated from the data of Figs. 2 and 3 using Eq. (1), a significant change in σ with time was observed. Starting from 2.9 mN/m, σ increased over the course of the experiment and eventually reached a plateau of about 4 mN/m. It was therefore decided to go further in the analysis of the drop shape and to evaluate if the other fluid properties needed to calculate σ from Eq. (1), i.e., the viscosity of the continuous phase and the viscosity ratio, also changed with time. In fact, the former is unlikely to change due to the small mass transfer from the drop to the surrounding fluid and it was considered to be constant with time (apart from the effect of the small temperature variations recorded during the experiment, which was accounted for in the calculations). On the other hand, changes in the viscosity ratio with time, brought about by possible variations of the drop viscosity during the experiment, cannot be excluded a priori.

Since Eq. (1) predicts a rather weak dependence of D on λ, the observed change of σ during the experiment cannot be explained by even substantial variations of λ. Nevertheless, for the sake of precision, an attempt was made to evaluate λ as a function of time over the course of the experiment. To this purpose, we used the data of drop orientation, expressed as the angle θ that the drop's major axis makes with respect to the velocity gradient direction. At steady-state, the angle θ is related to the

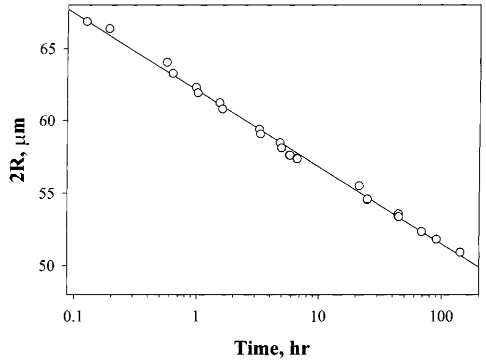


Fig. 2 Size variation as a function of time for the same drop as in Fig. 1

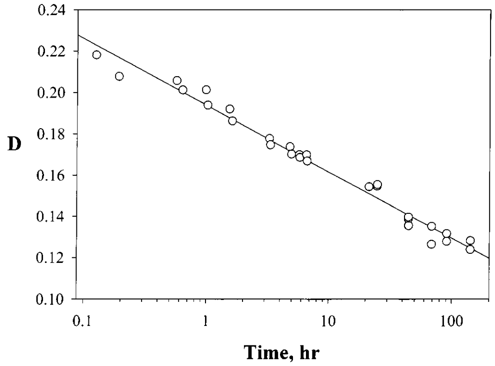


Fig. 3 The deformation parameter D as a function of time for the same drop as in Fig. 1

deformation parameter by the following equation, derived by Cerf (1951):

$$\theta = \frac{\pi}{4} + \frac{2\lambda + 3}{5} D \qquad (2)$$

which can be used to determine λ from the experimental data of θ versus D. Equation (2) takes into account a small error in Cerf's analysis pointed out by Roscoe (1967) and is valid in the limit of small deformations, a condition which is satisfied in the experiment described so far (as shown by Guido and Villone (1998), when λ is close to 1 the small deformation theory is valid up to values of D around 0.25).

The plot of θ as a function of D is presented in Fig. 4. Since the deformation parameter decreases during the experiment, later times are represented by lower values of D. The variation of θ during the experiment can be described as a gradual increase followed by a levelling off to a value of 62°. From the data shown in Figs. 3 and 4, λ can be calculated as a function of time and the results are presented in Fig. 5.

It can be seen that the initial value of λ ($\sim$0.9) does not coincide with the value that one would expect from the viscosities of PIB and PDMS ($\sim$0.5). This is due to the fact that the first shear, which was taken as the origin of the time scale, was applied some time after drop injection. The main feature of Fig. 5 is the large increase in the viscosity ratio, which goes from the initial value of 0.9 to a plateau level of 4.4. Furthermore, such a value is higher than the critical value of λ for breakup in shear flow (about 3.7).

The interfacial tension was then re-calculated using Eq. (1) with the correct values of λ presented in Fig. 5. The results, which are plotted as a function of time in Fig. 6, show that, as expected, a significant change of σ during the experiment is still present after the correction to the viscosity ratio.

The trend displayed by σ was an increase with time, starting from 2.9 mN/m, until an apparent plateau of about 4.2 mN/m was reached. It can be seen that the total change in σ is significantly above the experimental error, which is mainly due to uncertainties in the measurements of D and can be estimated as the difference between the two points corresponding to each time.

