

Rheo-optical investigation of immiscible polymer blends

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Linear conservative dichroism has been investigated as a potential tool for tracking (*in situ* and in real time) the flow-induced microstructure of immiscible polymer blends. Dilute mixtures of poly(dimethylsiloxane) in poly(isobutene) and vice versa have been used as model systems. It is demonstrated that different mechanisms for structural changes can be identified with this technique: droplet deformation, droplet retraction, fibril break-up and coalescence. Time-resolved *in-situ* SALS measurements support the structural interpretation of the dichroism data. Breaking up of stretched filaments by Rayleigh instabilities can be deduced from dichroism measurements. The resulting strings of droplets can be detected with SALS. The time scales for the structural changes can be determined by dichroism, which makes it possible to study *in situ* the effect of the various process and material parameters. As an illustration, the effect of shear rate on fibril break-up and on droplet coalescence after sudden changes in shear rate has been considered. Break-up times decreased only slightly with increasing shear rate; coalescence times scaled with the square of shear rate rather than with strain under the conditions of the present experiments. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Properties of immiscible polymer blends are known to depend strongly on the detailed morphology (see e.g. Ref. 1). During processing, flow can cause drastic changes in the microstructure in two-phase fluids. The resulting morphology will depend on process parameters and on material parameters such as viscosity η and elasticity of the components and their interfacial tension Γ . The evolution of the microstructure in fluid–fluid systems has been the subject of many theoretical and experimental studies since the early work by Taylor^{2,3}. The majority of the direct experimental evidence has been obtained by microscopic observation of single droplets. For real polymer blends, which are processed at elevated temperatures, most of the structural information has been derived from the analysis of specimens which have been cooled-down from the melt after processing (see e.g. Refs 4 and 5). Scattering techniques have been suggested to study morphology in real time during flow. This topic has been reviewed recently⁶, and it turns out that collecting scattering patterns is not always the most optimal manner with which to probe structural changes.

Here we will investigate the possibility of using rheo-optical techniques, in particular linear conservative dichroism $\Delta n''$, to follow *in situ* the time evolution of the microstructure. Dilute mixtures of immiscible polymers subjected to simple shear flow are used for this purpose. Conservative dichroism measures polarisation-dependent attenuation of light. In a non-absorbing material the transmitted light intensity in perpendicular polarisation

directions will be different if the scattering is anisotropic. In this manner dichroism probes changes in the microstructure. Dichroism measurements during flow have been used successfully to detect flow-induced structural changes in particulate^{7–10} and phase-separating systems¹¹. In immiscible polymer blends, the flow will affect size, shape, orientation and relative position of the droplets. This will normally generate a change in the global anisotropy and hence in dichroism. Therefore it should be possible to follow the various structural changes in such a system by the said technique. The dichroism measurements will be supplemented here by flow-SALS to support structural interpretation of the data and to provide additional information.

EXPERIMENTAL

The measurements of the conservative linear dichroism have been performed on an Optical Analyzer (ROA) from Rheometric Scientific Inc. This instrument uses a polarisation modulation technique to measure linear birefringence and dichroism¹². An He–Ne laser serves as a light source with a wavelength of 633 nm. Before the light reaches the sample it is modulated by a halfwave plate rotating at 2000 revolutions per second. Only the light that leaves the sample at zero angle is detected. Phase-locking amplifiers demodulate the signal and determine the in-phase and out-of-phase components of the high frequency part of the light intensity. The DC-component of the transmitted light (I_{DC}), which represents the transmittance of the sample, is also measured. Data can be collected at a rate of around 100 Hz. Because of the substantial turbidity of the samples a parallel plate geometry has been used for the flow cell with an optical beam parallel to the rotation axis. In this manner the

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optical path length can be minimised: 0.2 mm in the present investigation. It will be shown later that the droplet size in the blends is small enough to avoid gap size effects in this geometry. Even with such a small gap, only blends with concentrations of 1.0% by weight dispersed phase could be investigated. This suffices however to assess the role of process and material parameters in the evolution of the droplet structure during flow¹³. Rheological investigations on relatively concentrated blends of the same homopolymers have been published elsewhere^{14,15}. A drawback of this set-up is that only the velocity–vorticity plane can be probed and not the shear plane in which the orientation angle of the deformed droplets could be measured. For the present purpose, i.e. studying the major morphological changes in blends during flow, this will prove to be adequate. More detailed information about the evolution of the droplets would be obtained with more transparent samples, in which case the shear plane could be viewed.

