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PHASE BEHAVIOUR OF SMA/PMMA BLENDS: THE INFLUENCE OF PROCESSING AT LOW AND HIGH DEFORMATION RATES

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SUMMARY

The influence of processing parameters (deformations) on SMA/PMMA blend phase behaviour is studied. It is found that injection moulding does change polymer blend phase behaviour. Phase separation kinetics are important to understand the injection moulding experiments and the kinetics are probably influenced by the deformations caused by the injection moulding proces. Capillary flow causes a complex change of polymer blend phase behaviour showing both deformation induced mixing and redemixing. Short capillaries, causing almost only uniaxial elongation in combination with pressure, cause no change to polymer blend phase behaviour. This is probably due to the short time the deformation is imposed to the material: it is expected that elongation is a main parameter causing changes in polymer blend phase behaviour. Parallel plate rheometer experiments show that applying only shear causes a complex change of phase behaviour showing both shear induced mixing and redemixing.

INTRODUCTION

During the last two decades, extensive research has been published on the influence of shear on the phase behaviour of binary or ternary systems, both theoretically [1] and experimentally [2, 3]. First shear induced mixing has been reported by several groups for several systems [1]. Subsequently shear-demixing has been observed [4]. More recent investigations have shown both shear-induced mixing and shear-induced demixing in the same system, leading to a very complex change of phase behaviour as a function of shear rate [2]. Mainly experimental studies are limited to polymer solutions. These systems are chosen because they were well defined and not too complex, in addition they are easy to handle at room temperatures and can be studied using existing rheo-optical apparatus. In the polymer industry, most of the systems of interest are blends of two or more polymers in the melt at high temperatures of typically, 200°C - 270°C. The SMA/PMMA system (SMA: polystyrene-co-maleic anhydride), subject of the present investigation, does have its LCST within the relevant processing temperature window and has a large difference in the two components glass transition temperatures (T_g). The large difference in refractive index allows for visual (or optical) detection of the change

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of phase behaviour. Also very important for experimental work on the influence of processing conditions on blend phase behaviour is to know which are realistic processing conditions used in industry. Most materials are extruded and injection moulded. Both shear and elongation do occur during extrusion and injection moulding processing processes. Additionally high pressures and viscous heating are involved, both factors known to be of influence on phase behaviour [5]. Most research up till now is concentrated on pure shear experiments as studied with cone and plate or parallel plate rheometers. A motivation to investigate the influence of deformations, involved in the injection moulding proces, on blend phase behaviour is given by the occurrence of locally phase separated material observed in injection moulded SMA/PMMA blends.

EXPERIMENTAL

Materials

The polymers used in this work were STAPRON® SMA, a copolymer with Styrene (S) and maleic anhydride (MA); produced on a commercial scale by DSM, and DIAKON™ PMMA , a PMMA with ethyl acrylate comonomer; supplied by ICI. Details on characteristics of both polymers are indicated in *Table 1*.

Table 1 Characteristics of the polymers used in this work

Polymer	M_w (g mol^{-1})	M_w/M_n	T_g (°C)	Refractive index, n_D^{20}	wt% MA in SMA
STAPRON® SZ28110	110 000	1.93	162	1.574	28
STAPRON® SZ32080	82 000	1.71	171	1.570	32
DIAKON™ PMMA	104 000	1.92	116	1.492	---

The blend investigated was melt blended on a ZSK30 extruder. Prior to experimental study samples were dried under vacuum and nitrogen atmosphere at 80°C until dry.

Experiments

The blend phase behaviour of the above mentioned blends was investigated under different processing conditions:

1: Stationary Phase Behaviour (no deformations)

2: Injection Moulding experiments

3: Kinetics of (spinodal) phase separation

4: Capillary flow experiments

5: Capillary flow experiments with a short capillary (mainly uniaxial elongation)

6: Parallel plate rheometer experiments (only shear)

RESULTS

1: Stationary Phase Behaviour (no deformation)

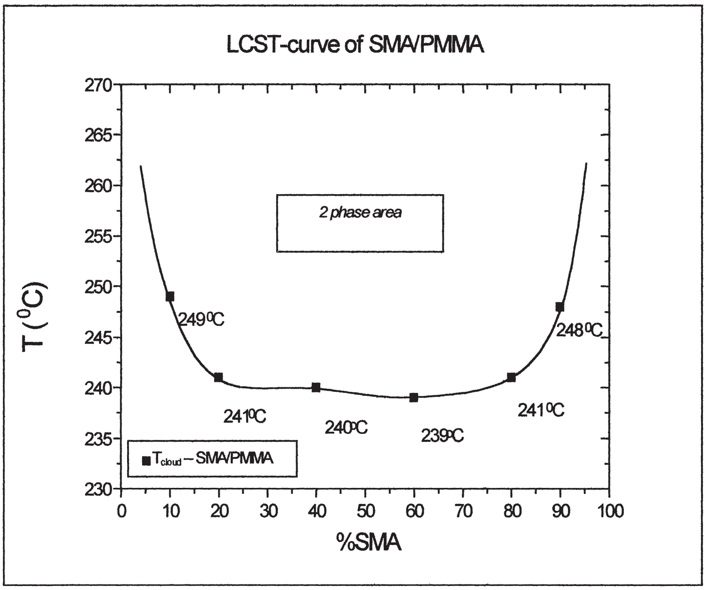


Figure 1: The LCST Phase behaviour of SMA/PMMA with SMA SZ28110.

