Influence of the Elasticity Ratio on the Point of Phase Inversion in an Immiscible Polymer Blend.

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SUMMARY: At a shear rate of 10 s^{-1}, a flow-induced phase inversion has been observed *in-situ* by optical microscopy on a blend of polydimethylsiloxane with solution of 50% of hydroxypropylcellulose in water for a range of concentrations. By increasing the shear rate up to $30s^{-1}$, the elasticity ratio of the components can be changed without changing the viscosity ratio. The resultant steady-state morphology is not influenced by the variation of the elasticity ratio, contrary to a theoretical model.

Introduction

For two-phases immiscible polymer blends, several parameters are important in determining the final morphology : composition of the blend, shear rate, viscosity and elasticity of the two phases, interfacial tension and time of mixing. Several authors as Paul and Barlow[1)], Miles and Zurek[2)] and Utracki[3)] have proposed semi-empirical equations based on volume fraction and viscosity of each component to predict the point of phase inversion. They assume that the least viscous component tends to constitute the continuous phase. But they do not describe satisfactorily the inversion in a general case, and more especially for viscosity ratios diverging from unity[3-5)] and for systems with large differences in elasticity of the components[6,7)]. More recently, a model where elasticity is explicitly included was devised by Bourry and Favis[8)]. Because the more elastic phase tends to encapsulate the less elastic one and to form the matrix, they proposed the following expression for the point of phase inversion:

$$\frac{\Phi_A}{\Phi_B} = \frac{G'_B}{G'_A} \cdot \frac{G''_A}{G''_B} \qquad (1)$$

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where Φ_i, G'_i and G''_i are respectively the volume fraction, the storage and the loss moduli of the component i.

In the literature, the lack of results about the influence of elasticity on the co-continuity conditions can be easily explained by the faced experimental difficulties in separating the influence of elasticity ratio from the influence of viscosity ratio. The only acceptable solution is to find a polymer blend that permits a variation of elasticity ratio with shear rate while keeping the viscosity ratio constant.

The aim of this work is to take advantage of the fact that a polydimethylsiloxane (PDMS) and a solution of 50 % wt. of hydroxypropylcellulose in water (HPC50%) responds to this criteria. We will first determine the concentration of flow-induced phase inversion at the shear rate where components have the same elasticity with optical observations during processing. Then we will evaluate at this concentration, the influence of elasticity ratio on the morphology by changing the shear rate, but keeping the viscosity ratio constant.

Materials

The experiments were performed on PDMS/HPC50% blends that are liquid at room temperature. The PDMS (Rhodorsil 47V200000, $\overline{M}_W = 149350$) is produced by Rhône-Poulenc and the HPC (Klucel L, $\overline{M}_W = 100000$) by Aqualon.

Rheological measurements were carried out at 18°C on a controlled stress Stresstech Rheologica rheometer, in parallel plate geometry. The results are presented in Table 1.

Table 1. Viscosity ratios and storage modulus ratios of the HPC50% and the PDMS at 18°C.

Shear rate 1/s	$\eta_{HPC\,50\%}/\eta_{PDMS}$	$G'_{HPC\,50\%}/G'_{PDMS}$	$G''_{HPC\,50\%}/G''_{PDMS}$
0.2	1.7	40	1.4
0.8	1	9.8	0.7
10	0.4	1	0.4
15	0.4	0.8	0.4
20	0.4	0.7	0.4
30	0.4	0.5	0.3

Before being introduced in the shearing device and let to relax 30 minutes, the blends are slowly hand mixed. Blends with concentrations of PDMS varying from 55 to 70% vol. have been prepared. The flow-induced morphology observations were performed on a Linkam CSS

450 transparent shearing device permitting the observation on the blends by optical microscopy during a simple shear-flow. The blends are visualized in the flow direction-vorticity plane, between crossed polarizers. Because the HPC50% solution is a liquid crystal, it appears bright between crossed polarizers, while the PDMS will be black. This will easily allow an identification of the phases.

Results and discussion

The at rest morphology is for all of our blends a continuous phase of PDMS with droplets of HPC50% that encapsulate droplets of PDMS (Fig. 1a). This morphology is in accordance with the viscosity ratio (see Table 1): the least viscous component (PDMS) is the continuous phase.

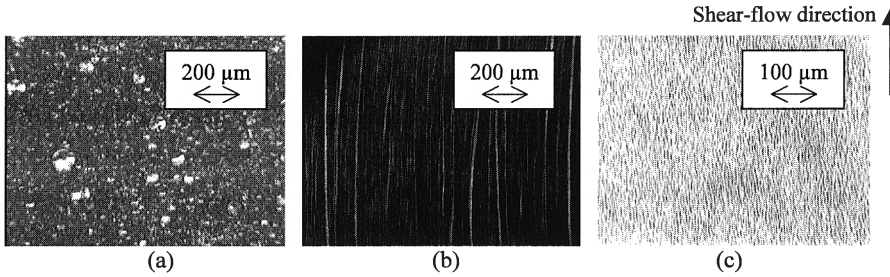

Fig. 1: Blends PDMS/HPC50% observed in the shearing device: (a) the at rest morphology of a 60/40 blend 30 min after filling; (b) final steady-state morphology of a 70/30 blend at 10 s^{-1} and (c) final steady-state morphology of a 60/40 blend at 10 s^{-1}.

