

Rheology and morphology of concentrated immiscible polymer blends

Jan Mewis*, Thomas Jansseune and Paula Moldenaers

Dept. Chemical Engineering K.U.Leuven, de Croylaan 46, 3001 Leuven, Belgium

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Abstract

The phase morphology is an important factor in the rheology of immiscible polymer blends. Through its size and shape, the interface between the two phases determines how the components and the interface itself will contribute to the global stresses. Rheological measurements have been used successfully in the past to probe the morphological changes in model blends, particularly for dilute systems. For more concentrated blends only a limited amount of systematic rheological data is available. Here, viscosities and first normal stress differences are presented for a system with nearly Newtonian components, the whole concentration range is covered. The constituent polymers are PDMS and PIB, their viscosity ratio can be changed by varying the temperature. The data reported here have been obtained at 287 K where the viscosities of the two components are identical. By means of relaxation experiments the measured stresses are decomposed into component and interfacial contributions. The concentration dependence is quite different for the two types of contribution. Except for the component contributions to the shear stresses there is no clear indication of the phase inversion. Plotting either the interfacial shear or normal stresses as a function of composition produces in some cases two maxima. The relaxation times of these stresses display a similar concentration dependence. Although the components have the same viscosity, the stress-component curves are not symmetrical with respect to the 50/50 blend. A slight elasticity of one of the components seems to be the cause of this effect. The data for the more concentrated blends at higher shear rates are associated with a fibrillar morphology.

1. Introduction

Mixing immiscible polymers in the liquid state can result in various phase morphologies. These depend on the nature and the relative amounts of the polymers used as well as on the flow history of the sample. Especially in rather dilute systems a droplet/matrix structure is quite common. In that case the results of emulsion theory, e.g. for the deformation of droplets, can be applied in principle to polymer blends, see the reviews by Rallison (1984) and Stone (1994). Polymers, however, have higher viscosities and lower interfacial tensions than common water/oil emulsions, they are also viscoelastic rather than Newtonian. More general models for droplet deformation in blends have been developed lately, still based on Newtonian components but including larger and more complex deformations. Maffettone and Minale (1998) included nonlinearities in their model through a phenomenological term that contains the capillary number Ca . This model description can be applied to flows with relatively small values of Ca . Alternatively, Almusallam *et al.* (2000) proposed a model that is based on affine deformation with an empirical modification of the

relaxation term. They used their model to describe step strain and subsequent relaxation experiments. These models have been developed for single droplets and consequently apply only to dilute systems. Simulations in 2D (Yuan and Doi, 1998) demonstrate that the droplet shape becomes much more complex in more concentrated blends, in agreement with experimental evidence.

At a critical capillary number, Ca_c , droplets break up. The value of Ca_c depends on the type of flow and on the viscosity ratio of the components (see e.g. Stone, 1994). Janssen *et al.* (2001) recently showed experimentally that Ca_c in simple shear flow decreases with increasing droplet concentration. When droplets are suddenly deformed in long filaments the break-up mechanism changes. Very long fibrils rupture by an interfacial instability involving capillary waves at the interface. Theoretical analyses (Khakar and Ottino, 1987) as well as numerical simulations (e.g. Cristini *et al.*, 1998; Li *et al.*, 2000) are available for the case of isolated droplets submerged in flowing fluids. In concentrated blends droplet interactions affect the breaking up (Loewenberg and Hinch, 1996). The interactions become quite complex in the case of fibrils (Knops *et al.*, 2001). In non-dilute blends droplets cannot only reduce their size by breaking up, they can also grow by means of coalescence. Available theories for coalescence in rather dilute systems

*Corresponding author: jan.mewis@cit.kuleuven.ac.be
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with Newtonian components have been reviewed by Chesters (1991) and Janssen (1993). Systematic coalescence experiments on model systems such as the ones used here have been reported by Vinckier *et al.* (1998), Lyu *et al.* (2000) showed the complex evolution of the particle size distribution in molten polymers.

