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Transient interfacial tension and dilatational rheology of diffuse polymer-polymer interfaces

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We demonstrate the influence of molecular weight and molecular weight asymmetry across an interface on the transient behavior of the interfacial tension. The interfacial tension was measured as a function of time for a range of polymer combinations with a broad range of interfacial properties using a pendant/sessile drop apparatus. The 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 the specific combination of polymers, the transient interfacial tension is found to increase or decrease with time. The results are interpreted in terms of a recently proposed model [Shi *et al.*, *Macromolecules* **37**, 1591 (2004)], giving relative characteristic diffusion time scales in terms of molecular weight, molecular weight distribution, and viscosities. However, the time scales obtained from this theoretical approach do not give a conclusive trend. Using oscillatory dilatational interfacial experiments the viscoelastic behavior of these diffusive interfaces is demonstrated. The time evolution of the interfacial tension and the dilatational elasticity 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. The dilatational elasticity and the dilatational viscosity show a frequency dependency that is described qualitatively by a simple Fickian diffusion model and quantitatively by a Maxwell model. The characteristic diffusion times provided by the latter show that the systems with thick interfaces (tens of microseconds and more) can be considered as slower diffusive systems compared to the systems with thinner interfaces (a few micrometers in thickness and less) can be considered as fast diffusive systems. © 2005 American Institute of Physics. [DOI: 10.1063/1.1856454]

I. 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 dynamics is a key issue for controlling processes such as drop break-up and coalescence. The mutual diffusion between two polymers that are not fully miscible is, at long times, restricted to a finite length scale.¹⁻³ 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 important factors determining the final morphology of a polymer blend.

The discrepancies between theoretical predictions on structure development and experimental results⁴⁻⁹ are, 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.^{4-6,10-12} This seems reasonable since the polymers consist of long molecules, and mixing of those molecules is thermodynamically unfavorable.¹³ Moreover, polymers possess a high (macroscopic) viscosity [typically from $O(1-10^3)$ Pa s] and therefore mutual diffusion if present, is

expected to be slow (the mutual diffusion coefficient is of the order of 10^{-13} cm²/s and smaller¹⁴). 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. Small molecules start to diffuse since they move faster than the slow entangled large molecules, creating in this way an increase in density in the interfacial zone that quickly settles down by the relaxation of the large chains, resembling osmotic pressure effects.¹⁴ Despite the fundamental and practical importance of the mutual diffusion effects on the interfacial properties of immiscible and partially miscible blends, only a limited number of experimental studies on these effects have been reported in the literature. LeGrand and Gains¹⁵ were first to report on mutual solubility of homologous series of polyisobutylenes (PIB) and polydimethylsiloxanes (PDMS) and on the molecular dependence of interfacial tension of these pairs. Grace¹⁶ observed a decrease in the interfacial tension with time for the liquid pair Vorite 125/Si 1000 (polymerized Castor oil/Silicon oil) and attributed this to a slow mutual diffusion in the highly viscous system. More recently, confirming these results, a decrease of the interfacial tension with time was found for several Newtonian systems.¹⁷ A fast decrease, followed by an increase of the interfacial tension was reported¹⁸ for a surfactant that is diffusing from the drop

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(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 in the drop and in the interfacial area. An increase of the interfacial tension with time was reported⁸ 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. Recently, Shi *et al.*¹⁹ reported experiments on similar material combinations as we used (PIB/PDMS). The experimentally observed decrease in interfacial tension, attributed to the transport of low molecular weight species across the interface, was described with a kinetic model.

Little experimental work has been done to the viscoelastic properties of pure polymer-polymer interfaces. 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 Ref. 20). None of these studies have included the effect of diffusion on the viscoelastic interfacial behavior. We report here the experimental results of non-Newtonian behavior of a diffuse polymer-polymer interface.

In this work, we investigate 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 dilatational deformations of the drop surface. All measurements 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 describe the oscillatory results.

II. 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 for this is that it is not possible to consider a diffuse interface layer as a discrete two-dimensional (2D) 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. We should instead rather think in terms of an averaged concentration.

Interfacial rheology²¹ is based on the well known bulk rheology²² 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 2D interfacial and 3D bulk rheology is that the former deals with open systems that are, in general, compressible. During dilatation/compression of a soluble adsorption layer 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.²³ The deformation of a diffuse interface gives rise to excess elastic and viscous stresses, related to the response of the changing interfacial tension γ . Both the elastic and the viscous contributions can be affected by diffusion, depending on the ratio of the characteristic deformation and diffusion times.

A. Radial oscillatory expansion/contraction of a sessile/pendant drop

The pendant/sessile drop technique²⁴ 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 this data the interfacial tension response function can be calculated using Fourier analysis.²⁴