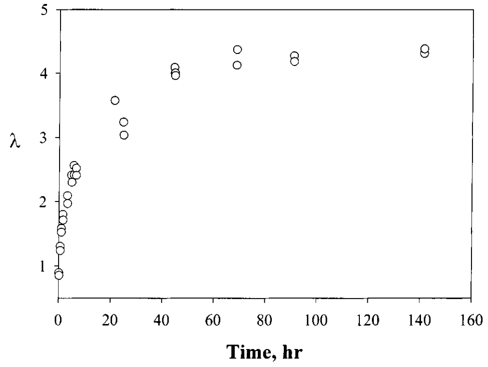


Fig. 5 The time evolution of the viscosity ratio λ calculated from the data presented in Figs. 3 and 4 using the Cerf Eq. (2)

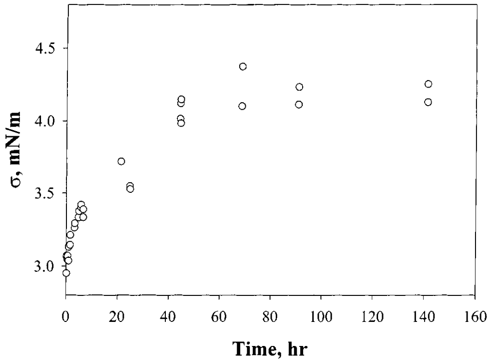


Fig. 6 The time evolution of the interfacial tension calculated from the data presented in Figs. 2 and 3 using the Taylor Eq. (1)

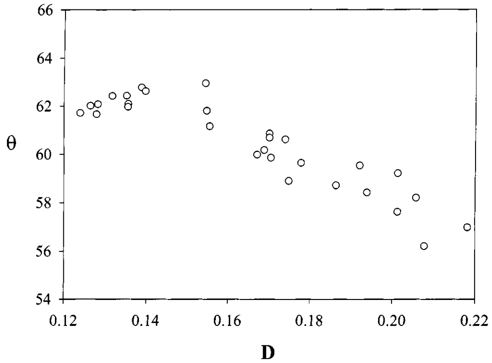


Fig. 4 Plot of the angle θ between the drop's major axis and the velocity gradient versus the deformation parameter D for the same drop as in Fig. 1

Drop of PIB in PDMS subjected to a shear rate sweep at different times

To confirm the results described so far, a second, more comprehensive set of experiments was carried out keeping PIB as the drop and PDMS as the continuous phase. In the previous experiments, the evolutions of λ and σ with time were calculated from the analysis of the stationary drop shape at a single value of shear rate. A higher accuracy would be achieved if data corresponding to several values of $\dot{\gamma}$ were available. To this purpose, the experimental protocol was changed in the following way. The drop was sheared at the lowest selected value of $\dot{\gamma}$ (around 0.05 s^{-1}) until the shape reached a steady-state configuration. At this point, the flow was stopped and the drop allowed to relax. The shear rate was then set at a higher value by adjusting the speed of the moving plate and the sample was sheared again, waiting as before for a stationary shape and then allowing the drop to relax. The same sequence was repeated several times (up to $\dot{\gamma}$ around 1 s^{-1}) and this modified protocol will be referred to as a shear rate sweep. In the course of an experiment the sample was subjected to several shear rate sweeps separated by a given time interval. The time required by a shear rate sweep was always small compared to the characteristic time of drop shrinkage. The number of shear rates applied in a shear rate sweep was four at the beginning of the experiment, where a faster drop shrinkage was expected, and was gradually increased (up to 10) over the course of the experiment.

The results from an experiment which lasted two days are presented in Figs. 7–9. The time evolution of the drop radius, which is shown in Fig. 7, was again linear when plotted on a logarithmic time scale. The initial radius was about 18 μm and a decrease in 16% was measured over the course of the experiment (41% volume change), with a faster rate of drop shrinkage relative to the previous experiment. Five shear rate sweeps were carried out during the experiment, starting about 1 h after drop injection. In Fig. 8, θ is plotted as a function of D and, for the sake of clarity, only data corresponding to the first and last shear rate sweeps are shown.

The shear rate ranged from 0.05 to 0.25 s^{-1} in the first sweep and from 0.08 to 1.6 s^{-1} in the last sweep. The lines in Fig. 8 were obtained by fitting Eq. (2) to the two sets of data (for the last shear rate sweep, only the first five points at the lowest values of $\dot{\gamma}$ were used in the fitting procedure in order to stay within the small deformation limits). The difference in slope between the two lines is a measure of the total change in λ measured over the course of the experiment.