Because of the interfacial tension the microstructure has a specific effect on the rheology of blends. In particular it causes viscoelastic phenomena even in blends with purely viscous components. For rather dilute systems a linear viscoelastic theory is available (Paliarne, 1990), Choi and Schowalter (1975) calculated the stationary flow properties, including the normal stresses in moderately concentrated systems with Newtonian components. For more concentrated systems accurate descriptions for the evolution of the microstructure are lacking and therefore the stresses cannot be calculated either. Doi and Ohta (1991) suggested a formalism to calculate the stress contributions from the continuous phase of a 50/50 mixture of equiviscous Newtonian polymers. Several scaling relations can be derived from the model, they have been proven to be valid over a wider range of conditions than the model itself (Takahashi *et al.*, 1994; Vinckier *et al.*, 1999). The equations that are used in the model to describe the evolution of the microstructure are, however, only first order approximations. Some extensions have been suggested later (Lee and Park, 1994; Grmela *et al.*, 1998) but a full analysis is still lacking.

The procedure, used in the Doi-Ohta theory to calculate the interfacial stress contribution from the shape of the interface (Onuki, 1987), can also be applied to droplet/matrix structures. For low capillary numbers the Maffettone-Minale model produces accurate predictions of the stresses in transient and stationary flows (Jansseune *et al.*, 2001). The model by Almusallam *et al.* (2000) showed good agreement for stresses resulting from fast changes in shape. Recently a new rheological model was proposed by Peters *et al.* (2001), it combines various existing descriptions of the microstructural changes during flow.

2. Experimental

The blends that have been used consist of two nearly Newtonian polymers: Parapol 1300, a poly (isobutene) (PIB) from Exxon and Rhodorsil 47V200.000, a poly (dimethylsiloxane) (PDMS) from Rhodia. Both are liquid at ambient temperature. The viscosities of the components match at 287 K (230 Pa.s). The PDMS sample is slightly viscoelastic, with an average low shear relaxation time of the order of 0.01 s at ambient temperature. The relaxation time of the PIB is even an order of magnitude smaller. The interfacial tension of such systems is 3 mN/m at room temperature (Sigillo *et al.*, 1997). There can be interference from diffusional phenomena on the interfacial tension but

this turns out to be unimportant in the concentration range of interest here (Guido *et al.*, 1999)

As the details of the interface affect the rheological properties, it is of paramount importance to use in all experiments samples with a controlled microstructure. For uncompatibilized blends the shear history can be used to generate the desired phase morphology. It has been observed repeatedly that shearing at a given shear rate, for a sufficiently long period of time, results indeed in reproducible structures, irrespective of the preceding shear history. Care should be taken at low shear rates in dilute blends, where the coalescence can become sufficiently slow to produce an apparent hysteresis (Minale *et al.*, 1998). In highly concentrated blends it becomes more difficult to generate a reproducible microstructure. Whereas a total strain of 3000-4000 seems in most cases to be adequate for blends with up to 20% of dispersed phase, a much larger strain is needed for more concentrated systems (e.g. Astruc and Navard, 2000). Strains of up to 80.000 have been used here in the most concentrated blends. In this manner an adequate degree of reproducibility could be achieved in most cases for the stationary stresses as well as for the subsequent relaxation curves.

The rheological measurements have been performed on a Rheometrics RMS800, using a cone and plate geometry with a cone angle of 0.1 rad and a radius of 25 mm. Steady state viscosities and normal stresses were recorded, respecting preshear periods as indicated in the previous paragraph. The global stresses can be divided in a contribution from the components and in one from the interface. When the components are purely viscous their contribution to the global stresses at each instant are determined by the instantaneous shear rate. When the flow is suddenly arrested, as in stress relaxation upon cessation of flow, these contributions should relax instantaneously to zero. The interfacial contribution is driven by the interfacial tension, which in a relaxation experiment drives the interface to its equilibrium shape. The viscous resistance in droplets and matrix makes that this movement requires a finite amount of time. Hence, relaxation experiments can be used to separate the two contributions. Even with a slightly elastic component the component relaxation is sufficiently fast to distinguish it from the interfacial one.

The relation between the shape of the interface and the resulting interfacial stresses is given by (Onuki, 1987):

$$\bar{\sigma} = -\frac{\alpha}{V} \left(\vec{n} \cdot \vec{n} - \frac{1}{3} \mathbf{I} \right) dS \quad (1)$$

where $\bar{\sigma}$ is the stress tensor, α the interfacial tension, \vec{n} a unit vector locally perpendicular to the interface and dS the area of an interfacial element. The interfacial contribution to the first normal stress is normally quite high and can be measured easily. The shear stress is strongly dominated by the component contribution but the relaxation procedure

allows one to extract even small interfacial contributions. In earlier work (e.g. Takahashi *et al.*, 1994; Vinckier *et al.*, 1997) the interfacial stress contributions were derived from measurements of the total stress by assuming a linear mixing rule for the component contributions.