The dilatational interfacial viscoelastic modulus E is defined as the change in the interfacial tension γ as a function of the interfacial area A , which is subjected to a dilatation or a compression:

$$E = \frac{d\gamma}{d \ln A/A_0}. \quad (1)$$

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

$$\Delta A(t) = A(t) - A_0 = \Delta A_0 \exp(i\omega t), \quad (2)$$

where A_0 is the initial or the equilibrium area, ΔA_0 and ω 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 case of a linear response of the interfacial tension to the oscillatory area change, i.e., restriction to relatively small deformation (a few percent), the frequency is the same and $\gamma(t)$ can be written as

$$\Delta \gamma(t) = \gamma(t) - \gamma_0 = \Delta \gamma_0 \exp(i\omega t + i\phi), \quad (3)$$

where γ_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

$$E = E'(\omega) + i\eta_d(\omega)\omega = E'(\omega) + iE''(\omega) = E_0 \exp(i\phi), \quad (4)$$

with

$$E_0 = [E'^2 + E''^2]^{1/2}, \quad \tan(\phi) = \frac{E''}{E'}, \quad (5)$$

where E' is the dilatational elasticity or (in phase) dilatational modulus, E'' is the (out phase) dilatational loss modulus (in analogy with the terminology in bulk rheology). The dilatational loss modulus is related to the dilatational viscos-

ity by $E'' = \eta_d \omega$. The dilatational viscosity contains all relaxation processes, i.e., intrinsic viscosity and, in this case, diffusion effects. The intrinsic elasticity and viscosity can, in principle, be separated from the apparent ones (due to diffusion) by applying an oscillatory interface deformation with period ($T = 2\pi/\omega$) much smaller than the characteristic relaxation time determined by the diffusion.

Combining Eqs. (1)–(4), after simple transformations the following relationship between $\Delta\gamma(t)$, E' , and η_d can be defined:

$$\Delta\gamma(t) = E' \alpha(t) + \eta_d \dot{\alpha}(t), \quad (6)$$

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 and out of phase contributions, E' and η_d , respectively, can be calculated. The range of oscillations that can be applied is limited to relatively small frequency, $\omega \sim 0\text{--}0.3 \text{ s}^{-1}$ and small amplitudes, $\alpha \sim 0\text{--}0.05$. The former is determined by the bulk viscosity of the materials while the latter is necessary in order to stay in the linear regime.

B. Models for the 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. However, 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 extent this relation (qualitatively) is applicable to diffuse interface. For a diffusion model with one characteristic time constant the in phase and out of phase dilatational moduli are given by

$$E'(\omega) = E_0 \frac{1 + \sqrt{\omega_0/\omega}}{1 + 2\sqrt{\omega_0/\omega} + 2\omega_0/\omega}, \quad (7)$$

and

$$E''(\omega) = E_0 \frac{\sqrt{\omega_0/\omega}}{1 + 2\sqrt{\omega_0/\omega} + 2\omega_0/\omega}, \quad (8)$$

respectively,^{25,26} where ω_0 is a material parameter related to a characteristic diffusion relaxation time of the system under consideration.

For fast deformations, i.e., a time period much shorter than the specific diffusion time ($\omega \gg \omega_0$), diffusion does not change the composition of the diffused layer, and a Kelvin model with a constant elastic modulus (equivalent to Marangoni elasticity) and a constant intrinsic viscosity (if present) applies [Eq. (6)]. For slow deformations, i.e., a period of time much longer than 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. (8), has a maximum, $E'' = 0.21E_0$ for $\omega = 2\omega_0$. So, if such a one-mode model applies and the experimental results for E'' show this maximum it is easy to determine the parameters, E_0 and ω_0 .

In case of multiple diffusion processes that take place at the same time and do not interfere with each other, a multi-mode model can be used, i.e., $E' = \sum E'_i$; $E'' = \sum E''_i$, where for every E'_i and E''_i Eqs. (7) and (8) apply with characteristic material parameters $E_{0,i}$ and $\omega_{0,i}$.

Another phenomenological 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:

$$E' = E_0 \frac{(\omega/\omega_0)^2}{1 + (\omega/\omega_0)^2}, \quad (9)$$

and

$$E'' = E_0 \frac{\omega/\omega_0}{1 + (\omega/\omega_0)^2}. \quad (10)$$

Again, for a one-mode model, E'' has a maximum, $E'' = 0.5E_0$ for $\omega = \omega_0$. In this case a multimode version reads:

$$E' = \sum_i E_{0,i} \frac{(\omega/\omega_{0,i})^2}{1 + (\omega/\omega_{0,i})^2}, \quad (11)$$

$$E'' = \sum_i E_{0,i} \frac{\omega/\omega_{0,i}}{1 + (\omega/\omega_{0,i})^2}, \quad (12)$$

in which every mode again has its own characteristic material parameters $E_{0,i}$ and $\omega_{0,i}$. The results in this work will be interpreted in terms of an effective diffuse layer thickness ξ as defined in the theory of diffuse interfaces.^{27,28} 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. (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 sections results will be presented that come close to these cases.

III. METHODS AND MATERIALS

The polymers used for 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 were covered by varying the asymmetry in molecular weight across the interface. Their number average molecular weight M_n and molecular weights polydispersity M_w/M_n are given in Table I. All materials were used as supplied.

The zero shear viscosities (μ_d for the dispersed phase and μ_c for the continuous phase) were measured using a rotational viscometer (Rheometrics, ARES) using a plate-

TABLE I. Materials and materials bulk characteristics.