The ROA device has been modified to perform SALS measurements during flow as well. For this purpose the detector is replaced by a semi-transparent sheet. The maximum accessible scattering angle is 15° in air. A CCD camera, Ikegami model ICD-810P, is used to record the transient scattering patterns. The images are sent to a monitor for observation and are also digitised and stored with a PC, which is equipped with a Data Translations DT3851 frame grabber for further data handling of the scattering patterns. SALS provides more detailed information than dichroism but at a slower rate (10 images per second in the present set-up) and only from relatively small angles in flow cells. The more global, numerical output of dichroism measurements, without a need for off-line data handling, can be more useful in some cases, e.g. to determine time scales for fast structural changes.

To study the potential of the rheo-optical technique the measurements were limited to near ambient temperatures thus avoiding the various difficulties associated with measuring melts at elevated temperatures. Devices for rheo-optical measurements at the latter conditions are available and hence the technique could eventually be extended to blends of melts. The polymers used here are liquid at ambient temperature, the use of polymer solutions has been avoided because the presence of solvents can interfere in several ways with the physical and physico-chemical phenomena that occur in mixtures.

The model blends consist of poly(dimethylsiloxane) (PDMS) from Rhône-Poulenc (Rhodorsil 47V200.000) and poly(isobutene) (PIB) from Exxon Chemical (Parapol 1300), no compatibilizer has been used. These polymers are immiscible and are indeed liquid at ambient temperature. The PIB is essentially viscous whereas the PDMS displays a small but significant elasticity. At 23°C the PDMS has a density of 975.0 kg m⁻³, for the PIB the corresponding value is 895.3 kg m⁻³. The interfacial tension between the two polymers amounts to approximately 2.8 mN⁻¹¹⁶. The refractive indices of the components at 23°C are 1.406 and 1.499 for PDMS and PIB, respectively. The polymers do not absorb light at the frequency of the laser used in the ROA device.

The steady-state rheological properties of both homopolymers were measured (*Figure 1*) with a Rheometric Mechanical Spectrometer 800 (RMS 800) using cone and plate geometry with a cone angle of 0.1 rad. Over the accessible range of shear rates ($\dot{\gamma}$) both materials behave approximately as second-order fluids. At 23°C, the PDMS is about twice as viscous as the PIB. The normal stresses N_1 in

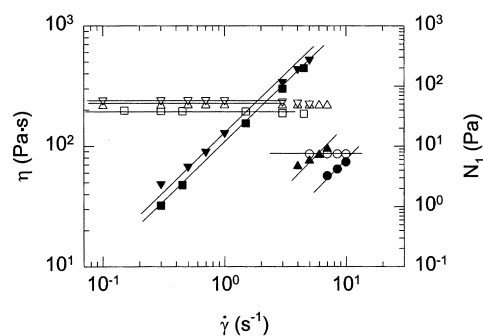


Figure 1 Rheological properties (η : open; N_1 : filled) of the component polymers: \square, \blacksquare : PDMS (23°C); \circ, \bullet : PIB (23°C); $\nabla, \blacktriangledown$: PDMS (15°C); $\triangle, \blacktriangle$: PIB (15°C)

the PIB are hardly measurable, even the PDMS is not very elastic, although its normal stresses are about two orders of magnitude larger than those of the PIB. Viscosity matching, which is assumed in some models, as in the Doi–Ohta one¹⁷, can be achieved with the present materials by performing the experiments at 15°C.

The blends were prepared by using a six flat-blade mixer. The mixtures were then submitted to vacuum at room temperature to eliminate air bubbles. When the sample was introduced in the ROA, it was first sheared at 2 s⁻¹ until steady state. This resulted in a reproducible dichroism reading. For the systems under consideration, dichroism could be detected quite accurately over a reasonable range of shear rates. This provides a means to control whether a particular structure has been achieved. By systematically increasing the shear rate a pseudo steady-state value for the dichroism could be obtained at each shear rate. At the higher shear rates the same value could be recovered by either starting from lower or higher shear rates, indicating that a truly steady state exists. At the lower shear rates this experiment becomes increasingly time consuming and therefore the value used does not necessarily represent a truly steady state.