3. Results and discussion

3.1. Relaxational phenomena.

Systematic data have been collected for the steady state behaviour at various concentrations and shear rates. Some results on more dilute blends with the same components have been discussed elsewhere (Jansseune *et al.*, 2000; Jansseune *et al.*, 2001). At 293 K, and with PDMS as the dispersed phase, the stresses in dilute blends could be described quite well by combining existing models for the evolution of the droplet shape with eqn. (1). Inversely, rheology can be used to obtain morphological information for such systems. This is only possible for well-defined structures. There is, however, one relation between rheology and morphology that only requires the inclusions to have a symmetry plane (with angle θ) with respect to the vorticity-velocity plane. The tangent of this angle is given by the ratio of the interfacial contributions to the shear stress $\sigma_{12,int}$ over the first normal stress difference $N_{1,int}$ (Almusallam *et al.*, 2000; Jansseune *et al.*, 2000):

$$\sigma_{12,int}/N_{1,int} = 2 \tan(2\theta) \quad (2)$$

During the relaxation of single droplets in Newtonian blends the orientation angle remains constant (Yamane *et al.*, 1998). Consequently, the interfacial components of the shear stress and the normal stresses should have identical relaxation curves. This has been observed in a number of dilute blends (e.g. Vinckier *et al.*, 1997). Here, relaxation measurements have been performed after steady state shear flow, for both shear and normal stresses, and this over the whole concentration range. The relaxation times calculated from these curves, for previous shear rates of 1 and 5 s^{-1} , are displayed in Fig. 1.

At the highest shear rate the relaxation curves were not always exponential. A similar behaviour has been observed for dilute blends in relaxation experiments after short shearing periods (Vinckier *et al.*, 1997). In this manner more deformed droplets were generated, which could relax by droplet break-up rather than by retraction. In the case of non-exponential relaxation curves an average relaxation time has been calculated. It corresponds to the time necessary for the stresses to drop to 1/e of their initial value.

For concentrated blends the relaxation curves for shear stresses and normal stresses are not identical anymore, as can be seen in fig. 1. Whenever there are differences the first normal stress difference relaxes slower than the shear stress. If eqn. (2) applies this means that the average ori-

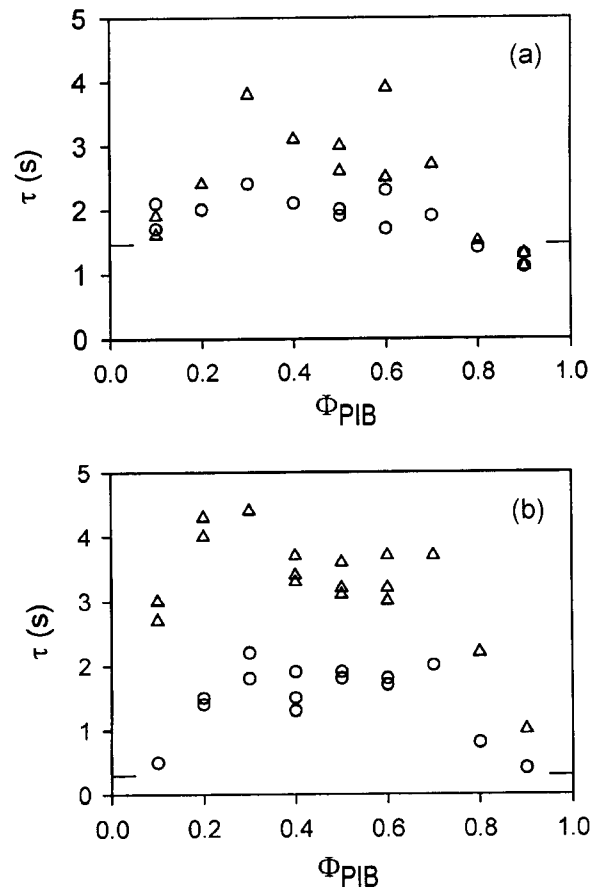


Fig. 1. Relaxation times for shear stress (circles) and first normal stress difference (triangles) after cessation of flow at: a) 1 s^{-1} ; b) 5 s^{-1} . Horizontal lines: values calculated with the Maffettone-Minale model.

entation angle decreases during relaxation. This even holds for rather dilute systems, especially after shearing at higher shear rates, as can be seen in the data for 10 and 90% PIB at 5 s^{-1} .