Polymer combinations	Dispersed phase/ matrix phase	μ_d/μ_c [Pa s/Pa s]	M_n^a	$\frac{M_w}{M_n}$
A1	PB635/PDMS28k	3/1.0	635/28 000	2.1 ^a /1.8 ^a
A2	PB635/PDMS60k	3/10	635/62 700	2.1/1.8 ^a
A3	PIB950/PDMS6k	30/0.1	950/6000	2.5 ^b /1.6 ^c
A4	PIB950/PDMS28k	30/1.0	950/28 000	2.5/1.8
A5	PIB950/PDMS60k	30/10	950/62 700	2.5/1.8
A6	PIB1300/PDMS60k	75/10	1300/62 700	2.2 ^b /1.8
B1	PBD1800/PDMS28k	0.7/1.0	1800/28 000	2.2 ^c /1.8
B2	PBD1800/PDMS60k	0.7/10	1800/62 700	2.2/1.8
B3	PBD8k/PDMS6k	12/0.1	8000/6000	1.1 ^a /1.6
B4	PBD8k/PDMS60k	12/10	8000/62 700	1.1/1.8

^aProvided by supplier.^bLight scattering.^cGPC based on polystyrene standards.

plate configuration and applying steady shear. For shear rates below 30 s^{-1} and $25 \text{ }^\circ\text{C}$ all polymers show Newtonian behavior, i.e., no shear rate dependency of the viscosity. In all oscillatory experiments, relatively slow deformation frequency (within the range of $0\text{--}0.3 \text{ s}^{-1}$) were used, ensuring Newtonian behavior of the materials. The interfacial tension γ (see Table II) of the polymer pairs was measured as a function of time with the pendant/sessile drop apparatus (PAT-1, Sinterface, Germany). For a few combinations the thickness of the diffusion interfacial zone was estimated by means of confocal Raman spectroscopy.²⁹

IV. RESULTS AND DISCUSSION

A. Transient interfacial tension and drop size reduction

The observations and results reported in this section are different and, therefore, we have chosen to demonstrate the general trends of the transient and oscillatory behavior of diffuse interfaces. The transient results are partially interpreted by using a recently proposed model for diffuse interfaces¹⁹ while the oscillatory results by Fickian diffusion and Maxwell model. In the following we limit ourselves to (i) a complete set of transient results, (ii) an extended set of oscillatory results for a few specific polymer combinations,

and (iii) the general trends with time of the dilatational moduli for two of the combinations. Limitations were also put forward by, for example, the high viscosities of the polymer combinations which restricted the frequency range that could be applied with the experimental system.

The mean values of the interfacial tension γ (with accuracy $\pm 0.1 \text{ mN/m}$) at three successive moments (0, 0.5, and 4 h, where 0 corresponds to a few minutes after the two phases were put into a contact; the time required to obtain a Laplacian drop shape) are given in Table II. The arrows in Table II indicate the tendency of the change of the interfacial tension with time. The “A” combinations, which have the lower values for the interfacial tension ($\gamma < 4 \text{ mN/m}$), show first a decrease of the interfacial tension that, for some of the combinations, is followed by an increase. The “B” combinations, which have the higher values for the interfacial tension ($\gamma > 4 \text{ mN/m}$), show increasing or stationary values. In Fig. 1 the long term behavior of the interfacial tension for a specific set of polymer combinations is shown; the matrix phase is kept the same ($M_n = 62\,700$) while the drop phase is changed by increasing M_n from 635 to 8000. It is observed that with increasing M_n and/or decreasing asymmetry in molecular weight of the components, the interfacial tension increases.

Although most of the polymers under consideration are,

TABLE II. Polymer pairs interfacial properties; γ is the interfacial tension and ΔR_{4h} is a characteristic length scale of drop size reduction.

Polymer combinations	γ_0 [mN/m]	$\gamma_{1/2h}$ [mN/m]	γ_{4h} [mN/m]	ΔR_{4h} [μm]
A1	1.9 ↘	1.6 ↗	2.5 ↗	237
A2	2.4 ↘	1.8 ↗	2.1 ↗	209
A3	2.6 ↘	2.4 ↗	2.5 ↗	67
A4	2.7 ↘	2.5 →	2.5 →	50
A5	2.8 ↘	2.6 ↘	2.4 ↘	34
A6	3.2 ↘	3.1 ↘	3.0 ↘	6
B1	4.0 →	4.0 →	4.0 →	20
B2	4.0 ↗	4.1 →	4.1 →	28
B3	4.2 →	4.2 →	4.2 →	≈ 5
B4	4.1 ↗	4.4 ↗	4.5 ↗	6

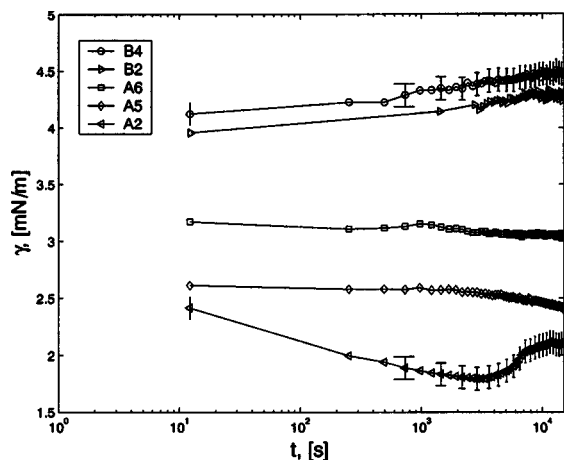


FIG. 1. Transient interfacial tension for a drop phase with different molecular weights. The matrix phase is kept the same (PDMS60k).

in the literature, assumed as immiscible, the decay and the increase of the transient interfacial tension as seen in Fig. 1 and in Table II can be explained by mutual diffusion. For apolar/apolar interactions 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, second, 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 of the polydispersity will not be discussed extensively hereafter.