The basic structural characteristic of the blend is the average droplet size, which can be expected to depend on shear rate. The droplet size has been estimated from the SALS patterns using the Debye–Bueche theory for isotropic systems with a random two-phase structure and sharp interfaces. This approach has been applied before to immiscible blends by Søndergaard and Lyngaae-Jørgensen¹⁸. It relates the q -dependence of the scattered light intensity $I(q)$ to the structure by:

$$I(q) = K \xi_d^3 F(q \xi_d) \quad (1)$$

where K is a function of the scattering contrast of the components, q is the magnitude of the scattering vector, ξ_d is a correlation distance for the structure and F is a scaling function which is given here by:

$$F(x) = (1 + x^2)^{-2} \quad (2)$$

Assuming an exponential correlation function, the average radius $\sqrt{R^2}$ of the droplets can be estimated ($=\sqrt{10\xi_d^2}$)⁶. The results for the two 1% blends are shown in *Figure 2*. At higher shear rates the SALS patterns become anisotropic (see further) and the analysis does not apply anymore. *Figure 2* also contains microscopic data on the droplet size during flow of a blend with 2.5% of PIB¹⁹. The data overlap hardly but the SALS data are at least in line with the microscopic results.

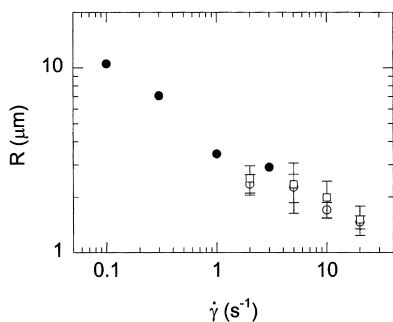


Figure 2 Droplet radius as a function of shear rate at 23°C for 1.0% PIB in PDMS (○) and 1.0% PDMS in PIB (□), comparison with microscopic data on a similar 2.5% PIB in PDMS blend from Ref. 19 (●)

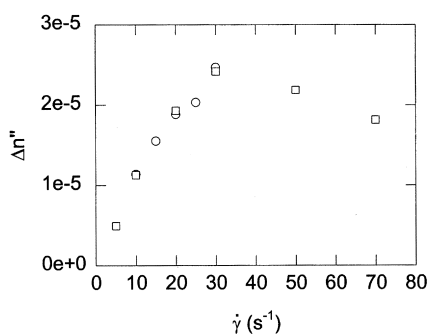


Figure 3 Steady-state values of dichroism versus shear rate at 15°C: ○: 1.0% PIB in PDMS; □: 1.0% PDMS in PIB

RESULTS AND DISCUSSION

Behaviour during steady-state shear flow

Figure 3 shows the dichroism as a function of shear rate for the two 1.0% blends at 15°C. The data have been obtained by the procedure described in the previous paragraph. At 15°C the viscosity ratio is unity. The accessible range of shear rates is limited by shear fracture, in particular when the more elastic PDMS constitutes the continuous phase. The two samples produce similar values for the dichroism during flow. As the viscosity ratio is unity, this result could be expected for blends with inelastic components. In the present case it implies that the slight elasticity of the PDMS does not affect the droplet size. From Figure 3 it is obvious that the flow-induced anisotropy of the droplets in the blends can be detected *in situ* by the dichroism.

Transient flows: step-down experiments

Although it is difficult to derive absolute information about size or even shape from rheo-optical measurements, the time scales for structural changes can be determined quantitatively. With the available equipment even fast changes in dichroism can be resolved. This is applied here to observe structural transients resulting from sudden changes in shear rate, i.e. either a sudden decrease or a sudden increase in shear rate.

When suddenly decreasing the shear rate, a distinction must be made between a step-down experiment and arresting the flow. In the former case the droplets are initially below their steady-state size once the shear rate has been lowered. Consequently, coalescence could gradually increase the droplet size. On the other hand, when stopping the flow, the lack of convection and the high viscosity make

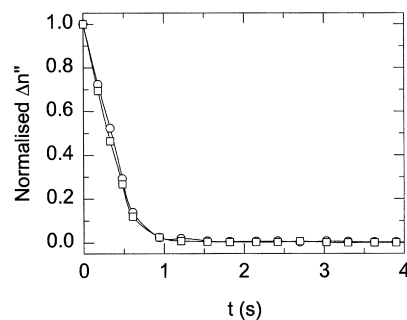


Figure 4 Time evolution of normalised dichroism for 1.0% PDMS in PIB at 23°C after cessation of flow: (○) 10 s⁻¹ and (□) 20 s⁻¹