A possible cause for a decreasing orientation angle would be a distribution of droplet sizes. The inclusions in a blend are never really monodisperse, but the degree of polydispersity varies (Friedrich *et al.*, 1995; Sundaraj and Macosko, 1995). Rather monodisperse samples could be generated in the hysteresis region. At 287 K, for the concentrations and shear rates used, this region was already outside the experimental window. Whenever there is a distribution in size, the smaller droplets will retract faster. These are also the ones that are less oriented towards the flow direction. As a result the average orientation angle will decrease in time, even when the orientation of the individual drops remains constant.

Theoretical relaxation times for dilute systems have been calculated with the Maffettone-Minale model (1998). For the values of the critical capillary number de Bruijn's empirical relation has been used (de Bruijn, 1989). In fig.

If the theoretical values are added as horizontal lines. They approach the values obtained by extrapolating the experimental results to zero droplet concentration. That the model does not very well describe the relaxation of even the most dilute blends that are used here is consistent with a larger polydispersity, where it is known (Friedrich *et al.*, 1995) that the simple rheology-morphology relations do not apply anymore.

Even if there is some scatter in the data, the results in fig. 1 suggest that the effect of composition is not symmetrical with respect to the 50/50 blend. With a viscosity ratio of one such symmetry could be expected. The only apparent difference between the two components seems to be that the PDMS polymer is slightly elastic (see section 2). This rather small effect seems to be sufficient to affect the balance between breaking up and coalescence of the inclusions.

In the regions of low and high PIB content, i.e. with a low concentration of disperse phase, the relaxation times become larger when the droplet concentration is increased. There are two possible mechanisms that can contribute to this slowing down. The first is related to an increase in drop size, as coalescence becomes more dominant at higher droplet concentrations. A second mechanism for slowing down the relaxation with increasing concentration is the hydrodynamic interactions between droplets. The significance of this effect has been demonstrated with numerical simulations (Li *et al.*, 1996).

The retarding effect of the hydrodynamic interactions on the stress relaxation should become more pronounced when the volume fraction of the inclusion is further increased, at least if there are no other structural changes. Nevertheless the relaxation times level off, or even decrease, starting roughly at concentrations of 30% dispersed phase. For equiviscous components the phase inversion is expected to occur at the 50/50 composition. The relaxation times do not show a particular change at that point. This holds for the shear stresses as well as the first normal force differences. The results strongly suggest that stress relaxation proceeds according to a different mechanism in highly concentrated blends.

Samples have been rapidly frozen, immediately after shearing, by submerging them in liquid nitrogen. They could then be observed by means of SEM. In concentrated blends that had been sheared at 5 s^{-1} a fibrillar structure is visible. The concentration region where this happens did, however, not completely coincide with the flat region of the relaxation curves in Fig. 1. Hence, there seems to be no obvious link between this region and a particular morphology.

From the initial values of the stress relaxation curves, taken after the quasi-instantaneous relaxation of the component stresses, an orientation angle can be calculated with eqn. (2). The results are shown in Fig. 2. Again, the theoretical values according to the Maffettone-Minale model