The change of the drop volume after 4 h was used to define a characteristic length scale, $\Delta R_{4h} = V_0^{1/3} - V_{4h}^{1/3}$ (see Table II). The accuracy of the determined ΔR is $\pm 3 \mu\text{m}$. The thickness of the diffusion layer around a drop can be estimated to be of the order of magnitude of ΔR . To support this statement we performed confocal Raman spectroscopy²⁹ on two different material combinations. Two liquids were put on top of each other on a standard microscope glass with the denser one (PDMS) beneath. This two layer system was scanned, in a confocal way, to measure the concentration of the double bonds in $\pm 50 \mu\text{m}$ range perpendicular to the interface. The double bonds, which demonstrate strong Raman absorption, are only present in one of the materials (in the PIB or PBD but not in the PDMS). The concentration profiles were normalized with the maximum concentration level for a given experiment. For combination A5, after 4 h of contact between the two phases, the thickness of the diffuse interface is measured to be around $100 \mu\text{m}$, while for B4 around $30 \mu\text{m}$ (see Fig. 2). For these combinations ΔR_{4h} is 34 and $6 \mu\text{m}$, respectively (see Table II). Notice that the measuring spot has a finite size which will give an apparent diffuse layer, even for a sharp interface. This apparent layer thickness is estimated to be about $\approx 15 \mu\text{m}$.³⁰ The size of the measuring spot depends on, among other things, the number of interfaces that have been passed (in our case the air-liquid and the liquid-liquid interface) and the depth of the spot

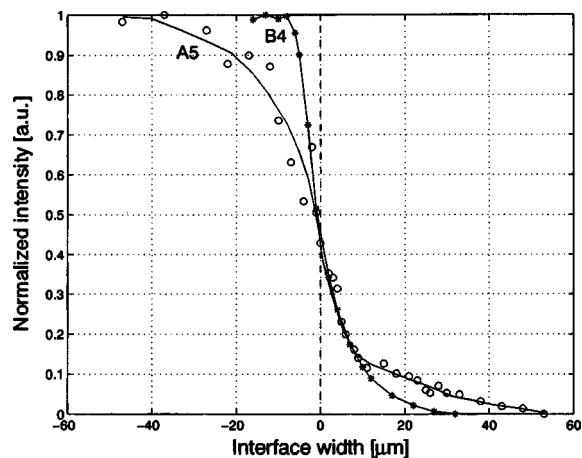


FIG. 2. Normalized intensity as a function of the scanning depth for two material combinations A5 and B4, after 4 h contact between the two phases. The solid lines are drawn to guide the eye.

below an interface. A detailed quantitative analysis of the effects of the varying measuring spot size can be found in Refs. 31 and 32. Such an analysis is beyond the scope of this paper. Here, a more direct and pragmatic approach is used. If we consider the B4 combination to be close to a sharp interface (or at least to have a thickness that stays within the resolution of the technique) then the measured intensity profile of this system can be considered as apparent and is used to correct the A5 intensity profile, resulting in an interfacial thickness for the latter of around $60\text{--}70 \mu\text{m}$ (after correcting the refraction the accuracy of every measurement in Fig. 3 should be $\pm 1 \mu\text{m}$).

Thus the change of the drop size can be used to demonstrate the diffusion process, see Table II. In most of the cases (with exception of B3 combination), the molecular weight of the drop phase is smaller than that of the matrix and the drops reduce in size. The observed trend is that the drop size change increases with lowering the molecular weight of the drop material while keeping the matrix material the same (A2/A5/A6 and B2/B4). For the A systems, keeping the drop materials the same and lowering the molecular weight of the matrix, the drop size change increases (A1/A2/ and

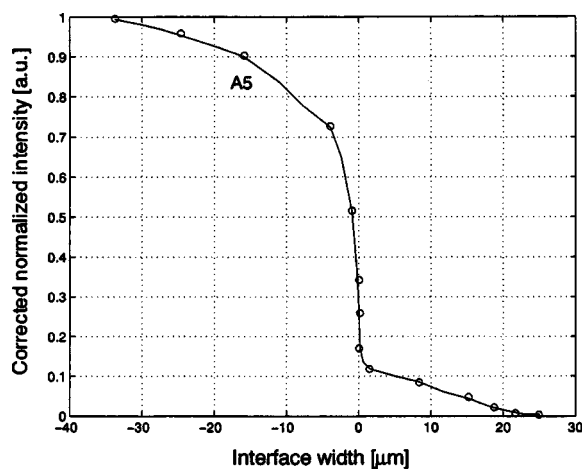


FIG. 3. Corrected intensity profile for the system A5 by subtracting the intensity profile of B4. The solid line is drawn to guide the eye.

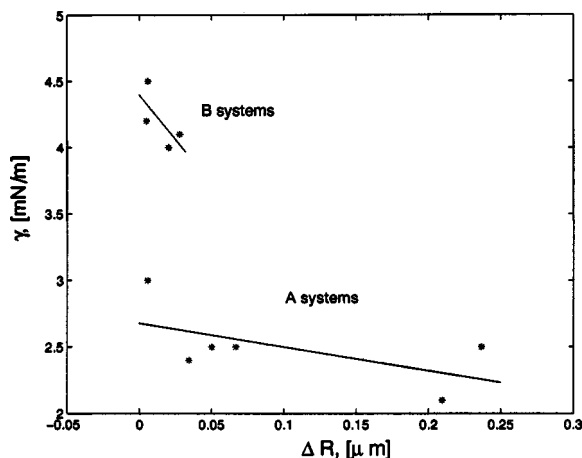


FIG. 4. ΔR correlation with interfacial tension for the A and the B systems.