coalescence unlikely. In that case the major structural change would be the retraction from the distorted droplets during flow into a spherical shape at rest. The change in shape can be deduced from the SALS pattern, which evolves from an elliptical shape into a circular one. The loss in anisotropy is also reflected in a decay of the dichroism (Figure 4). The latter provides a direct measure for a characteristic decay or relaxation time t_d , i.e. the time required for the dichroism to decrease to 1/e of its total change. The experimental values deduced from Figure 4 are about 0.4 s. Paliarne²⁰ has calculated a characteristic time, for droplet relaxation in polymer blends driven by interfacial tension, in the case of small deformations. Using this model and the estimated droplet size (Figure 2), theoretical values for t_d of slightly deformed droplets of the blend can be calculated as 0.21 s at 10 s⁻¹ and 0.16 s at 20 s⁻¹. The experimental values are larger than the theoretical ones. The difference can be explained on the basis of the deformation of the droplets, which is larger in the experiments than assumed in the model. Large deformations can be expected to result in larger relaxation times²¹.

When the shear rate is suddenly dropped to a non-zero value, the droplets will retract to a smaller deformation because of the reduced shear stresses. This should result in a decreasing dichroism. The size of the droplets is now, however, below the steady-state value at the new shear rate. Hence coalescence can occur, by which the droplets gradually grow in time to a new steady-state value. Even at the low concentrations of the disperse phase used here coalescence is possible¹³. Because of the low collision frequency, the growth rate will, however, be low. The growing droplet size at constant shear rate will give rise to a larger shape anisotropy and consequently the dichroism should increase again. Dichroism measurements therefore make it possible to separate quantitatively the time periods for shape relaxation and for coalescence. An example of the evolution of the dichroism during a step-down experiment is presented in Figure 5. This figure also contains the light transmittance (I_{DC}) during such an experiment. In the present case the evolution of shape during relaxation and of size during coalescence both cause a decrease in light transmittance. Hence a measurement of turbidity is less indicated than that of dichroism to distinguish the structural changes in step-down experiments.

The potential for probing coalescence with dichroism measurements is illustrated by evaluating the effect of shear rate. Step-down experiments similar to that of Figure 5 are used. Only the slowly increasing part of the dichroism curve is used as discussed above. The dichroism values of this part

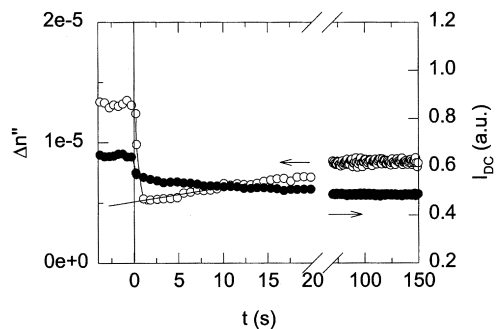


Figure 5 Dichroism (○) and I_{DC} (●) evolution for 1.0% PDMS in PIB in a step-down experiment from 50 to 30 s⁻¹ (23°C)

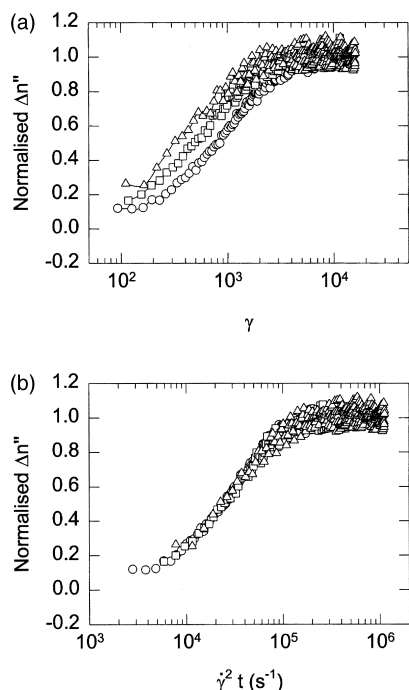


Figure 6 Coalescence after step-down in shear rate: normalised dichroism versus strain (a) and versus the product of strain and final shear rate (b) starting from the same initial shear rate (100 s⁻¹) at 23°C (1.0% PDMS in PIB). The final shear rates are 30 (○), 50 (□) and 70 s⁻¹ (Δ)

