Flow effect on phase separation during polymerisation of styrene containing dissolved HDPE

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Reactive diluents are used to enhance the processability of thermoplastic polymers. In one such system considered here, in situ polymerisation of monomer styrene results in phase separation of the initially dissolved polyethylene.

On-line turbidity measurements during the polymerisation show that an externally imposed shear flow delays the beginning of phase separation, i.e. flow-induced phase mixing takes place. The observed influence on the mechanical properties indicates a possible effect on final blend morphology also.

(Keywords: reactive diluent; flow-induced phase mixing)

Introduction

Since polymer blending provides a rapid and economic means of property modification by way of controlling the multiphase morphology, it has been the subject of intense interest. One important example is rubber-toughened plastics like high-impact polystyrene (HIPS). This is made by polymerising styrene (S) containing dissolved polybutadiene (BD) rubber, represented conveniently in a typical ternary diagram (Figure 1) of a partially miscible system. As the styrene polymerises into polystyrene (PS) along the line AB, polymerisation-induced spinodal decomposition into rubber-rich and PS-rich phases takes place at point C. Many other useful examples of polymerisation-induced phase separation have been reported, such as the synthesis of interpenetrating polymer networks, rubber- or thermoplastic-toughened epoxy-7,8, macroporous epoxy networks,7 reactive diluents,8 polymer-dispersed liquid crystals,10,11 polyurethane elastomers and cementers5,6.

Goossens et al.5 recently examined the miscibility of the S/high-density polyethylene (HDPE)/PS system, while using styrene as a flowability-enhancing diluent. As the styrene undergoes in situ polymerisation, liquid–liquid phase separation occurs. For a system containing HDPE in concentration as low as 7 wt%, HDPE was found to form a continuous phase. The authors considered reaction temperature and starting concentrations as the most important parameters responsible for controlling the morphology and mechanical properties of the blend. Many other workers12–16 have considered the use of crosslinkers and graft copolymers as compatibilisers for control of phase separation and dispersion morphology in the PS/PE system.

Here we analyse experimentally whether a polymerisation-induced phase separation process can be influenced by an externally imposed shear flow. Since polymeric mixtures are frequently processed under flowing conditions, the importance of such an effect is clear. The influence of flow fields on the phase transition of mixtures of polymers (or with small molecules), although without simultaneous polymerisation, has been subject of much research interest lately17,18. The effects are often analysed in terms of the shift in phase transition temperatures or coexistence curves, and both flow-induced mixing and demixing have been reported. The mixing effect has been attributed to flow-induced breaking of the dispersions to sizes comparable to the dimensions of the polymer molecule or to sizes smaller than a certain thermodynamically stable critical size.9,20 The demixing effect of flow has been attributed to the deforming polymer molecule’s elasticity contribution to the free energy.21

Experimental

Here, polymerisation of styrene containing dissolved, high-density polyethylene is carried out at elevated temperature in a constant shear rate apparatus, and phase separation is monitored by on-line measurement of turbidity as the polymerisation proceeds in the continuously shearing conditions.

As shown in Figure 2, the polymerisation reactor consists of a coaxial cylinder-cum-cone and plate, which induces flow fields of uniform shear rate, $\gamma$. The hollow inner cylinder, made from stainless steel (ss) but with its upper and bottom plates made of glass, is rotated at the desired rate with a constant-speed motor. The stationary outer ss cylinder is heated electrically by nichrome coils wound on it, and the reactor temperature is controlled at 120°C ± 2°C. To this outer cylinder is fixed the ss conical bottom; the latter has a glass peg through which a laser beam is passed in order to measure the turbidity of the polymerising shearing system by using a photodetector, as shown.