Under a shear rate of 10 s^{-1}, the elastic ratio of PDMS and HPC50% equals unity while viscosity ratio equals 0.4 (Table 1). Depending on concentration, two different final steady-state morphologies are observed.

- Above 70% of PDMS, the steady-state morphology is a continuous phase of PDMS with filaments and droplets of HPC50% (Fig. 1b). Phase inversion did not occur since PDMS is the continuous phase, as before shearing. We just observe a refinement of the at rest morphology after a long time of shear.
- Below 60% of PDMS, we can distinguish, droplets of PDMS dispersed in a continuous phase of HPC50% once the steady-state is reached (Fig. 1c). A phase inversion of the at rest morphology is induced by the flow.

Between these two boundaries, there is a range of concentrations where the two morphologies can occur. So we cannot measure a point but a region of phase inversion. With 63% of PDMS, a phase inversion is observed on half of our carried out experiments.

The concentration of PDMS at the phase inversion versus the applied shear rate were calculated with the model of Bourry and Favis (equation **1**). We made the assumption that the Cox-Merz rule is verified for each of the individual component. The curve is shown on Fig. 2. Our experimental points are plotted with squares and circles. The increase of shear rates from 0.8 to 30 s^{-1} is only slightly varying the viscosity ratio, but strongly varying the elasticity ratio (see Table 1).

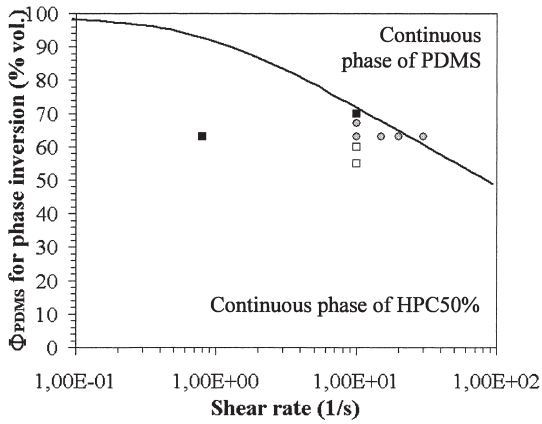

Fig.2: Concentration of PDMS that will give a phase inversion versus shear rate as predicted by the model of Bourry and Favis (——). Comparison with the experimental data: observation of shear-induced phase inversion (□), refinement (■) or the two morphologies (°).

At 10 s^{-1} where elasticity ratio equals unity, equation **1** predicts a phase inversion below 71% of PDMS. It just slightly overestimates the experimental data. But for shear rates below unity where the elasticity ratio and viscosity ratio are greater than unity and should act in opposite effect on the morphology, the model of Bourry and Favis predicts at low shear rates (shear rates under 10 s^{-1}) a continuous phase of HPC50% for our concentration range. This is not experimentally observed: the at rest matrix is always the PDMS component. The model of Bourry and Favis is not in agreement with the experimental data at low shear rates, for example at 0.8 s^{-1} for a blend with 63% of PDMS. For this blend, the components have same

viscosity whereas the elasticity ratio equals 9.8. The theory predicts a phase inversion that we did not observe.

Between 10 and 30 s^{-1}, the elasticity ratio is changing with the shear rate (from 1 to 0.5) while the viscosity ratio keeps a constant value of 0.4. By increasing the shear rate and so decreasing the elasticity ratio, elasticity should strongly suppress the phase inversion as predicted by equation **1**. On the contrary, we observed with the 63% vol. of PDMS blend either phase inversion or refinement with even a slight increase of rate of occurrence of phase inversion (Table 2).

Table 2. Number of cases of phase inversion at different shear rates for blends with 63% vol. of PDMS.

Shear rate	Number of cases of phase inversion
1/s	%
10	50
15	66
20	57
30	63

Conclusion

It is shown that viscosity ratio strongly influences the morphology of PDMS/HPC50% immiscible polymer blends, but not the elasticity ratio. A variation of viscosity ratio from 1 to 0.4 is sufficient to invert the morphology of a blend of 63% of PDMS with HPC50% even if elasticity acts in the opposite effect (elasticity ratio varying from 9.8 to 1). By varying the elasticity ratio from 1 to 0.5 at the point of phase inversion (concentration of PDMS fixed at 63% and viscosity ratio at 0.4), we observe an inverse influence of the elasticity ratio. These results are not in agreement with the model proposed by Bourry and Favis which places on the same level the influence of elasticity and viscosity ratios. The experimental data that have been published do not allow a decoupling of viscosity and elasticity.

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