Polymer Bulletin 16, 83–88 (1986)

Polymer Bulletin

Polymer Blends

Extensional flow induced miscibility in a polymer blend

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SUMMARY

Extensional flows can induce miscibility in a polymer blend of polystyrene with poly(vinyl methyl ether). Miscibility is observed as a change from turbidity to optical clarity when a phase separated blend flows isothermally in planar extension. In a start-up experiment at temperatures above the LCST, optical clarity does not appear instantaneously but after a time which depends on the rate of extension and the temperature, and it appears first near the region of highest extension. This effect is opposite to the observation for polymer solutions which exhibit shear-induced demixing. We attribute this to the fact that enthalpic effects largely determine blend miscibility, while the phase behavior of solutions is essentially controlled by entropic contributions. Since a deformation field decreases the configurational degrees of freedom of a polymer molecule, demixing is favored in solutions. However, the alteration of specific interactions rather than this entropic effect appears to be much more important in blends.

INTRODUCTION

Many studies of polymer-polymer miscibility have been made under equilibrium conditions (e.g., 1,2), however, little is understood about the phase behavior far from equilibrium. An understanding of the effect of flow on blend miscibility is potentially important in processing technology as well as in understanding the fundamental behavior of the blends.

Flow induced demixing in dilute polymer solutions has been known to occur at least since the work of Silberberg and Kuhn (3); an excellent review is given by Rangel-Nafaile, Metzner and Wissbrun (4). Changes in the apparent critical solution temperature for polymer blends in the presence of an external field such as shear flow (5), an electric field (6), and a pressure field (7) have recently been reported. The effects of these external fields are interpreted as the results of changes in molecular conformation and the cumulative strengths of the specific interactions that are necessary for miscibility between two homopolymers. Mazich and Carr (5) interpreted an abrupt change in the rheological behavior of a blend in shear flow as a phase transition. They found that the shearing of a blend of polystyrene with poly(vinyl methyl ether) could increase its lower critical solution temperature by 2 to 7 K.

The deformations studied so far have been restricted to steady shear in a concentric cylinder Couette, a capillary tube, or a cone-and-plate geometry. A shear flow stretches flexible macromolecules, inducing orientation which may cause the observed shift in phase stability. For example, the conformational change may enhance interactions that are effectively screened in a coiled molecule. However, because shear flows also provide rotational motion as a result of vorticity, the changes in conformation and orientation are generally limited. In contrast, extension provides a stronger flow without vorticity (8) and therefore should be significantly more effective in stretching and orienting chains.

A thermodynamic approach has been used to interpret flow induced phase transitions in polymeric liquids, despite the potential difficulties arising from the nonequilibrium circumstances. A relationship for the "free energy" elevation of dilute solutions in a flow field based on rheological parameters has been developed (4,9,10). Another estimate for free energy changes in flowing polymer solutions was based on the reduced flexibility of the stretched chain and is independent of rheological parameters (11). Expressions for the free energy elevation due to flow stems largely from the development of Marrucci (12). In this description, an infinitely extendable elastic dumbbell model was used; thus the effect of deformation on the phase stability of polymer blends and significant effects on the intermolecular interactions between two polymers cannot be described.

Miscibility in polymer blends is primarily the result of specific intermolecular interactions which occur between the components. The compressibility of the blend can also be significant (13). Therefore, enthalpic contributions can be expected to be much more important than the entropic effects. This is reflected in the free energy of mixing:

$$\Delta G = \Delta H - T\Delta S = \Delta E + P\Delta V - T\Delta S. \qquad [1]$$

A negative free energy of mixing is a necessary but insufficient condition for blend miscibility. Estimates of the changes due to flow in the enthalpic contribution through ΔE and compressibilty $P\Delta V$, along with the entropic contribution $T\Delta S$ can be used to interpret the free energy changes of a flowing polymer blend.

EXPERIMENTAL

The polymer blend used in preliminary studies is polystyrene (PSt M_w = 84,000, polydispersity = 1.8) supplied by Monsanto (Lustrex 101) with poly(vinyl methyl ether) (PVME M_w = 30,000, polydispersity = 1.6) supplied by Scientific Polymer Products. Both polymers were dissolved in toluene (~ 30-50% wt/wt solutions) and mixed in a Baker-Perkins planetary mixer for 12 hours. After mixing, the dissolved blend was placed in a Teflon-coated pan in a hood until most of the toluene was evaporated (about 10 days). The material was dried to a constant weight (less than 0.1 gram weight change) in a vacuum oven at 70 °C for about two weeks. The toluene content in a dried blend is less than 0.1%. Blends of 54/46% and 39/61% PSt/PVME were used in the experiments reported here.

