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# Shear influences on polymer blends: experimental, theoretical approaches and technical implications

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SUMMARY: We examine the effects of shear on polymer blends consisting of partially miscible components, i.e. systems close to the phase boundary. The eminent phenomenon is the shift of the phase boundary, either extending the homogeneous area (flow-induced mixing) or the opposite effect (flow-induced demixing). The kinetics of the demixing process and concentration fluctuations are also influenced by flow fields, inducing anisotropy due to the flow direction. Experiments (scattering, rheology, in-situ flow-scattering, microscopy, DSC) are carried out with the academic model blend polystyrene/poly(vinyl methyl ether) and the industrial poly(styrene-co-maleic anhydride)/poly (methyl methacrylate) blend. The experimental results are rationalised in terms of a generalised Gibbs energy of mixing by including the energy which is stored in the sheared fluids.

## Introduction

Blending is a method increasingly used to improve the properties of polymeric materials$^{1)}$. The most commonly used industrial way of blending is melt-mixing in which pellets, or particles, of two (or more) pure components are thermally and mechanically mixed. Depending on the experimental procedure and the system the final processed materials exhibit different structures, from domains of a pure component dispersed in a second component matrix (immiscible polymer blends) to apparently mixed (at a mesoscopic - a few nanometers - level at least) polymer blends. One of the main interest in controlling processing lies in the fact that the resulting structure may be either unstable or metastable under quiescent conditions as is the case for certain partially miscible polymer blends$^{2\text{-}4)}$ but also for some immiscible polymer blends that seem to exhibit miscibility for very high shear rates$^{5)}$. For industrial blends with high enough glass transition temperature $T_g$ this unstable state may be retained in the final product through the rapid quench below $T_g$ that occurs after processing. The effect of flow on the structure of the blend during processing is then of dramatic

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importance especially in the case of partially miscible blends for which the observed flow-induced mixing or demixing may affect the mechanical and optical properties of the final product. The aim of this study was to study the effect of simple shear flow on the structure of partially miscible polymer blends and to develop experimental and theoretical tools to eventually permit a better control of polymer blends processing.

## Rheological Determination of Phase Diagrams

Our work has shown that for binary blends whose components present a sufficient dynamic asymmetry (difference of glass transition of constituents) some rheological measurements in the linear viscoelastic regime permit the determination of both binodal and spinodal curves. As the phase separation temperature is approached for a given composition, the viscoelastic properties of the blend change substantially, because of the enhanced concentration fluctuations. At low temperatures an increase of temperature results in a decrease of G' due to an increased distance from the $T_g$ of the blend. However, as the temperature increases further, the phase boundary approached, and the thermodynamic slowing-down of concentration fluctuations outbalances the mobility forces and gives rise to an enhancement of G'. As already discussed in detail elsewhere[6,7], the change of slope in the G'-T curve is identified with the rheological demixing temperature ($T_r$), i.e., the binodal point. This assignment of $T_r$ is in harmony with the observed thermorheological complexity[6].

A quantitative analysis of the linear viscoelastic properties of the polymer blends in the pretransitional regime leads to the determination of the spinodal temperature $T_s$[6] based on the use of the theoretical approach of Frederickson and Larson[8] which eventually leads to the consideration of the ratio[6,7]:

$$\frac{G'(\omega)}{[G''(\omega)]^2} = \frac{30\pi}{k_B T}\left\{\frac{b_1^2}{36\phi} + \frac{b_2^2}{36(1-\phi)}\right\}^{3/2} (\chi_s - \chi)^{-3/2} \qquad \mathbf{1}$$

Assuming that $\chi$=A+B/T, a linear dependence is predicted of $\left\{G''^2(\omega)/\left(G'(\omega)T\right)\right\}^{2/3}$ versus 1/T, leading to an intercept with the 1/T axis denoting the spinodal temperature, $T_S$.