are normalised between 0 and 1. The normalised zero value refers to the dichroism which is obtained by extrapolating the coalescence branch of the curve back to the instant the shear rate has been suddenly decreased (see Figure 5). The normalised values are plotted against total strain $\gamma (= \dot{\gamma}t)$ at the final shear rate after step-down (Figure 6a). Strain could be expected to be the dominating factor in the process. Indeed, flow-induced coalescence should be controlled by the collision rate rather than by Brownian motion in these very viscous fluids²². If the collision rate were the only determining factor, the representation of Figure 6a would superimpose the results from experiments performed at different final shear rates. This is not the case here, where coalescence is completed at somewhat lower strains when the shear rate is increased. Actually, the curves superimpose when the strain is multiplied by the final shear rate (Figure 6b), which corresponds to coalescence times that are proportional to the inverse of the shear rate squared, at least over the range of shear rates covered here. An increased collision efficiency at higher shear rates is not a

straightforward result of the available theories, but a similar relation has been suggested by Utracki²³ for flow-induced coagulation of latex. It should be pointed out that the effect of particle size and particle size distribution can be different for different probing techniques. Hence the shape of the coalescence curves is not necessarily identical for all techniques²⁴.

Transient flows: step-up experiments

Various structural changes can occur in a blend when flow is suddenly applied or when the shear rate is suddenly increased. Dichroism can detect the resulting changes in anisotropy. Combining this information with the available insight in the effect of shear on blend structure, substantial structural information can be gathered from dichroism measurements.

Suddenly applying or increasing the shear rate will cause a stretching of the droplets. The corresponding increase in anisotropy will be picked up as a growing dichroism. If the extended droplets should break up, a more isotropic structure would develop and consequently the dichroism would drop again. Coalescence could also proceed during flow; a growth in size can be detected indirectly because larger droplets will deform more at a given shear rate and hence increase the dichroism. The experimental results for a large step-up in shear rate are shown in Figure 7a. In such an experiment all the mentioned structural changes could occur because droplet break-up will proceed via an interfacial instability, resulting in many small droplets that can subsequently coalesce. Indeed, three regions can be distinguished in the measured dichroism curve. A rapid increase, indicating droplet stretching, is followed by a decrease that reflects the break-up and by a slow gradual increase that identifies the coalescence period. In this manner the necessary time scales for the different structural changes can be obtained directly. The turbidity is also affected by these structural changes, but as in step-down experiments it turns out to be less sensitive than dichroism.

The evolution of the transient flow-SALS patterns in step-up experiments is illustrated in Figure 7b. They confirm the structural interpretation of the dichroism data and provide some additional information. The existence of fibrils or stretched droplets is confirmed by the appearance of a bright streak perpendicular to the flow direction. The streak is most pronounced when the dichroism is near its maximum value, as a comparison of Figure 7a and b shows. The streak decreases during fibril break-up but does not disappear totally, this will be discussed below.

Considering that the initial increase in dichroism in Figure 7a can be attributed to the development of extending filaments, an attempt can be made to model this part of the curve. For a dilute suspension of anisometric, dielectrically isotropic particles that do not absorb light, the dichroism can be expressed as²⁵:

$$\Delta n'' = \frac{1}{2k} \sum_{i=1}^N (C_{sca,1} - C_{sca,2})_i \quad (3)$$

where N is the number of particles per unit volume, k the wavenumber ($= 2\pi n_m/\lambda$) in a matrix of refractive index n_m with wavelength λ in vacuum. The terms $C_{sca,i}$ represent the scattering cross-sections in two orthogonal directions perpendicular to the direction of incident light. In a strong shear flow, filaments of radius a and length l are formed which will orient towards the flow direction. The scattering cross-sections of the filaments can be written, within the