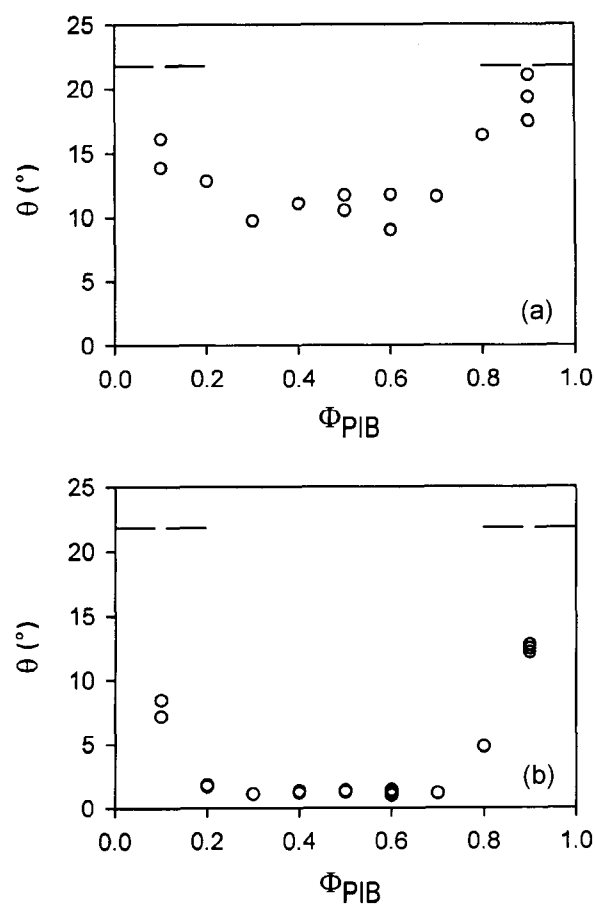


Fig. 2. Orientation angles of the inclusions, calculated from eqn. (2) at: a) 1 s^{-1} ; b) 5 s^{-1} , lines calculated with the Maffettone-Minale model.

have been added in the figure. The measured values for the samples with 10% dispersed phase, either PIB or PDMS, are much lower than the theoretical ones. As was the case for the relaxation times, extrapolating the measured values to zero concentration gives results that are consistent with the model. In the region between 0 and 20% disperse phase the orientation angle drops drastically. Above 20% of disperse phase the angle remains very low and hardly changes with concentration.

Fig. 3 shows a more detailed picture of the evolution of the orientation angle, as calculated from eqn. (2), with shear rate. The two upper curves represent the two blends with 10% of disperse phase. Their difference confirms the systematic lack of symmetry with respect to concentration for the rheological properties in this system. The flat minimum at higher concentrations occurs at the various shear rates investigated here. It gradually decreases with increasing shear rate. At 4 s^{-1} the inclusions seem to be nearly completely parallel to the flow direction. This is in agreement with the orientation of the fibrillar structure in the frozen samples.

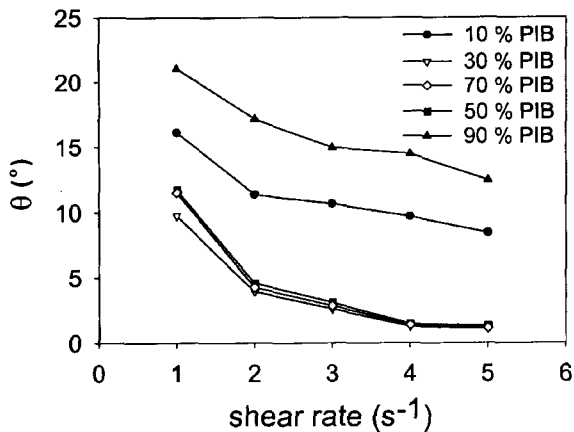


Fig. 3. Shear rate dependence of the orientation angles calculated from eqn. (2) at different blend compositions.

3.2. Stationary flow

From the relaxation curves the interfacial and component contributions for the steady state values of the shear stresses and the first normal stress differences have been calculated as discussed in section 2. The results for the interfacial contributions are given in Fig. 4. When several data points are given for a single concentration they have been obtained on different samples, the scatter therefore includes sample variability. The interface contributes only a very small fraction of the total shear stress. Even so the

data points show only a limited amount of scatter. The lines represent the predictions of the Maffettone-Minale model, calculated according to the same procedure that has been followed for calculating the theoretical values of the relaxation times (section 3.1). The model is for dilute systems and therefore is linear in droplet concentration if the droplet size is assumed to be constant.

There are some similarities between the results for the relaxation times (Fig. 1) and those for the interfacial stresses. Both increase with increasing concentration of the dispersed phase, at least in dilute blends. The experimental values of the interfacial stress contributions also differ from the theoretical ones. This is the case for shear stresses as well as normal stresses. Hence the structural feature that is responsible for the deviation from the theoretical value should affect both types of stresses. The magnitude of the interfacial area is the most logical common feature. This would mean that the average droplet size is somewhat larger than assumed in the calculation of the theoretical values. Larger droplets entail a lower orientation angle. According to eqn. 2 a lower angle would decrease the shear stresses more than the normal stresses. The results of fig. 2, which have been obtained by applying eqn (2) to the data, are consistent with this argument. Once the concentration of the dispersed phase becomes larger than 10-20%, the interfacial contributions level off or actually even decrease with concentration. The ratio between shear and