Miscibility was detected by a change in turbidity of the blend. Although optical clarity is not an absolute criterion for homogeneity (14), a decrease in turbidity indicates an increase in compatibility. Thus, flow experiments should provide the capability to observe turbidity changes. Because the phase transitions are detected by optical clarity, we believe that they occur on the binodal line. Spinodal decomposition may be occurring, but it presently cannot be detected in this analysis.

Extensional flow experiments were done in a planar extensional flow apparatus; Winter et al. (15) described such a device and gave a description of the flow. A recent review of extensional flow induced changes in polymers is given by Keller and Odell (16). The die used in this study has a depth $l=12$ mm. The geometry of the die is set by a constant that dictates the shape of the hyperbolic walls ($A=xy$, where A is 10 mm^2). The die was constructed with a circular glass window on each of the die faces to allow for optical studies.

A Goettfert Rheograph 2001 Capillary Rheometer was used to feed the blend through the die. The rheometer cylinder is 25 cm long and 2.0 cm in diameter. Material can be extruded through the die at linear speeds that range continuously from 0.01 to 20 mm/s. The average deformation rate can be estimated from the expression for the ideal rate of extension $\dot{\varepsilon}$ in the die (14):

$$\dot{\varepsilon} = Q/2Al \qquad [2]$$

where Q is the volumetric flow rate. The extension rates were approximately 0.013 s^{-1} to 26 s^{-1}.

RESULTS AND DISCUSSION

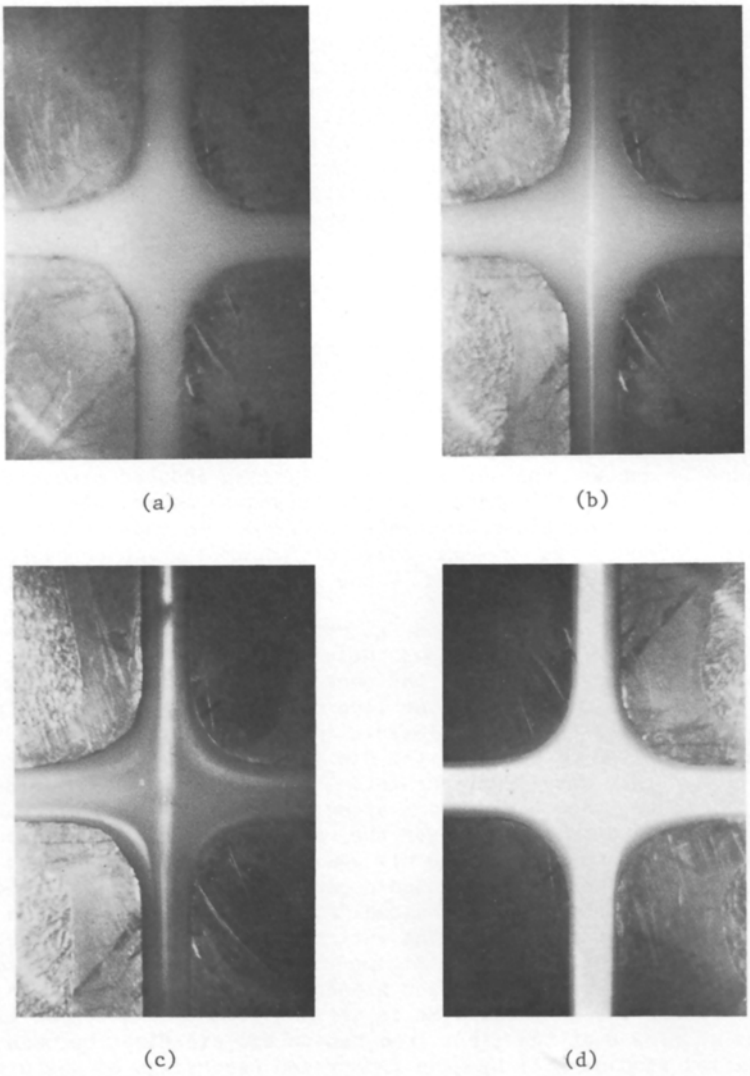
Figure 1 shows the development of flow induced miscibility. The temperature is 109 °C which is six degrees above the cloud point temperature for this blend of 54/46% PSt/PVME. In these experiments, the blend was extruded at a ram speed of 2.5 mm/s which corresponds to an average extension rate of 3.3 s^{-1}; the flow enters horizontally and exits through the top and bottom.

