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Shear Induced Mixing/Demixing: Blends of Homopolymers, of Homopolymers plus Copolymers, and Blends in Solution

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SUMMARY: Shear may shift the phase boundary towards the homogeneous state (shear induced mixing, SIM), or in the opposite direction (shear induced demixing, SID). SIM is the typical behavior of mixtures of components of low molar mass and polymer solutions, SID can be observed with solutions of high molar mass polymers and polymer blends at higher shear rates. The typical sequence with increasing shear rate is SIM, then occurrence of an isolated additional immiscible area (SID), melting of this island into the main miscibility gap, and finally SIM again. A three phase line originates and ends in two critical end points. Raising pressure increases the shear effects. For copolymer containing systems SID is sometimes observed at very low shear rates, preceding the just mentioned sequence of shear influences.

Introduction

In technical applications it is often necessary to handle multi-component fluid mixtures. During injection molding the influences of shear flow, elongational flow and pressure occur simultaneously. The accurate knowledge of their phase state as a function of temperature, pressure, composition, and flow rates is essential to optimize the properties of the blends and to design adequate extruders and mold geometries. Many studies, experimental and theoretical, deal with this research field.[1)]

Calculated Phase Diagrams for Homopolymer Blends

The basic idea for the theoretical treatment of shear influences on the miscibility behavior is to add E_S, the energy the system stores via chain entanglements until it reaches the steady state at the given shear rate $\dot{\gamma}$, to ΔG_z, the Gibbs energy of mixing of the stagnant system (zero shear).[2)] This yields $\Delta G_{\dot{\gamma}}$, the generalized Gibbs energy of mixing of the flowing mixture.

$$\Delta G_{\dot{\gamma}} = \Delta G_z + \Delta E_S \tag{1}$$

The flowing mixture represents a steady state, not an equilibrium. The tools of thermodynamics may not be applied in such a situation, and the technical terms, like binodal,

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critical point etc. should not be used. Nevertheless, since ΔG_Z is much greater than ΔE_S it is possible to treat the steady state of flow same as an equilibrium. Even if it is not correct, the normal technical terms are used in order to avoid the introduction of new ones.

The implementation of an alternative method[3)] for the calculation of phase diagrams enables a more exact calculation of phase diagrams for polymer blends, the results of which will be shown in the next paragraph. In the original paper[4)] some simplifications were used which can be avoided now. The recalculation for polymer solutions has already been reported.[5)] This publication contains a detailed discussion of all the phenomena which will not be given here. A very comprehensive description of similar phase diagrams as shown in the following can be found in ref. 6.

The stored energy per mole of segments can be calculated as

$$\overline{\overline{E_s}} \doteq V_S\, J_e^0\, (\eta\, \dot{\gamma})^2 \tag{2}$$

where V_S is the molar volume of the segment, J_e^0 the steady state shear compliance, η the viscosity and $\dot{\gamma}$, the shear rate. All eqs. and the values of parameters not given here can be found in ref. 4. ΔG_Z is given by the Flory-Huggins-Model[7)], the interaction parameter is

$$\chi = 0.00015 + 0.5\left(N_1^{-0.5} + N_2^{-0.5}\right)^2 + 5 \cdot 10^{-6}\left(T/K - 400\right) + 0.001\, \varphi_2^3 \tag{3}$$

with N being the Number of segments and φ_2 the volume fraction of component 2. The molar masses are 75 and 100 kg/mol, and $K = 10^{-4}$ Pa s at $T = 400$ K. This complicated equation for χ is needed to generate all effects that can occur.

With the chosen parameters five critical points (CP) can occur. For some $\dot{\gamma}$-values all of them occur, as can be seen in Figs. 1 and 2. At low shear rates both components show Newtonian flow behavior. Under these conditions the curvature of E_S is positive and SIM has to be expected. Therefore the original CP 1 at $\varphi_2 = 0.696$ and $T_c = 395.0$ K for the stagnant blend shifts to higher temperatures when the system flows (Fig. 3). At higher $\dot{\gamma}$ and low temperatures component 2 starts to show non-Newtonian flow behavior yielding a negative curvature of E_S inducing SID. At 76.45 s^{-1} an island of immiscibility emerges below the main miscibility gap. The maximum of this island is CP 3, the minimum CP 2. Both develop from a homogeneous double critical point (DCP). Since the area of positive curvature of E_S shifts to higher temperatures with higher shear rates, both CPs shift to higher T as well. CP 2 finally is found at higher temperatures than the original CP and one finally observes SIM.