Particles of HDPE (3.4 g; melt-flow index = 6.5; particles finer than 1 mm) are suspended in purified styrene (75 ml) and transferred to the preheated reactor. The inner cylinder is rotated at 1250 rev min$^{-1}$ for about 3 min, during which time the HDPE dissolves and the transmitted laser intensity becomes steady. The speed of the cylinder is now brought to the desired value (50 or 1000 rev min$^{-1}$; i.e. $\gamma = 5.5$ or 110 s$^{-1}$, respectively), and the intensity of the transmitted laser beam is monitored as polymerisation proceeds under shear. After 15 min of polymerisation, the polymerisation rate is increased by adding cumyl peroxide initiator (0.34 g) freshly dissolved in styrene (5 ml). The shearing is continued for another 15 min. The viscous reaction mixture
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Figure 1 Schematic ternary phase diagram. Additive is (i) PB for HIPS and (ii) HDPE for the present case.

Figure 2 Schematic of the polymerisation reactor.

Figure 3 Decreases in transmitted intensity with the appearance of turbidity during polymerisation-induced phase separation at two different shear rates, $\gamma$.

is transferred to sheet moulds, and maintained at 120°C for 4 h to enable polymerisation to complete in quiescent state. The sheet is cut into dumb-bell shaped specimens, and analysed for tensile properties.

Results and discussion

During the first 3 min of heating and mixing in the reactor, the HDPE dissolves in the polymerising styrene, forming a homogeneous solution. After this, as the polymerisation proceeds under shear, the intensity of the transmitted beam decreases with time and approaches extinction (Figure 3). The decrease in intensity is attributed to the development of turbidity as a consequence of phase separation resulting from the increasing PS concentration in the polymerising system. From Figure 3, we notice that increasing the shear rate causes the turbidity to occur at a later time. In other words, at the higher shear rate, the polymerisation mixture remains homogeneous for a longer time of polymerisation, or a higher critical concentration of PS. Interestingly, we also find that the phase separation phenomenon is reversible by a change of $\gamma$ in the range where a single-phase solution is obtained at the existing polymer concentration. For example, the reaction mixture polymerising at $\gamma = 110$ s$^{-1}$, which is clear to light transmission at $t = 300-400$ s, immediately develops turbidity on reduction of $\gamma$ to 5.5 s$^{-1}$, and becomes clear again on increasing $\gamma$. Thus, a flow-induced phase mixing during polymerisation is seen to occur in this polymerising system, with a downward shift in the liquid–liquid phase separation curve of Figure 1. As discussed above, the phenomenon of flow-induced mixing observed in non-reactive polymeric systems has been attributed to higher $\gamma$ resulting in increased breakage rates of dispersed droplets, eventually into sizes close to those of single polymer molecules. Alternatively, Beyens et al. suggested that shear-induced mixing occurs when $\gamma$ exceeds the rate of relaxation of concentration fluctuations. It has also been attributed to elasticity contributions to the free energy, and to increased concentration of intermolecular sites.

The effect of flow strength, $\gamma$, during initial phase separation on the tensile properties of the fully polymerised samples is shown in Table 1. We find that although the tensile modulus is affected only marginally, the tensile strength and the elongation to break are significantly reduced if $\gamma$ during initial phase separation is high. As reported above, phase separation during the early stages of polymerisation is seen to be affected by $\gamma$. Thus, it appears that once phase separation has taken place at higher $\gamma$, some of its influence is retained even during subsequent quiescent polymerisation. In an earlier study reported in the literature, agitation during polymerisation to HIPS is also reported to affect the final particle size, particle size distribution, particle morphology and eventually the properties of the rubber-modified polystyrene.

We conclude that, during polymerisation-induced phase separation processes, externally imposed flow provides an additional control for phase separation, and perhaps.

<table>
<thead>
<tr>
<th>Shear rate (s$^{-1}$)</th>
<th>Modulus (MPa)</th>
<th>Strength (MPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>1616</td>
<td>38.0</td>
<td>2.6</td>
</tr>
<tr>
<td>110.0</td>
<td>1725</td>
<td>27.0</td>
<td>1.67</td>
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morphology and property development. We attempted direct electron microscopy examination of the morphology by solution etching to enhance contrast. However, this was rendered difficult owing to the major component, PS, being more soluble in etching solvents. We aim to examine alternative systems in greater detail.

References