A3/A4/A5). For the B systems this is the opposite, although the differences in the results are close to the measuring accuracy. Moreover, for the A systems the larger changes in drop size correlate with lower interfacial tensions which, in turn, indicates thicker diffuse interfaces (see Fig. 4). In this figure we have drawn two lines (least square fits in the log-log plot) as the results suggest a clear separation between the A and B combinations. Finally, small changes in drop size also correlate with small changes in time of the interfacial tension, see Figs. 1 and 4.

Relating the interfacial tension to the interfacial thickness, it follows that, for the time period used, thick interfaces become initially thicker, and then for some combinations (A1–A3) thinner, while the thin interfaces only become thinner (B combinations). Moreover, the effects are much stronger for the thick interfaces (low interfacial tension) than for the thin interfaces (high interfacial tension). With increasing M_n of the dispersed phase and/or decreasing the asymmetry across the interface, the diffusion of the small molecules is restricted to a smaller fraction of the molecular distribution. 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 (A1–A3). Accumulation occurs when the initial diffusion builds the diffuse layer and depletion occurs when the finite amount of small molecules in the drop spreads out in the matrix. Analogous, the increase of the interfacial tension for the B combinations is explained by the diffusion of a much smaller fraction of molecules and it is faster as only the increasing part of $\gamma(t)$ is captured in the time window of the measurement. Hence, the interfacial width for B combinations is expected to be much smaller than for A combinations. This is confirmed by the fact that the equilibrium value for γ for the B pairs is reached faster than for A pairs. For example, for the B4 combination the equilibrium value $\gamma=4.6$ mN/m is reached after 4–5 h while for the A5 pair the equilibrium value $\gamma=3.2$ mN/m is reached after, at least, 24 h.

With an increase of the average molecular weight of both phases, the value of the interfacial tension also increases and, moreover, slows down the diffusion substantially as is observed from the change of γ with time (Table II and Fig. 1). This is understood from the fact that mixing of long mol-

ecules is less favorable,¹³ a well known phenomenon that was reported earlier.^{33,34} 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 .

For binary systems, as we are dealing with, the model of Shi *et al.*¹⁹ expresses the changes of the interfacial tension in terms of two characteristic times describing the diffusion of the low molecular weight components of both phases into an (assumed) interphase. It is not possible to determine from our results, unambiguously, these two characteristic terms. The model is based on the existence of a stationary value of the interfacial tension that is reached after sufficient long time that is only possible if the concentration of the low molecular components in the source is constant. For droplets, this is certainly not the case; they form a finite source. However, we still can use this model as a first approximation to compare the different systems that we used and in this way to estimate trends that can be expected and to interpret the influence of the system parameters such as the molecular weights and viscosities of the dispersed and matrix phases. For comparable systems (for example, combination A5 used in this work and the PIB wide/PDMS 55n system used in the work of Shi *et al.*¹⁹) and comparable conditions (room temperature) the times in which changes take place are comparable. The model of Shi *et al.* allows for estimating the ratio of characteristic diffusion times of different systems when the diffusion constants k_1^* and k_2^* , which describe the diffusion of low molecular species in and out of the interphase region, are known [Eqs. (21) and (22) in their paper]. The influence of polydispersity of the dispersed material is taken into account by means of a disproportionate factor f_{\min} that is given in terms of the polydispersity index, $D=M_w/M_n$, by

$$f_{\min} = \{2D - 1 + 2[D(D - 1)]^{0.5}\}^{0.5}. \quad (13)$$

Since the values of the rate constants are not available, we assume them to be identical. The ratio is then given by

$$\frac{\tau_1}{\tau_2} = \left(\frac{f_{\min,2}}{f_{\min,1}} \right)^d \frac{E_2}{E_1} \quad (14)$$

with

$$E_i = \left[\frac{\eta_\alpha \eta_\beta}{\eta_\alpha + \eta_\beta} \right]_i \quad (15)$$

in which η_α and η_β are the viscosities of the source and receiving phase. With the material data given in Table I, the value of the d parameter equals 3, and taking the most diffuse system A2 of the series with a 60 k matrix material (see also Fig. 1) as the system to compare with, we determine the ratios as given in Table III.

As can be seen, “most diffusive” in terms of the lowest interfacial tension (see Fig. 1) and in terms of decreasing droplet radius (see Table II) does not mean the shortest dif-

TABLE III. Diffusion times relative to the time τ_{A2} of system A2 and the weight factor ω_α expressing the influence of the viscosities on the diffusion (see text for explanation).