In Fig. 9, D is plotted as a function of $\dot{\gamma}$ for the first and last shear rate sweeps. The two lines in Fig. 9 represent a fit of Eq. (1) to the data (with the values of λ calculated from Fig. 8) and the slopes are inversely proportional to the interfacial tension. It can be seen that the data taken in the last shear rate sweep show a strong deviation from linearity at high values of $\dot{\gamma}$, where the deformation parameter seems to level off to a value of around 0.4. Even at the highest values of $\dot{\gamma}$, a stationary shape was observed and the drop did not show any tendency to break up. Such a trend of D versus $\dot{\gamma}$ is characteristic of systems with λ exceeding the critical value for drop breakup (which is ca. 3.7 in shear flow). The values of the drop diameter, percentage volume reduction, σ and λ corresponding to the five shear rate sweeps are shown in Table 1.

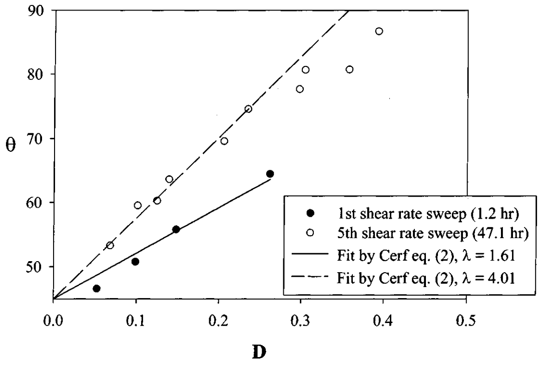


Fig. 8 Plot of θ versus D for the first (*filled circles*) and the fifth (*open circles*) shear rate sweep of the experiment of Fig. 7. The corresponding times are 72 min and 46 h 30 min (starting from drop injection)

It can be seen that the final values of both σ and λ are in good agreement with the values of the experiment at a single shear rate described earlier. The difference of the initial values compared to the previous experiment can be attributed to the faster kinetics of drop shrinkage already pointed out.

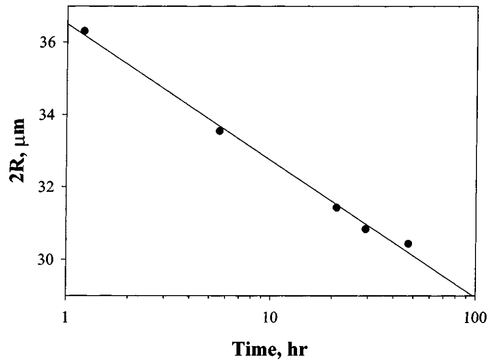


Fig. 7 Plot of diameter as a function of time for a drop of PIB in PDMS. At each time a shear rate sweep was run in the parallel plate apparatus

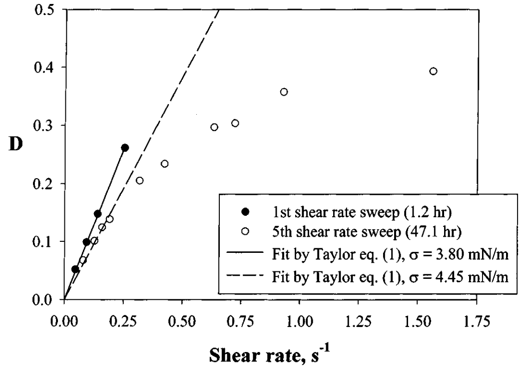


Fig. 9 Plot of D versus shear rate for the same experiment as in Fig. 7. Data for the first (*filled circles*) and the fifth (*open circles*) shear rate sweep are shown, as in Fig. 8

Table 1 Variation of drop diameter, percentage volume reduction, viscosity ratio λ and interfacial tension σ with time for the experiment of Figs. 7–9

Time (h)	Drop diameter (μm)	Volume reduction (%)	λ	σ (mN/m)
1.2	36.3	0	1.61	3.80
5.6	33.5	21	3.00	4.12
21.1	31.4	35	3.80	4.29
29.2	30.8	39	3.59	4.49
47.1	30.4	41	4.01	4.45

Drop of PDMS in PIB subjected to a shear rate sweep at different times

When drops of PDMS were injected into PIB no significant variation of size with time was observed, neither were significant changes of σ and λ with time found in experiments of drop deformation under shear flow such as the ones described for PIB drops. As an example, in Fig. 10, θ is plotted as a function of D for an experiment on a PDMS drop of initial radius equal to 55 μm.