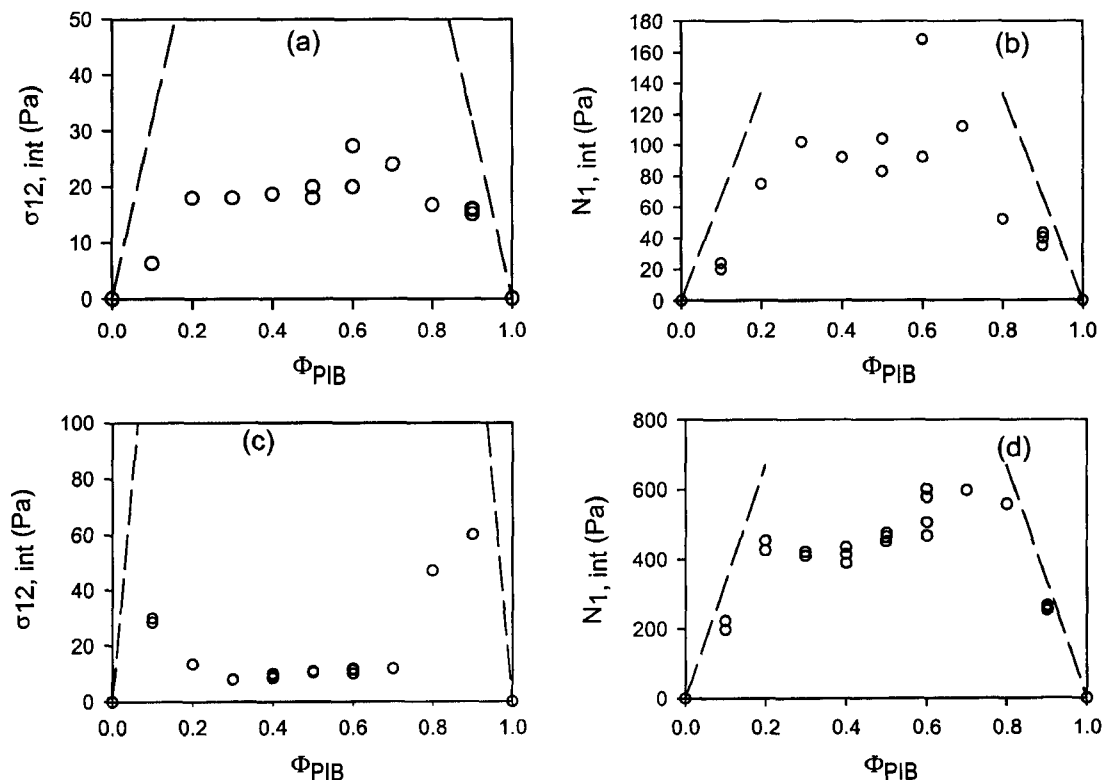


Fig. 4. Interfacial stress contributions: a) σ_{12} at 1 s^{-1} ; b) N_1 at 1 s^{-1} ; c) σ_{12} at 5 s^{-1} ; d) N_1 at 5 s^{-1} .

normal stresses hardly changes with concentration and consequently may reflect a droplet size that grows with concentration.

A comparison of the results for 1 and 5 s⁻¹ (Fig. 4) shows a significant effect of shear rate. The shear stresses are found to decrease rather than increase with shear rate, except for the most dilute blends. Small shear stresses can be expected for fibrils oriented in the flow direction, i.e. the morphology that has been observed at the higher shear rate (see 3.1). The curves are not totally symmetrical with respect to the 50/50 composition, a characteristic that was also observed for the relaxation times. Equally similar to Fig. 1 is the lack of a maximum in the curve near the phase inversion, which should occur at a 50/50 composition in this equiviscous system. The presence of two peaks at intermediate concentrations (Figs. 1 and 4) has been reported in some cases for rheological features of immiscible polymer blends, e.g. for the extent of shear thinning (Ziegler and Wolf, 1999) and for the zero shear viscosities (Huitric *et al.*, 1998). These data referred to the total stresses, whereas here the double peaks can be associated with the interfacial contribution.

A more systematic picture of the effect of shear rate on the shear stresses is presented in Fig. 5. Only for dilute blends with 10% of disperse phase do the shear stresses grow continuously with shear rate. For the other concentrations the shear stresses actually decrease gradually with increasing shear rate. As the interfacial contribution to the total shear stress is quite small the evolution of the latter will be determined by the component contribution. The results with 10% PDMS are systematically higher than those with 10% PIB. Hence the stress-composition curves remain asymmetrical at the different shear rates. The first normal stress differences are not shown, they increase regularly with shear rate.