For concentration independent χ the CPs 1 and 3 would vanish in a homogeneous DCP when the island melts into the main miscibility gap. For χ as given by eq. (3) CP 1 is shifted to very high values of φ_2, much higher than those of CP 3 (Fig. 4). Therefore a shoulder in the spinodal, a heterogeneous DCP, is induced at 386.1 s^{-1}. From this DCP the CPs 4 and 5 develop. CP 5 is unstable, the spinodal is concave to the (meta)stable area at this point. CPs 3 and CP 4 vanish in a homogeneous DCP at 386.36 s^{-1}. In the $\dot{\gamma}$ range between these two DCPs all five CPs exist. The shear rate of Figs. 1 and 2 is chosen within this range. The projection of the critical line into the T-$\dot{\gamma}$-plane (Fig. 3) is smooth at a homogeneous DCP, but sharp at a heterogeneous DCP. The three-dimensional critical line is smooth in all DCPs, as well as the projection of it into the φ_2-$\dot{\gamma}$-plane (Fig. 4). Finally the CPs 5 and 1 vanish in a heterogeneous DCP at 407.4 s^{-1} so that only CP 2 remains.

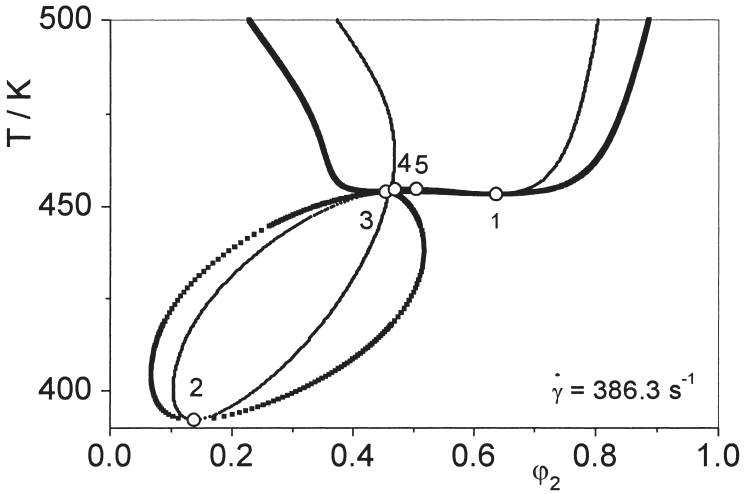

Fig. 1: Phase diagram for 386.3 s^{-1}; lines: spinodal and binodal; open circles: critical points. At this shear rate all five critical points can be found.

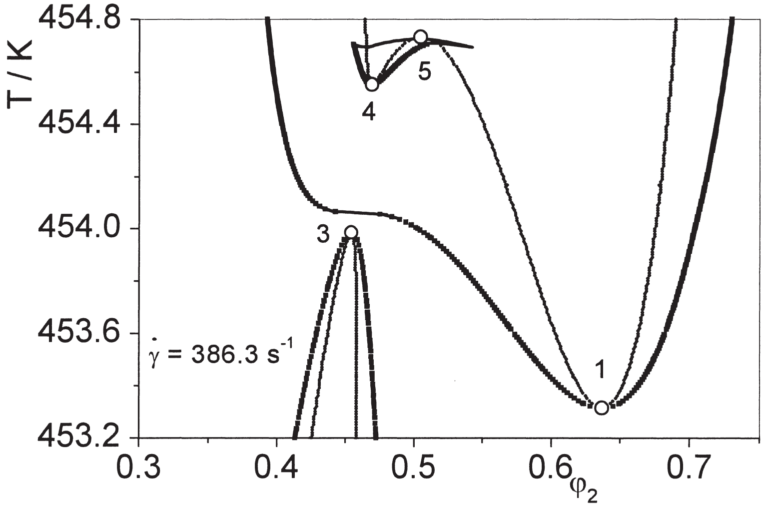

Fig. 2: Detail of Fig. 1. The stable and unstable binodals at the critical points 4 and 5 form a double sigmoidal curve.

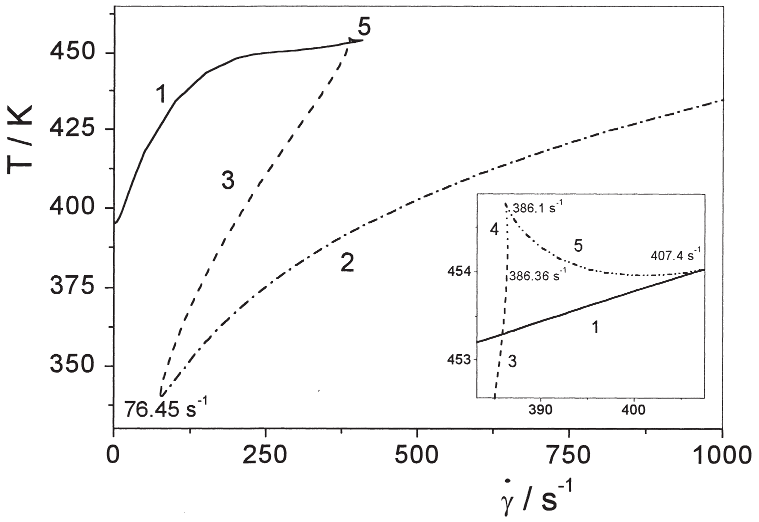

Fig. 3: Projection of the critical lines into the T-$\dot{\gamma}$-plane. Except for 5 all are stable. The shear rates, where double critical points can be found are given in the graph.