The two sets of data shown in Fig. 10 correspond to two shear rate sweeps carried out, respectively, at 7 h (filled circles) and at 17 h (empty circles) after drop injection. The continuous line and the dashed line were obtained by fitting Eq. (2) to the data at 7 h and 17 h, respectively. The slight difference between the slopes of the two lines is probably not significant, i.e., within the accuracy of the fit. The values of λ determined from the fit are 2.01 at 7 h and 1.90 at 17 h and these coincide, within experimental error, with the values calculated from the viscosity of the two polymers (taking into account a change of about 1 °C in the sample temperature during the experiment), which are 2.09 at 7 h and 1.89 at 17 h. Furthermore, the drop radius did not change in an appreciable way (the value measured at 17 h was 54.8 μm) and the difference between the values of σ, which were 2.58 mN/m at 7 h and 2.50 mN/m at 17 h, was well within the experimental error (the plots of D versus $\dot{\gamma}$, which are linear throughout the range of $\dot{\gamma}$, were not included for the sake of brevity).

Experiments of diffusion in PIB/PDMS blends

In the experiments described so far a significant variation of interfacial tension and viscosity ratio was associated with the diffusion of PIB from an isolated drop to the continuous PDMS phase. These results motivated a final set of experiments, which were carried out on blends of the two polymers where PIB was the dispersed phase. Here, the goal was to evaluate, at least qualitatively, the extent of PIB diffusion which, by analogy with the isolated drop case, is expected to take place upon mixing the two polymers. The experimental approach was to inject a drop of pure PIB into the PIB/PDMS blend and measure its size reduction until equilibrium was attained. By comparing this reduction to the case of an isolated drop one can estimate the actual values of the viscosity ratio and the interfacial tension of the blend. PIB/PDMS blends were prepared by mixing and stirring by hand appropriate amounts of the two polymers. The blends were allowed to equilibrate for a few weeks before use. A sample of a blend was placed between two microscope slides separated by two rectangular spacers (thickness 1 mm). A drop of PIB was injected into the sample and images were recorded at several times to monitor the drop size evolution. The size of some drops of the dispersed phase was also measured as a function of time and no variation was found, thus confirming that equilibrium had been attained. Only dilute blends (up to 3% by weight of PIB) were studied, since in concentrated blends it was difficult to distinguish the injected drops from the ones constituting the dispersed phase, due to the high turbidity of the sample.

In Fig. 11 the variation of diameter with time is presented for two drops, one injected into a 1% PIB

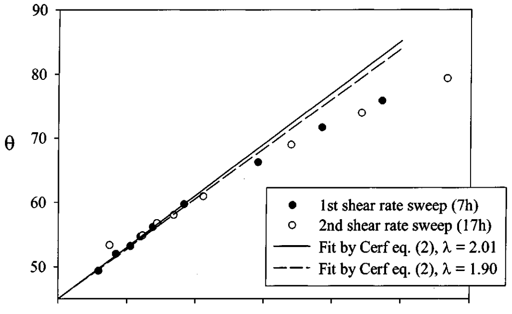


Fig. 10 θ as a function of D for a PDMS drop in PIB. *Filled* and *open circles* refer, respectively, to shear rate sweeps run 7 and 17 h after drop injection

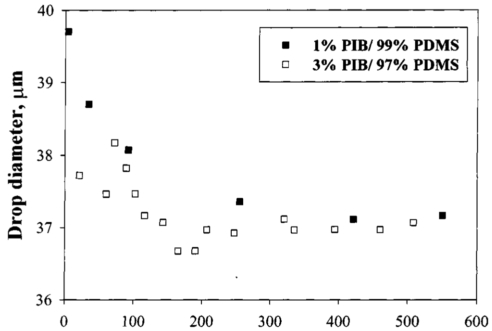


Fig. 11 Size evolution with time of PIB drops injected into PIB/PDMS blends. *Filled* and *open squares* refer, respectively, to blends containing 1 and 3% by weight of PIB

blend and the other into a 3% PIB blend (all the percentages are by weight). The initial diameter of the two drops was around 40 μm and a significant change in size can be observed for both drops. Even though the data of the 3% blend are somewhat scattered, owing to the difficulties of focusing in a turbid sample, it can be seen that in either blend both the rate and the extent of shrinkage are smaller compared to the case of an isolated drop. Volume reduction is 20% in the 1% blend and 11% in the 3% blend and the characteristic time of shrinkage is of a few hours.