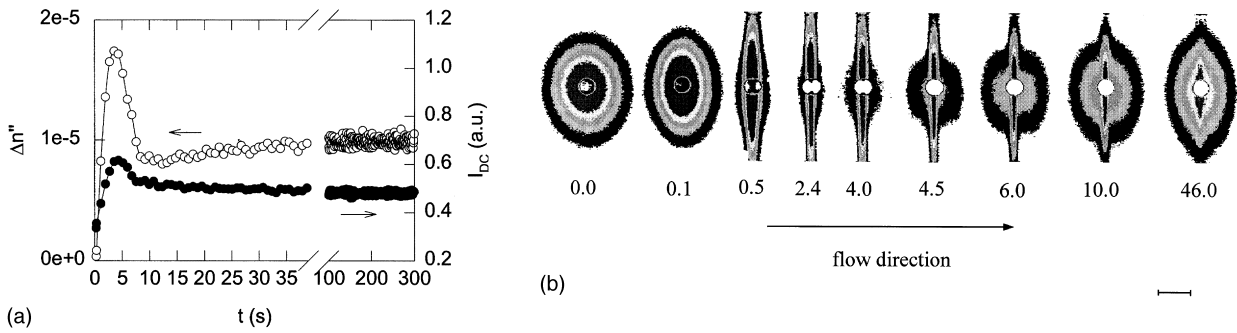


Figure 7 Time evolution of dichroism (○) and I_{DC} (●) (a) and the corresponding SALS patterns (b) for 1.0% PDMS in PIB at 23°C in a step-up experiment from 2 to 30 s^{-1} . Numbers under the patterns indicate the time elapsed since the increase in shear rate. The line segment in the corner represents $2 \mu m^{-1}$ of q

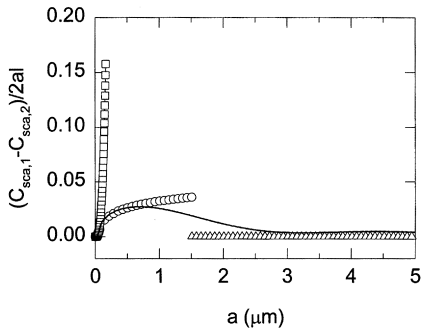


Figure 8 Scattering efficiency $(C_{sca,1} - C_{sca,2})/2al$ as a function of filament radius for PIB in PDMS within different approximations: Rayleigh (□); RGD (○); diffraction (Δ). The full line represents the numerical calculation result

Rayleigh–Gans–Debye (RGD) approximation, as²⁵:

$$C_{sca,1} = \pi(m-1)^2 k^3 a^4 l \int_0^\pi F^2 \left(2ka \sin \frac{\theta}{2} \right) d\theta \quad (4)$$

$$C_{sca,2} = \pi(m-1)^2 k^3 a^4 l \int_0^\pi F^2 \left(2ka \sin \frac{\theta}{2} \right) \cos^2 \theta d\theta \quad (5)$$

where m is the ratio of the filament refractive index to the matrix refractive index, F is defined as $2J_1(u)/u$ with $J_1(u)$ the Bessel function of the first kind. The subscripts represent the electric fields of the incident light parallel (1) or transverse (2) to the filament axis. As an example, Figure 8 shows a calculation result of $(C_{sca,1} - C_{sca,2})/2al$ for PIB in a PDMS matrix. When a is very small, equations (4) and (5) can be simplified as (Rayleigh approximation):

$$C_{sca,1} = \frac{\pi^2}{4} (m^2 - 1)^2 k^3 a^4 l \quad (6)$$

$$C_{sca,2} = \frac{\pi^2}{2} \frac{(m^2 - 1)^2}{(m^2 + 1)^2} k^3 a^4 l \quad (7)$$

On the other hand, when a is very large, the difference in the scattering cross-sections goes to zero, as equations (4) and (5) become (diffraction approximation):

$$C_{sca,1} \equiv C_{sca,2} = \frac{16}{3} (m-1)^2 k^2 a^3 l \quad (8)$$

In order to avoid the need for using the various approximations, a numerical calculation of $(C_{sca,1} - C_{sca,2})/2al$ ²⁶ is also shown in Figure 8. Within the range of filament radii a of interest here, the RGD approximation can be applied.

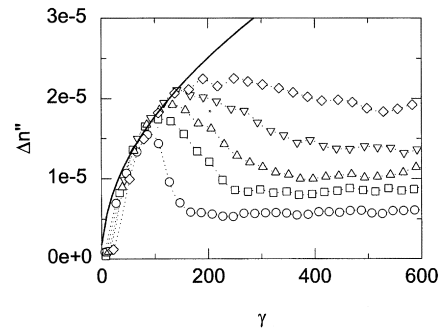


Figure 9 Dichroism versus strain for 1.0% PDMS in PIB at 23°C starting from the same initial shear rate in step-up experiments, Ca/Ca_{crit} : 1.8 (○); 2.7 (□); 3.6 (Δ); 4.5 (∇); 6.3 (◇). The full line is the theoretical prediction for the initial part

Moreover the value of $\zeta = (C_{sca,1} - C_{sca,2})/2al$ remains approximately constant in this region and amounts to 0.027 for PIB in PDMS and 0.017 for PDMS in PIB. The dichroism from equation (3) can now be written as:

$$\Delta n'' \approx \frac{\zeta NV}{\pi ka} \quad (9)$$

where V is the volume of the filament.