The relaxation technique also provides the values of the component contributions. These are shown in Fig. 6 for a

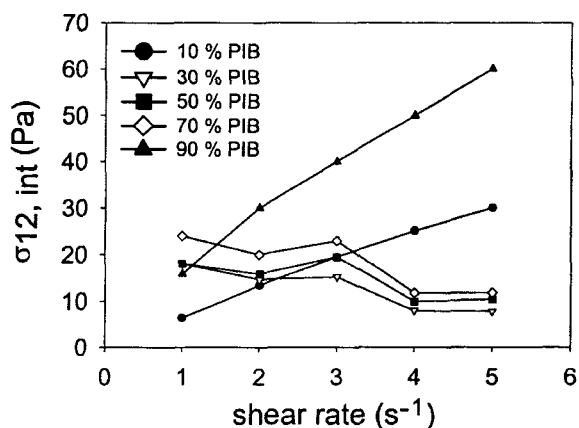


Fig. 5. Shear rate dependence of the interfacial contribution to the shear stress at different blend compositions.

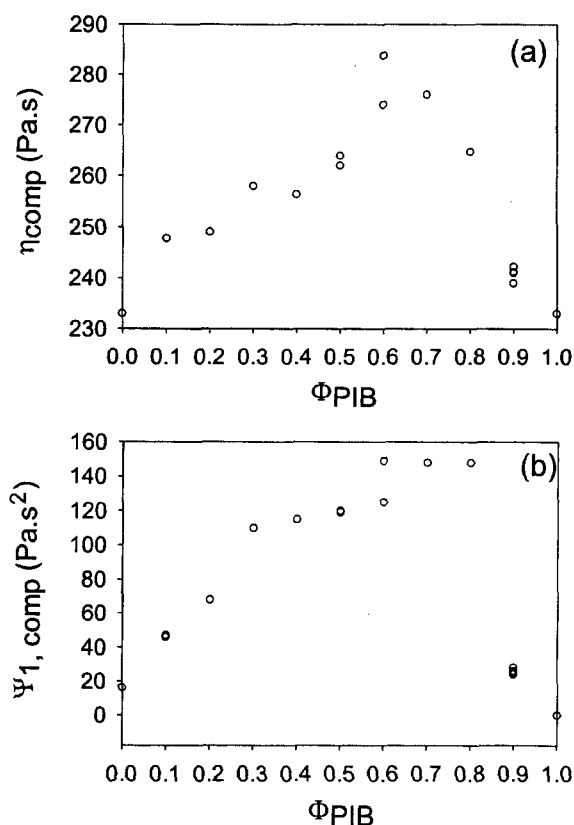


Fig. 6. Component contributions at 1 s⁻¹ for: a) viscosity; b) first normal stress coefficient.

shear rate of 1 s⁻¹. Using a linear mixing rule, as is commonly done, would predict the same viscosity at the different concentrations. Applying this procedure here would result in errors of less than 20%. The shape of the curve for the shear stresses, or viscosities, differs qualitatively from that for the interfacial contributions (Fig. 4). The component contribution increases continuously with the concentration of the dispersed phase. The curve displays a single maximum now. Similar shapes of curves have been obtained repeatedly for rheological features associated with the total stress in blends (e.g. Utracki, 1991; Takahashi *et al.*, 1994; Jeon *et al.*, 2001). Considering the small effect of the interfacial contribution, the similarity between the total shear stress and the component contribution is logical. The single maximum is normally associated with the phase inversion. The components have the same viscosity in the present case and hence the phase inversion is expected at the 50/50 blend composition. This is not the case, the lack of symmetry confirms the results for the interfacial stress contributions.