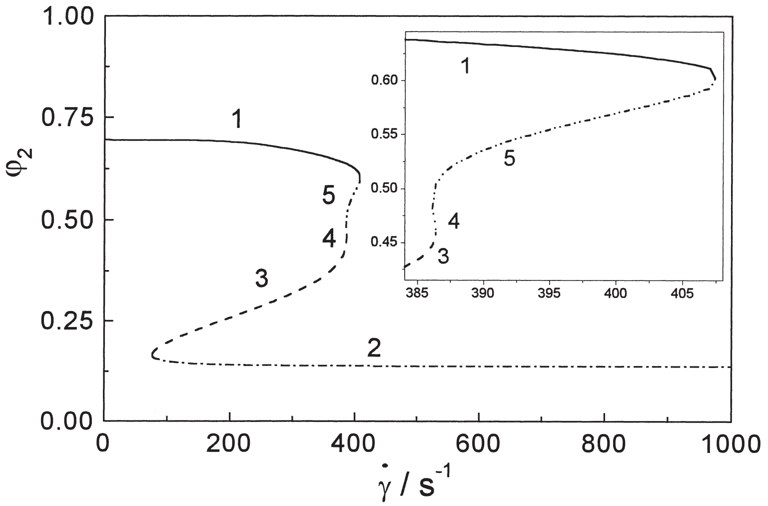

Fig. 4: Projection of the critical lines into the φ_2-$\dot{\gamma}$-plane.

A further phenomenon is the occurrence of a three phase line. At 386.32 s^{-1} CP 3 will protrude the binodal envelope and change from stable to metastable, at this shear rate CP 3 is a critical end point (CEP). The CEP is also the starting point for the three phase line. The middle composition runs from this point to a second CEP, when CP 1 is located exactly on the binodal at 392.65 s^{-1}.

Experiments for Homopolymer Blends and their Solutions

The most studied blend is PS/PVME.[8,9] It can exhibit two cloud points at one $\dot{\gamma}$, one higher than that of the stagnant blend, the other at lower temperatures. These two demixing points correspond to critical lines 1 and 2 in Fig. 3. Another blend showing the complex behavior of Fig. 3 is SMA/PMMA.[10]

The solution of a blend of PS (M_w = 196 kg/mol)and poly(*n*-butyl methacrylate) (PBMA 2050) in cyclohexanone shows shifts in the cloud point temperature (SIM) of 100 K and more.[11] The effect is more pronounced in PBMA-rich solutions, since PBMA has the higher molar mass.

Pressure Influences

To include pressure influences into the theoretical considerations, it is necessary to use a description for ΔG_z which takes volume changes with pressure variations into account. The Sanchez-Lacombe model[12] was chosen to calculate the combined effects of pressure and shear on phase separation.[13] The experimental observation, that SIM increases as pressure is raised, was also found in the calculated curves.

Copolymer Containing Blends A/AB

For mixtures of PDMS and a random copolymer of dimethylsiloxane and methylphenylsiloxane SID can be observed even at the lowest shear rates.[14] This can be rationalized by assuming, that for copolymer containing systems A/AB with very unfavorable interaction between A and B the stagnant blend does not exhibit random mixing but shows some clustering of like segments as a result of energetic preferences.[15] Flow can randomize the contact statistics and results in an additional mode of energy storage. Accounting for these contributions in eq. (1) leads to SID preceding the previously described sequence of shear effects.

References

1. A. I. Nakatani, M. D. Dadmun (Eds.), *Flow-Induced Structures in Polymer*, ACS Symposium Series No. 597,Washington, DC 1995.
2. B. A. Wolf, *Macromolecules* **17**, 615 (1984)
3. R. Horst, *Macromol. Theory Simul.* **4**, 449 (1995) and **5**, 789 (1996)
4. R. Horst, B. A. Wolf, *Macromolecules* **26**, 5676 (1993)
5. R. Horst, B. A. Wolf, *Polymer Bulletin* **40**, 353 (1998)
6. K. Šolc, R. Koningsveld, *J. Phys. Chem.* **96**, 4056 (1992)
7. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca NY 1953
8. M. L. Fernandez, J. S. Higgins, R. Horst, B. A. Wolf, *Polymer* **36**, 149 (1995)
9. J. D. Katsaros, M. F. Malone, H. H. Winter, *Polym. Eng. Sci.* **29**, 1434 (1989)
10. N. J. J. Aelmans, V. M. C. Reid, J. S. Higgins, *Macromol. Symposia*, this volume
11. C. Krause, R. Horst, B. A. Wolf, *Macromolecules* **30**, 890 (1997)
12. I. C. Sanchez, R. H. Lacombe, *J. Phys. Chem.* **80**, 2352 and 2568 (1976)
13. L. An, B. A. Wolf, *Macromolecules* **31**, 4621 (1998)
14. A. Hinrichs, B. A. Wolf, *Macromol. Chem. Phys.* **200**, 368 (1999)
15. B. A. Wolf, *J. Chem. Phys.* **110**, 7542 (1999)