When the ratio of final over initial shear rate is sufficiently large, meaning that the ratio of capillary number $Ca (= \eta_m R \dot{\gamma} / \Gamma)$ over critical capillary number Ca_{crit} is larger than 2, the droplets may be assumed to deform affinely²⁷. In that case the radius a of the filaments is a unique function of strain for all shear rates²⁷:

$$a = \left(1 + \frac{\gamma^2}{2} + \frac{\gamma}{2} \sqrt{4 + \gamma^2} \right)^{-1/4} R \quad (10)$$

Hence, dichroism is given by:

$$\Delta n'' \approx \frac{\zeta \lambda v_2}{2n_m \pi^2 R} \left(1 + \frac{\gamma^2}{2} + \frac{\gamma}{2} \sqrt{4 + \gamma^2} \right)^{1/4} \quad (11)$$

with v_2 the volume fraction of the droplets. When the dichroism curves are plotted versus strain rather than time (Figure 9), the initial parts for different shear rates indeed superimpose. Equation (11) describes the experiments quite well. A description of the transient normal stresses under similar kinematics has been given elsewhere¹⁵.

As in step-down experiments, the time scales for different structural changes during step-up experiments can be deduced from the dichroism. The total time that elapses between the instant the shear rate is increased and the time at which the minimum in dichroism is reached is considered

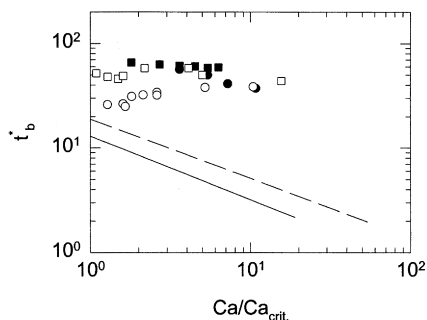


Figure 10 Dimensionless break-up time as a function of Ca/Ca_{crit} for 1.0% PIB in PDMS (●) and 1.0% PDMS in PIB (■) at 23°C. The lines represent the experimental results from Grace for viscosity ratios: 0.0169 (solid) and 0.107 (broken). The open symbols represent the experimental results from Elemans with viscosity ratios: 0.135 (○) and 0.933 (□)

to be the break-up time t_b for the fibrils. This time decreases slightly and monotonically with increasing shear rate. Figure 10 shows a dimensionless break-up time $t_b^*(= t_b\Gamma/2R\eta_m)$ as a function of Ca/Ca_{crit} for the two blends. The present break-up times compare quite well with the data by Elemans²⁷. They are, however, much larger than those of Grace²⁸. The discrepancy is attributed to interference of end pinching in Grace's case^{27,29}.

Transient flows: interrupted step-up experiments

In the step-up experiments of Figure 7 fibrils are formed and subsequently ruptured during shear. Alternatively, one could use a shearing motion to stretch droplets into fibrils, but then stop the flow before rupture has occurred. If the fibrils were long enough they would still rupture rather than retract back to the original spherical shape²⁹. A comparison between such an experiment of interrupted flow and the usual step-up experiment makes it possible to evaluate the effect of shear on fibril break-up. The results of dichroism and flow-SALS measurements during an interrupted shear flow experiment are shown in Figure 11. A shear rate of 30 s^{-1} has been applied during 4 s after the sample had been sheared at 2 s^{-1} until steady state. From normal step-up experiments (Figure 7) it is known that a shearing time of 4 s would nearly stretch the droplets to fibrils with maximum length. When the flow is stopped at that moment it takes 2.5 s for the dichroism to decay (Figure 11a). During shear the corresponding time lapse is about 5 s (Figure 7a). The delay in fibril break-up during shear is caused by the damping of the disturbances on the fibril and by a change of their period^{30,31}.