The rheologically determined binodal and spinodal temperatures are summarised in the phase diagram of Fig. 1. In this diagram we also show independent measurements of the binodal temperature (by turbidity[9]) and the spinodal temperature (by Light Scattering (LS)[9]), which confirms the effectiveness of the proposed methodology to determine the complete phase diagram of a polymer blend. This procedure was proven successful in both LCST[6,10,11] and Upper Critical Solution Temperature[12] polymer blends.

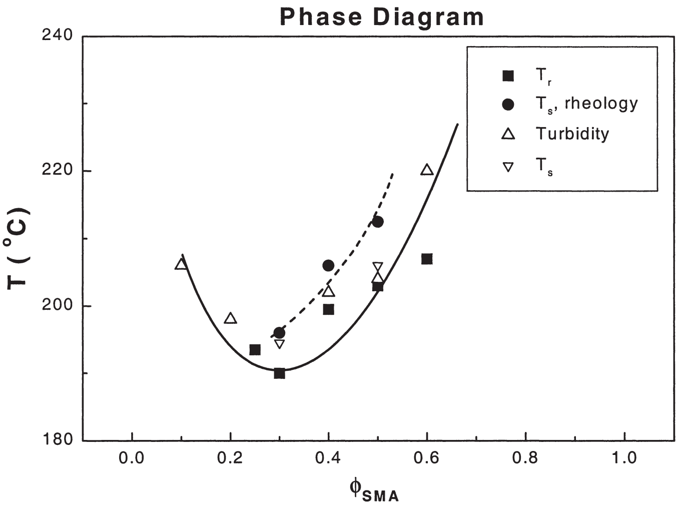

Fig. 1 Phase diagram of SMA/PMMA based on the rheologically determined temperatures and their confirmation from light scattering and turbidity measurements [see legend]

## Kinetics of Shear Induced Demixing

Earlier experiments allowed us to observe Shear Induced Mixing and Demixing (SIM and SID) in several systems through a shift under shear of the cloud temperature determined when heating the sample from the one phase up to the two phase region[4]. Here we focus on the kinetics and the influence of temperature and polydispersity. The only studies on the development of structures after a shear jump at constant temperature were carried through fluorescence on a limited range of shear rates[13] and through LS in a narrow temperature and shear rate range[14].

Our LS shear study carried out below the spinodal temperature $T_s$ for several PS/PVME blends and a broader range of shear rates (or shear stresses) allowed us to obtain first quantitative results on the SID process[15]. This process, observed above a temperature dependent critical shear rate, presents spinodal-like features. A wave-vector dependent growth rate can be extracted form LS intensities. Figure 2 displays the maximal observed growth rates (because of the q range limitation of LS experiments, this growth rate is likely to be inferior to the classical spinodal decomposition early stage maximal growth rate $R_m$) observed for different temperatures, shear rates and two blends. One of the main feature of the observed process is that, for a given shear rate, a lower experimental temperature or a higher polydispersity (both blends have similar $T_s$) leads to higher growth rates.

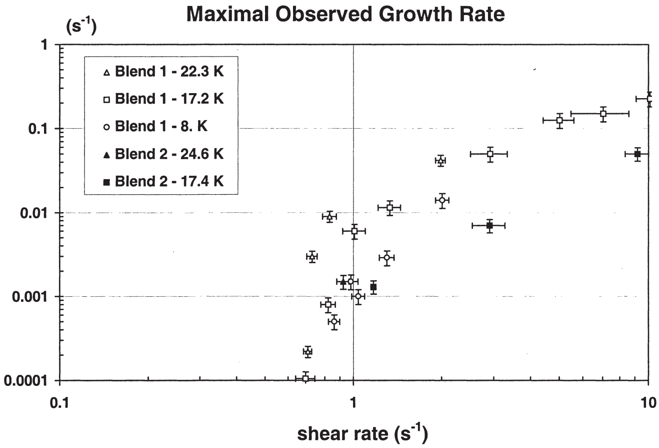

Fig. 2: Maximal growth rates observed through LS under shear for two 30/70 %w/w PS/PVME blends at different $\Delta T = T - T_s$. Blends 1 and 2 differ in the PS used, both having similar $M_w$ (~ 280 kg/mol.) but different $M_w/M_n$ (~4 for blend 1, ~1.3 for blend 2).