Discussion

The experiments described in the previous section show that a drop of PIB immersed in PDMS undergoes a reduction of size with time, the process being faster for a smaller initial radius. A simultaneous, significant increase in the viscosity ratio and the interfacial tension is observed. In this section, a possible explanation of the results found in this work will be proposed, starting with the time dependence of the drop size and the viscosity ratio.

Drop shrinkage is clearly driven by the solubility, though small, of PIB in PDMS. The parallel increase in λ with time might be explained by invoking a selective diffusion with respect to molecular weight. Indeed, mass transfer from the drop to the surrounding medium is expected to be faster for the lower molar mass PIB fractions. Upon shrinking, the drop becomes enriched with the higher molar mass material, while the change in composition of the surrounding PDMS can be considered negligible, given the small size of the drop. As a consequence, the viscosity of the drop tends to increase, whereas the viscosity of the continuous PDMS phase stays constant. The overall result is then an increase of the viscosity ratio with time. Furthermore, the progressive decrease of the rate of shrinkage with time might be attributed to the slower diffusion of the higher molar mass material still remaining inside the drop.

The trend of σ, i.e., an increase followed by an apparent plateau while the drop appears still to be shrinking, can be explained by this selective migration of molecular weights, which makes the drop more and more enriched with higher molar mass material. We propose that such an increase in molecular weight leads to the observed trend of σ, based on previous studies in the literature showing that the interfacial tension of polymer pairs increases with molecular weight with a power law dependence, reaching an apparent plateau above the entanglement chain length (LeGrand and Gaines 1975; Gaines and Gaines 1978; Anastasiadis et al. 1988; Ellingson et al. 1994; Kamal et al. 1994). Further support to this explanation is given by the work of Wagner and Wolf (1993), who measured the interfacial tension between PIB fractions with narrow molecular weight distributions and PDMS by means of spinning-drop and sessile-drop techniques. For a given PDMS sample, it was found that at room temperature σ increased with the molecular weight of the PIB fractions used in the mixture. The values of σ went from about 2.5 to 4.0 mN/m, which is the same range experienced in this work. More evidence of the effect of partial solubility on the interfacial tension of immiscible polymer blends can be found in the work of Anastasiadis et al. (1986), who measured σ between polybutadiene (PBD) and PDMS as a function of temperature and molecular weight by means of the pendant drop technique. These authors found that σ increased significantly with PBD molecular weight, while a relative insensivity to PDMS molecular weight was observed. To explain such a dependence, it was suggested that in an highly polydisperse system, such as PDMS, the lower molecular weight material may reside preferentially at the interface, thus giving rise to an interfacial tension relatively independent of the average molecular weight. An excess of small chains at the interface of polydisperse systems, lowering the interfacial tension, has been predicted theoretically by Broseta et al. (1990).

The time dependence of the interfacial tension found in this work when the drop was made of PIB is the opposite of that reported in previous studies (Smith et al. 1961; Grace 1981; Varanasi et al. 1994), as mentioned in the Introduction. The discrepancy might be explained if the polydispersity of the samples used in such studies was small. In the absence of polydispersity, indeed, it has been shown theoretically that the interfacial tension of two interdiffusing liquids is a decreasing function of time (Smith et al. 1961). Distributions of molecular weights were not provided in the studies mentioned in the Introduction, but polydispersity should be rather limited, given the much lower molecular weights of the samples as compared with the ones used in this work.

Let us now consider the case of PDMS drops in a PIB sample. Variations of drop size with time were negligible on the time scale of the experiments performed in this work. Similarly, neither the interfacial tension or the viscosity ratio changed significantly, the latter quantity being equal to the value calculated from the viscosities of the pure components (see Fig. 10). In fact, as it was the case when the phases were reversed, some PIB will surely diffuse inside the PDMS drop. However, due to the small solubility of PIB in PDMS such diffusion is not expected to produce a significant increase in drop size. On the other hand, PDMS will also diffuse out of the drop, due to its solubility, though small, in PIB and this process should lead to a reduction in drop size. The lack of drop shrinkage over the course of the experiment might be explained by the small diffusion coefficient which is expected for PDMS, given its high molecular weight (relative to PIB). It is likely that drop shrinkage will be observed only on time scales longer than the ones adopted in this work.