Polymer combinations	$\frac{\tau_i}{\tau_{A2}}$	ω_α
A1	0.3250	0.250
A2	1.0000	0.770
A3	0.0305	0.003
A4	0.2959	0.032
A5	2.2931	0.250
A6	3.4755	0.118
B1	0.1622	0.588
B2	0.257 74	0.935
B3	0.2634	0.008
B4	14.4843	0.455

fusion time, i.e., fast diffusion, according to the model. Actually, the correlation seems to be disappointing. Looking at the A systems, the systems A5 and A6 have a longer relative diffusion time compared to A2 and this correlates with the smaller change in the droplet radius, see Table II. However, systems A1, A3, and A4 have lower values (A3 even a much lower value) and this does not correlate with the changes in the droplet radius. One of the causes could be in the assumed equal diffusion constants k_1^* and k_2^* . However, even when we follow the suggestion by Shi *et al.* to take the k_1^* much larger than k_2^* (typically $k_1^*=100k_2^*$) the results show hardly any change; the trends are the same. Varying the exponent d in Eq. (14), which takes values between 2.9 and 5.1 in the work of Shi *et al.*, has also only a minor effect. A closer look at the results shows that the correlation fails when the matrix material is changed, but that the results are according to the expectations when the matrix material (PDMS60k) is kept the same, see systems A2, A5, and A6. In addition, when we keep the drop material the same the model seems to work also; compare A3, A4, and A5, although the correlation between the change in the droplet radius and the calculated relative diffusion time is the opposite of what is seen for the combination of systems A2, A5, and A6. Notice that for the (A2, A5, A6) set, the large differences in the change of the drop size [$O(10^2)$] correspond to relatively small changes [$O(1)$] in the calculated diffusion time, while for the (A3, A4, A5) set small differences [$O(1)$] in the change of the drop size correspond to large changes [$O(10^2)$] in the calculated diffusion time. It is clear that the influence of changes in the asymmetry of the system, especially when accomplished by changing both phases, are more complicated and cannot be captured with this model. Considering this, we still can compare systems B1 with B2 and B3 with B4, but we should be careful with comparing model results from B systems with those from the A systems. A complicating factor is also the change of the polymer for the dispersed phase (PBD instead of PB or PIB). The high value for the (relative) diffusion time of the B4 system is according to expectations; the low values for the other B systems are not. This characteristic time scale of system B4 is due to the symmetry in the

molecular weight and the monodisperse character of the drop phase (no low molecular weight components that diffuse fast, into the relatively high molecular weight matrix). On the other hand, the short characteristic time of the comparable B3 system is fully determined by the low viscosity of the matrix.

This can also be seen from the factor ω_α , which expresses to which extent the diffusion process is dominated by the viscosities of dispersed ($\omega_\alpha=1$) or matrix phase ($\omega_\alpha=0$), defined by

$$\omega_\alpha = \frac{k_1^* \eta_\omega}{k_2^* \eta_\alpha + k_1^* \eta_\omega}. \quad (16)$$

Again, the diffusion constants k_1^* and k_2^* are not known but we assume, in a first approximation, them to be equal. The calculated values are given in Table III. Special cases are B2 and A2, which are fully dominated by the dispersed phase (the source material), and A3 and B3 which are fully dominated by the, relatively low molecular weight, matrix material. System B4 with the highest characteristic time is, in terms of ω_α , an intermediate case.

The model is certainly too limited to explain all the phenomena observed, and more experimental and theoretical work is required.

However, the results presented here are sufficient to state that for polydisperse systems, with the drop phase having the smaller molecular weight, the diffusion will lead initially to a decrease in the interfacial tension followed by an increase and, eventually, a leveling off. This is most clearly demonstrated by the transient behavior of the interfacial tension of system A2 (see Fig. 1). For some material combinations the diffusion process is too slow (systems A5 and A6) or too fast (B combinations) to capture the full transient behavior of the interfacial tension, within the experimental time range. The fast initial diffusion process cannot be detected since, due to the drop formation in the initial stages of the measurements, the measuring technique does not work yet; it requires a Laplacian shape.

B. Oscillatory experiments

Oscillatory experiments were performed on the pendant/sessile drop apparatus as well. From these experiments the dilatational elasticity E' and dilatational viscosity η_d (or the equivalent E'') were determined. Figure 5 gives two 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 result for combination A2 is a typical example of a mainly elastic response while the result for combination B2 shows elastic and viscous aspects resulting in a large hysteresis loop.

For the material combinations A2, B2, and B4 the viscoelastic response was measured over a range of frequencies. The A2 system is considered as one of the most diffusive systems (see Fig. 1 and the change in drop size: Table II), the

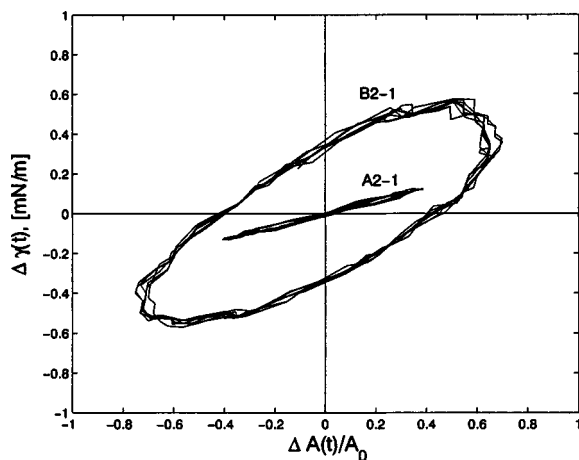


FIG. 5. Typical interfacial tension vs interface deformation curves for two experiments with different polymer combinations and frequencies (A2-1, $\omega=0.16$; B2-1, $\omega=0.16$).

B2 and B4 systems as medium and little diffusive, where B4 has also the special property of a nearly monodisperse drop phase.

For all results presented here the deformation amplitude was in the linear range. The range of linearity of the response was checked by varying the amplitude. Some of the measurements were repeated to demonstrate the reproducibility. For all three systems the results show the expected trends for a diffusion controlled interfacial response.