## Near Equilibrium Theoretical Approach

The shear influences on phase diagrams can be rationalised by treating all effects of flow as a perturbation of $\Delta G_z$, the Gibbs energy of mixing of the stagnant system (zero shear)$^{16)}$. Adding $E_S$, the energy the system stores until it reaches the steady state of the given shear rate $\dot{\gamma}$, to $\Delta G_z$ gives $\Delta G_{\dot{\gamma}}$, the generalised Gibbs energy of mixing of the flowing mixture. The basic equation therefore reads

$$\Delta G_{\dot{\gamma}} = \Delta G_z + \Delta E_S \qquad 2$$

It has to be kept in mind that, strictly speaking, the normal tools and technical terms of thermodynamics cannot be applied to a flowing mixture, since this is a steady state, not an equilibrium. But since $E_S$ is very small as compared to $\Delta G_z$, one should be able to treat the flowing system as being in equilibrium without much loss of accuracy.

The miscibility between two components is governed by the second derivative of $\Delta G$ with respect to the composition. Where it is negative, the homogeneous state is unstable, the system demixes instantaneously. Since the derivatives are also additive, the two effects of shear can be explained as follows: For Newtonian flow conditions the curvature of $E_S$ is positive and a slight negative curvature of $\Delta G_z$ can be compensated. The system demixed at rest becomes homogeneous when it flows (SIM). Under certain conditions, e.g. when the component with the longer relaxation time shows non-Newtonian flow behaviour at the given $\dot{\gamma}$, the curvature of $E_S$ can become negative leading eventually to SID.

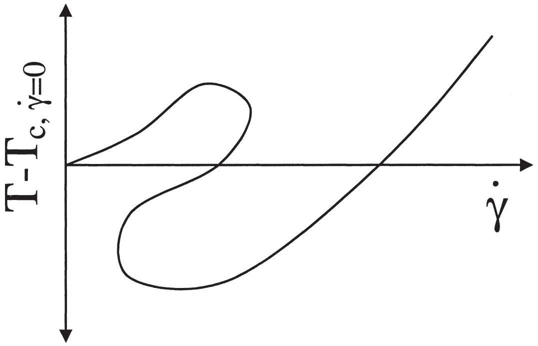

Fig. 3: Shear influences on the miscibility behaviour. The line starts at the critical point of the stagnant mixture and connects all "critical points" of the flowing blend. The two-phase area is above the "critical line".

Because of the just now mentioned reasons the effects of shear should obey the following sequence[17)], discussed for a LCST-system and shown schematically in Fig. 3: At low $\dot{\gamma}$ both components behave Newtonian, the curvature of $E_S$ is positive, one observes SIM. At a certain $\dot{\gamma}$ a closed miscibility gap emerges below the main miscibility gap (SID). This island shifts to higher temperatures and finally merges into the main two-phase area. At the highest $\dot{\gamma}$ only SIM is observed.

Experiments[18)] for PS/PVME support the validity of this scheme. These experiments correspond to the initial part of the curve of Fig. 3 and the part close to the minimum. The results displayed on Fig. 3 should correspond to the same $\dot{\gamma}$ zone but further away from the minimal $T_c(\dot{\gamma})$.

## Conclusions

Shear flow, by having a strong influence on the structure of polymer blends, is one parameter that needs to be adjusted in order to control the processing of polymeric materials. Our results on various blends allow a first quantification of flow induced structural changes that can be, qualitatively at least, described through a near-equilibrium thermodynamics approach taking into account the energy stored by the blend under flow.

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