Figure 1a shows the blend at rest where it is phase-separated and appears cloudy. Figure 1b shows the blend 12 s after the onset of flow. Light that is directed from the back of the die through the windows is faintly visible along the center line of the exiting stream. This shows that the blend is becoming miscible in the region of highest extension. Note that the material entering the die is still cloudy, thus the pressure generated by the cappilary rheometer is not inducing the miscibility. Figure 1c shows the blend 16 s after the onset of flow. A much larger region is clear and is located near the region of highest extension. There is also some clearing near the die walls, which we attribute to shearing near the wall. Shear flow is also capable of inducing blend miscibility, but is not as effective as extensional flow. Figure 1d shows the blend 20 s after the onset of flow, when the entire flow region is completely clear.

The development shown in Figure 1 is typical of the observations at other flow rates, temperatures, and blend compositons as listed in Table 1. In this table, the critical time is defined as the duration of time after the onset of flow that the light from behind the die first becomes visible. More detailed studies will be made from video recordings of the experiments and/or by continuously measuring the intensity of light passing through the die. The critical strain is the product of the average extension rate and the critical time, which gives the average strain experienced by the material before the phase transition. Actually, the strain and the residence time in the die are inhomogeneous even during ideal flow.

There is no apparant correlation between the critical strain and the extension rate or temperature. In fact, within experimental error, the critical strain is practically constant. This would imply that the onset of flow induced miscibility depends only on the total deformation applied to the material. After flow was stopped, phase-separated condition was restored within 20 to 70 s, depending on the temperature and the previously applied extension rate. Experiments were also run in the homogeneous region at temperatures below the cloud point, but no effect was observed.

We estimate that the pressure in the die is approximately 10 to 20 atm, which could affect miscibility. We do not know the precise pressure



(a) (b)

(c) (d)

Figure 1: A 54/46 PSt/PVME blend, 6 K above the cloud point temperature of 103°C. Flow enters horizontally and exits vertically at an average extension rate of 3.3 s^{-1}. (a) No flow; the blend is cloudy, (b) 14 s after the start-up of flow, (c) 16 s after the start-up of flow, (d) 20 s after the start-up of flow.

Flow Rate	ε	Temperature	T - Tc	Critical Time	Critical Strain	Blend Comp.
[mm/s]	$[s^{-1}]$	[°C]	[K]	[s] (±4)		[PSt/PVME]
0.2	0.26	106	3	80	21	54/46
0.5	0.65	106	3	56	36	54/46
1.5	2.0	106	3	20	39	54/46
2.5	3.3	106	3	8	26	54/46
5.0	6.5	106	3	4	26	54/46
0.5	0.65	109	6	50	33	54/46
1.5	2.0	109	6	24	48	54/46
2.5	3.3	109	6	14	46	54/46
5.0	6.5	109	6	8	52	54/46
0.5	0.65	109	3	>60	--	39/61
1.0	1.3	109	3	>60	--	39/61
1.5	2.0	109	3	24	48	39/61
2.0	2.6	109	3	24	62	39/61
4.0	5.2	109	3	12	63	39/61
5.0	6.5	109	3	8	52	39/61
2.0	2.6	112	6	>60	--	39/61
4.0	5.2	112	6	12	62	39/61

Table 1
Results of extensional flow experiments
Tc = cloud point temperature
$\dot{\varepsilon}$ = average extension rate

dependence of the critical solution temperature for the PS/PVME blends. However, blends of poly(ether sulfone) and poly(ethylene oxide) were studied by Walsh and Rostami (7) who found that the LCST changes by 0.046 K/atm. For similar behavior, the cloud point temperature in our experiments would be raised by approximately 1 K for pressures of 20 atm. The most dramatic effect, however, occurs along the axis of the exiting stream in the planar extensional flow die, where pressure is believed to be very low. Thus, we expect pressure effects to be of secondary importance.

Further experiments are needed to quantify the relationship between average extension rate, critical strain, and temperature above the cloud point. More precise measurement of the temperatures and pressures in the material, as well as studies of chemically different blend systems, are needed. It is also important to study the regions in the extensional flow where the effect is strongest and behavior near the upper critical solution temperature in blends where the UCST is present.

ACKNOWLEDGEMENTS

We would like to thank Scientific Polymer Products and Goettfert for their help. Partial financial support from the Materials Research Laboratory at the University of Massachusetts is also acknowledged.

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Accepted June 4, 1986 *K*