The description of E' and E'' using a Fickian diffusion model [Eq. (7) and Eq. (8)] is only qualitative, see Fig. 6 and Table IV for the parameters values. For example, the crossing of the experimental curves of system B4 is a feature that is not described by the Fickian diffusion model. The E' of system A2 is captured rather well but the corresponding predicted E'' is unsatisfactory. A multimode approach does not improve this.

The Maxwell model [Eqs. (9) and (10)] does give a much better description for all three systems, see Fig. 7 and Table IV for the parameters values. System A2 was best fitted with a one-mode model, system B2 and B4 with a two-mode model. Also, the crossover of E' and E'' for system B4 is captured well. For comparative reasons, i.e., to have one characteristic time for each system, also one-mode fits are given next to the two-mode fits. Using these values, one can see that systems B2 and B4 have characteristic diffusion time that is around five times lower than for the A2 system. This leads to the conclusion that systems with a thin interface (a few micrometers and less) can be considered as

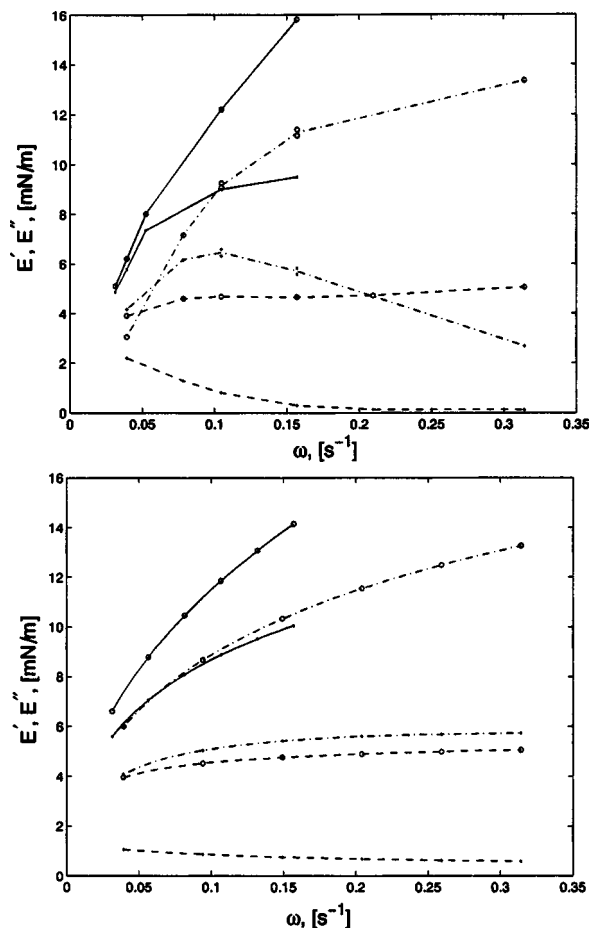


FIG. 6. Top: Measured E' (\circ) and E'' (\bullet) as a function of ω for systems B2 (solid lines), A2 (dashed lines), and B4 (dashed dot lines). Bottom: Predictions with a one-mode Fickian diffusion model.

fast diffusive systems, while systems with a thick interfaces (tens of micrometers and more) as slow diffusive systems.

Comparing the (one-mode) time scales obtained from fitting the results from oscillatory experiments with those obtained from the model of Shi *et al.*¹⁹ one big difference in the observed trend can be seen. In all cases the characteristic time for the B2 system is, compared to the A2 system, much smaller. However, for the B4 system the model of Shi *et al.* predicts a much larger characteristic time when compared to the A2 system while those found from oscillatory experiments are much smaller. Notice that the characteristic time of the A2 system together with the small characteristic time for the B2 system and the high characteristic time for the B4 system give the same trend in the time scales as found from

TABLE IV. Model parameters for the Fickian diffusion model and Maxwell model. The numbers in parenthesis refer to one-mode Maxwell model.

Polymer combinations	Fickian		Maxwell	
	$\tau_{ch} = 2\pi/\omega_0$ [s]	E_0 [mN/m]	$\tau_{ch} = 2\pi/\omega_0$ [s]	E_0 [mN/m]
A2	7540	5.8	319	4.9
B2	41	74	50, 1340 (87)	18.6, 4.6 (18.7)
B4	217	27.7	70, ∞ (82)	12.9, 1.5 (13.7)

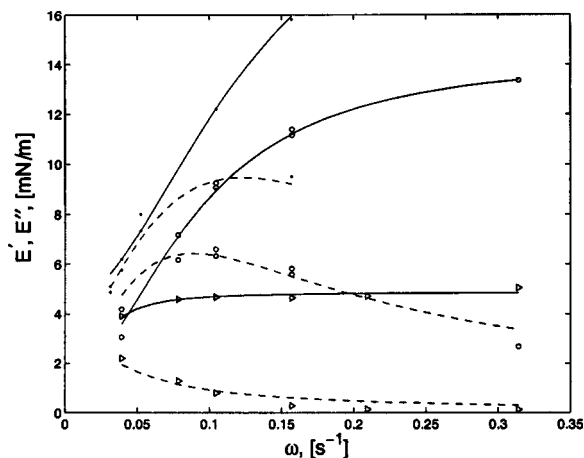


FIG. 7. Predicted E' (solid lines) and E'' (dashed lines) as a functions of ω using a one- or two-mode Maxwell model. Measured values are given for comparison; system A2 (\triangleright), B2 (\bullet), and B4 (\circ).

the predictions from the model of Shi *et al.* It seems that the oscillatory experiments can give more information, i.e., multiple time scales, especially when the frequency range would be extended.