Whereas droplet growth by coalescence can be observed during flow, the low concentration of droplets, the high matrix viscosity and the negligible Brownian motion all act to slow down coalescence at rest enormously. As a result the slow increase in dichroism, observed after fibril break-up in a step-up experiment (Figure 7a), does not appear at all in an interrupted shear experiment (Figure 11a). The corresponding SALS patterns are also different (compare Figure 7b and Figure 11b). When fibrils rupture during flow the streak gradually disappears more or less in the background scattering. When the rupture occurs after the flow has been stopped, the streak decreases somewhat during the break-up period but remains nevertheless a dominant feature of the scattering pattern. It actually remains very visible many hours after the flow has been halted. Nevertheless, the dichroism relaxes nearly totally shortly after the flow has been stopped. This result seems to indicate that the dichroism closely follows the break-up of the filaments but that the streak in the scattering pattern does not. Rupture of a fibril by Rayleigh instability will result in a string of droplets, which might be gradually disturbed by flow but which will persist at rest. At rest inclusions will always retract to a spherical shape in dilute blends, hence shape anisotropy should decay to zero. A string of droplets, however, causes a structural anisotropy which, in the absence of form anisotropy, can dominate the scattering pattern without necessarily entailing a strong dichroic effect. Strings of droplets have recently also been suggested as an explanation for streaks observed in the SALS patterns of phase-separating systems³².

CONCLUSIONS

The flow-induced changes of the microstructure in immiscible polymer blends can be investigated by means of rheo-optical techniques. Linear conservative dichroism and flow small-angle light scattering are particularly useful for that purpose. It has been demonstrated that these techniques can detect detailed changes in microstructure in real time during flow. The various mechanisms for structural change could be distinguished: droplet deformation, fibril formation, droplet break-up and coalescence. The measurement of dichroism in particular makes it possible to determine rapidly and quantitatively the time scales for the different structural changes during flow or after stopping the flow. Hence this technique is very suitable to study the effect of material and process conditions on structural changes. As an illustration, dichroism measurements have been performed during stepwise changes, either step-down or step-up, in

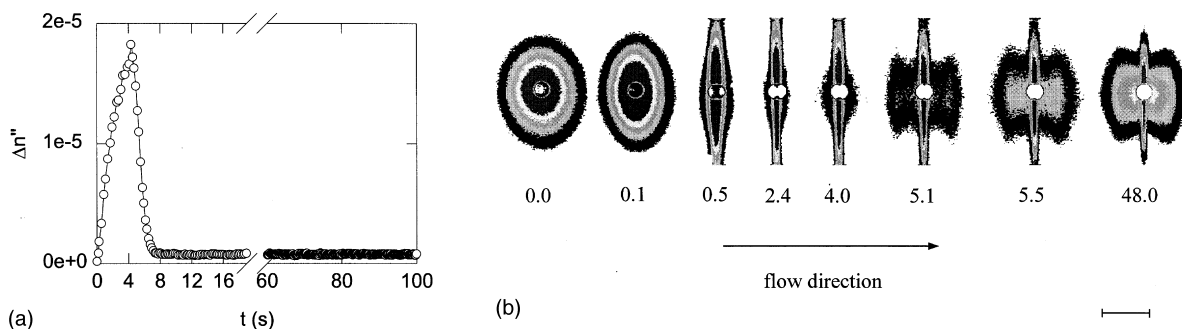


Figure 11 Time evolution of dichroism (a) and the corresponding SALS patterns (b) for 1.0% PDMS in PIB in an interrupted step-up experiment from 2 to 30 s^{-1} at 23°C. The flow was interrupted 4 s after the increase in shear rate. Numbers under the patterns indicate the time elapsed since the increase in shear rate. The line segment in the corner represents $2\text{ }\mu\text{m}^{-1}$ of q

shear rate. The rate of coalescence after a sudden decrease in shear rate is found to be essentially determined by the value of the final shear rate. The corresponding time scales are inversely proportional to the shear rate squared, indicating an increased coalescence probability per droplet collision with increasing shear rate. In step-up experiments at large capillary numbers, fibril formation, fibril break-up and subsequent coalescence can be distinguished. The affine nature of deformation can be assessed by measuring the dichroism. Fibril break-up proceeds slower during flow than at rest. The break-up time decreases slightly with increasing shear rate. The measured values are much larger than those obtained by Grace for lower viscosity ratios. They compare very well with the data by Elemans. The streak, which develops in the SALS pattern during fibril formation, persists after the fibrils break up at rest. This is attributed to the formation of a string of droplets. The dichroism detects mainly the form anisotropy and relaxes to very small values after fibril break-up. Interrupted flow provides a suitable means to study Rayleigh instabilities in polymer systems. It can be concluded that rheo-optical techniques make it possible to follow changes in microstructure *in situ* and in real time during flow in dilute immiscible polymer blends.

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