The first normal stress differences for the pure components at 1 s⁻¹ are small for PDMS and non-existing, within measuring accuracy, for PIB. Nevertheless there is a substantial component contribution in the blends, comparable or even larger than that from the interface. The discrepancy

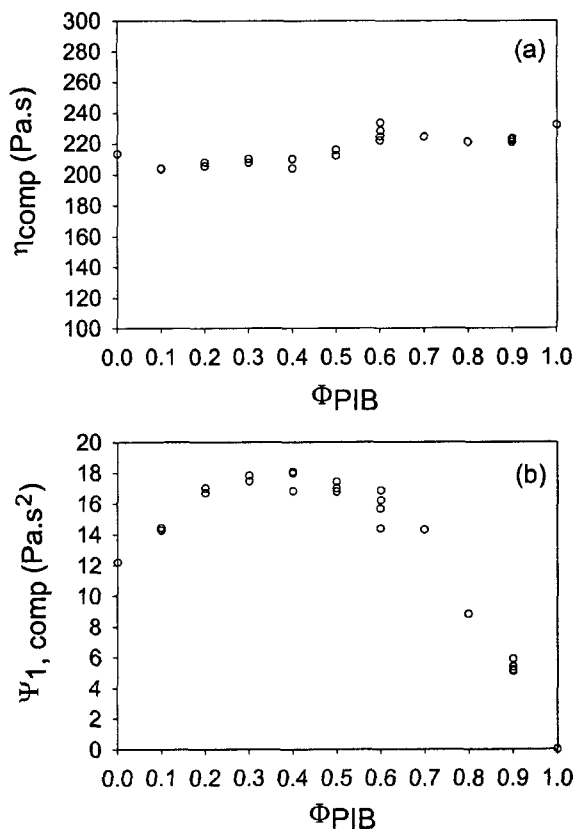


Fig. 7. Component contributions at 5 s^{-1} for a) viscosity; b) first normal stress coefficient.

between the behaviour of the pure components and that of the blends seems surprising. Some published data on model blends (e.g. Vinckier *et al.*, 1999) also show a substantial instantaneous relaxation of N_1 , indicating a similar behaviour as that observed here. This is, however, not a general result. A component contribution to N_1 from Newtonian components is possible, as demonstrated by the numerical analysis of Wetzel and Tucker (2001) for systems with zero interfacial tension.

At 5 s^{-1} (Fig. 7) the maximum in the viscosity-composition curve has disappeared. It is a general trend in blends that, for the total stresses, a linear mixing rule is better satisfied at higher shear rates. As mentioned above, for the system under consideration a fibrillar structure has been observed for the concentrated blends at 5 s^{-1} , oriented nearly parallel to the flow direction. A constant viscosity is consistent with this structure. In some cases viscosities have been reported to be smaller than the predictions from a linear mixing rule. Such a negative deviation has been attributed to interfacial slip (Utracki, 1991). Comparing the values at 5 s^{-1} with those at 1 s^{-1} , one observes a small drop in viscosity with shear rate. Contrary to the interfacial contribution the component shear stresses themselves increase with increasing shear rate over the whole concentration range.

For N_1 the data at the higher shear rate in Fig.7 show a single maximum and do not obey a linear mixing rule. With a fibrillar structure parallel to the flow direction and second order behaviour for the components one could expect component N_1 stresses for the blends which approach the linear mixing rule. The data for the interfacial contributions indicated that the fibrils seemed to make on the average a slight angle with the flow direction. In that case the viscous forces in the components could contribute a stress in the normal direction.

4. Conclusions

Steady state viscosities and first normal stress differences are reported for model blends containing nearly Newtonian components of identical zero shear viscosities. Relaxation after cessation of flow has been used to determine average relaxation times and also to decompose the stresses during flow in interfacial and component contributions. The effect of composition is quite different for the two contributions, the only common factor being that the effect of composition is not symmetrical around the 50/50 blend. This seems to be associated with a slight elasticity of one of the components.

The interfacial contributions only increase with the concentration of the dispersed phase up to 20% of dispersed phase. When the concentration is further increased the stresses level off or even decrease. In the latter case the concentration dependence contains two local maxima. This pattern seems not to be associated with any particular blend morphology. In the concentrated blends the interfacial shear stresses decrease in absolute value with increasing shear rate. The decrease is associated with a reduction of the interfacial area and an alignment of the inclusions in the flow direction, both are brought about by a transformation of the droplets into long fibrils. An orientation angle for the inclusions has been estimated from the ratio of the interfacial normal stresses over the shear stresses.

The component contributions to the shear stresses display a single maximum, that is associated with the phase inversion. At higher shear rates the component shear stresses become independent of composition, which is consistent with an aligned morphology under these circumstances. There is a substantial component contribution to the first normal stress difference, even with only one of the components being slightly viscoelastic.

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