Finally, we measured the long term (for 10^4 s) dilatational modulus behavior for system A2 (Fig. 8). This system showed the most pronounced transient behavior for the interfacial tension (see Fig. 1) and, therefore, is considered as a good test of the posed correlation between interfacial tension and dilatational modulus. The frequency used was $\omega = 0.16 \text{ s}^{-1}$ for which the interface response was mainly elastic (see Table IV and Fig. 7). As explained before, for fast enough deformations, the dilatational modulus should follow the same trend as the interfacial tension. In Fig. 8 the time evolutions of the interfacial tension and the dilatational elastic modulus are plotted. It is observed that, indeed, this expected coupling between the interfacial tension and the dilatational elastic modulus is present for this system. Similar measurements were done for system B2 with the same frequency $\omega = 0.16 \text{ s}^{-1}$, Fig. 9. This time the oscillations have to be considered as slower compared to system A2, i.e., the (fast) diffusion processes contribute more to the interfacial

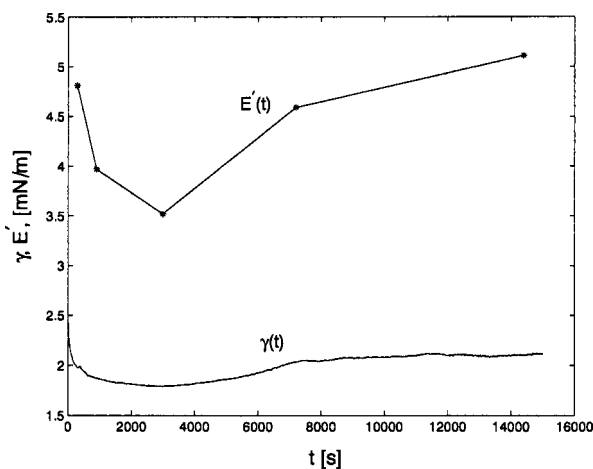


FIG. 8. Comparison between the transient behavior of γ and E' for system A2.

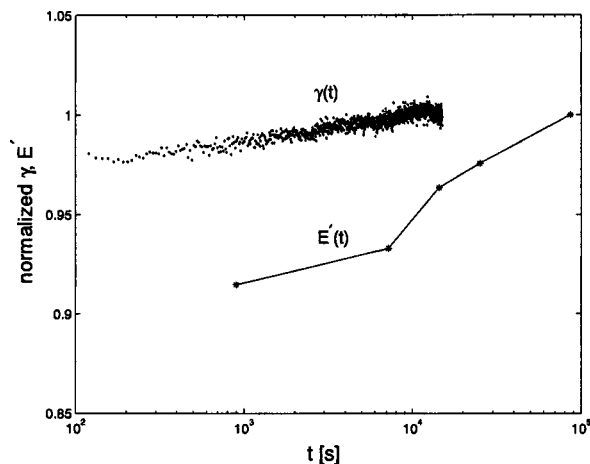


FIG. 9. Comparison between the transient behavior of γ and E' for system B2. A log scale is used for the abscissa to make the effects more clear.

behavior. It is seen that the correlation between interfacial tension and dilatational elastic modulus is not as strong as for system A2 but it is still clear, i.e., both rising in time (Fig. 9).

V. CONCLUSIONS

In summary, we have determined that diffusion can lead to either a decreasing or an increasing transient interfacial tension, in the time scale of the first few hours, depending on the material combination used. In the first case, thick diffuse interfaces (in the order of tens of microseconds) are formed while in the second case thin interfaces (in the order of $1 \mu\text{m}$) are formed. These properties were obtained by varying the asymmetry in molecular weight across the interface of polymer combinations. The model proposed by Shi *et al.*,¹⁹ although limited due to some strong assumptions, is useful for the interpretation of the influence of different material properties, especially if one of the phases is kept the same. Refinements of this model, such as a finite source for diffusing low molecular weight species and including the effect of the asymmetry across the interface, will probably make this model more predictive. Oscillatory experiments show that the rheological behavior of both type of systems (A and B) is frequency dependent. For three different systems this frequency dependency was qualitatively described by a simple diffusion model and quantitatively described by a (one- or two-mode) Maxwell model. Using the characteristic times provided by the latter model, one can conclude that the systems with thin interfaces are fast diffusive while the systems with thick interfaces are slow diffusive. Moreover, the transient interfacial tension and dilatational elasticity show the same trend as predicted by the theory of diffuse interfaces, 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 since 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' . As it is known that the most important mechanism for stabilization of emulsions (blends) are interfacial tension gradients which are determined by the interfacial elasticity and viscosity, it is clear that diffuse interfaces can have, in principle, a marked influence on morphology development during polymer blending, similar to the effects of surfactants. By using the full Palierne model the effects of the interfacial viscoelastic and bulk viscoelastic properties can be studied. However, very often decoupling of these two effect is very complicated. In forthcoming publications we will show that the diffusion length scale and the interfacial viscoelastic properties have 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 thin diffusive layers (the B combinations), show pronounced viscoelastic behavior that has to be considered during structure development experiments.

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