As described in the Results Section, some experiments were performed on dilute PDMS/PIB blends. The goal was to ascertain how representative of the value of σ for a polymer blend the results obtained from measurements on isolated drops were. It was found that PIB drops injected into blends decreased in size with time, even though at a smaller rate than for the isolated drop case, the shrinkage being faster for the more dilute blend. Such results might be explained as follows. Upon mixing the two polymers, some diffusion between dispersed and continuous phase is expected to take place due to mutual solubility. If such diffusion is selective with respect to molecular weight, some fractionation between the coexisting phases occurs. On the time scale of the experiments, actual phase equilibrium might not be attained for all the molecular weights, due to the slow diffusion of the high molar mass species. The extent of fractionation might depend on blend composition, since, by increasing PIB concentration, the low molar mass material diffused in the continuous phase will eventually be enough to reach an equilibrium with the dispersed phase. In such a scenario, the viscosity ratio and the interfacial tension between the two phases are not equal to the values that can be obtained from the pure components. Furthermore, at higher PIB concentrations the low molar mass fraction diffused out of the dispersed phase becomes smaller, and therefore the viscosity ratio should tend to the value calculated from the pure components. The interfacial tension is then expected to be close to the value extrapolated to a zero time of contact in isolated drop experiments.

A rough estimate of the values of λ and σ for a given PIB/PDMS blend can be obtained from the data reported in Table 1, which refers to an isolated PIB drop subjected to a shear rate sweep experiment. In fact, according to the proposed interpretation, the values of λ and σ, either for a blend or an isolated drop, should depend only on the amount of drop volume reduction, if transient effects are neglected. For a blend, the volume reduction experienced by the dispersed phase drops, in the equilibration process after mixing, can be taken as equal to the volume reduction measured for a fresh PIB drop injected into the blend. One can then use data taken for an isolated PIB drop, such as the data in Table 1, to get values of λ and σ corresponding to the measured volume reduction and take such values as estimates for the blend. For example, for the 1% blend (20% volume reduction) one finds $\lambda \sim 3$ and $\sigma \sim 4$ mN/m from Table 1. Of course, this is just a qualitative estimate, the aim being to point out that diffusion effects can be significant not only for isolated drops, but even for blends.

A possible way of measuring the interfacial tension of a blend is to separate somehow the two phases coexisting at equilibrium and to use the shear apparatus (or any other isolated drop method) on a drop of one phase injected into the other one. In this work, an attempt was made to achieve phase separation by ultracentrifugation of the PIB/PDMS blends. However, due to the small density difference and to the high viscosity of the two polymers, full separation was not attained even after extensive centrifugation at high speed (several days at 100,000 *g*).

Conclusions

In this work, diffusion effects on the interfacial tension between two immiscible polymers have been investigated by the analysis of drop deformation in shear flow. In spite of the possible influence on the measured values of σ, such effects have so far been generally overlooked in the literature. The main contribution of this work is the development of an experimental procedure, based on an advanced video imaging and analysis system, which allows one to monitor simultaneously the drop size, the interfacial tension and the viscosity ratio as a function of time. For the PIB/PDMS system investigated, it was found that the measurements can be significantly influenced by mutual solubility, even if small as in the case of a polymer pair which is considered immiscible for practical purposes. When the drop was made of PIB, both the interfacial tension and the viscosity ratio increased with time, at a rate dependent on drop size. Upon inverting the phases, no significant transient effects were observed in the time scale of the experiments.

Similar complications are expected in the application of other methods based on the analysis of the shape of a drop under the action of gravity or flow, such as the pendant drop or the spinning drop. A careful monitoring of drop size with time is required as a preliminary test for a proper measurement of the interfacial tension by any of these methods. Furthermore, the results of this work show that possible ways of minimizing transient effects are an appropriate choice of which polymer is to be used as the continuous or the drop phase, and of initial drop size, since shrinkage is slower for bigger drops.

Even when transient effects are minimized, you should still assess if the measurements of interfacial tension are representative of the actual values for the blends investigated. Fractionation of molecular weights between the coexisting phases might lead to values of σ and λ significantly different from those measured by isolated drop experiments, and the effect might be dependent on blend composition. In some cases λ might become higher than the critical value for drop breakup in shear flow, with the consequence that no size refining of the dispersed phase can be obtained by shearing the sample.

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