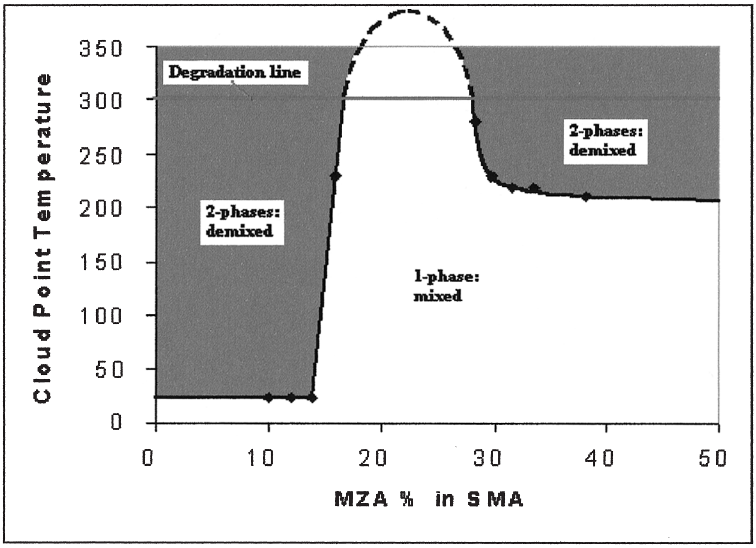
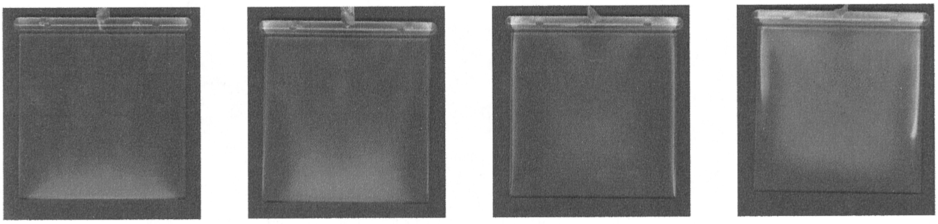


Figure 2: The influence of MA wt% in SMA for a 20/80 SMA/PMMA blend (SMA SZ28110).

With microscopy and light scattering techniques the following phase diagram could be constructed for a SMA/PMMA with a SMA SZ28110. Figure 1 shows the LCST for a SMA/PMMA blend for infinitely slow heating rates. Figure 2 shows the change of phase behaviour with MA wt% in SMA for a 20/80 SMA/PMMA blend at a heating rate of 10 °C/min (this results in higher values for the cloud point temperature).

2: Injection Moulding experiments

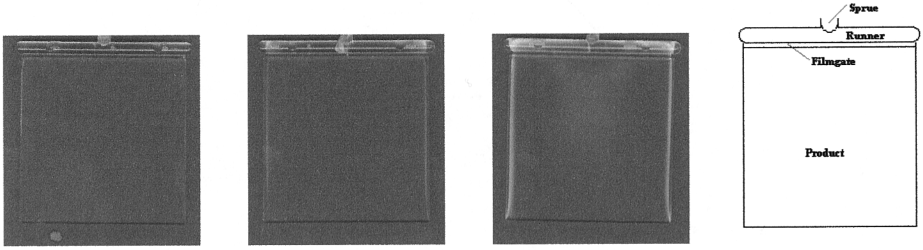
If the above mentioned blends (with a SMA SZ28110) are injection moulded under different processing conditions, the phase behaviour changes with processing conditions while having the same melt temperature (no friction heating effect). Some examples are shown below:



t_{inj} = 4 sec t_{inj} = 2 sec t_{inj} = 1 sec t_{inj} = 0.6 sec

20/80 SMA/PMMA blend, T = ± 250 °C, nozzle = ø 3 mm.

Figure 3: Change of product appearance as a function of injection time.



t_{inj} = 4 sec t_{inj} = 2 sec t_{inj} = 1 sec

60/40 SMA/PMMA blend, T = ± 250 °C, nozzle = ø 3 mm.

Figure 4: Change of product appearance as a function of injection time.

As one can see, increasing the injection speed causes a transparant sample (t_{inj} = 4 sec) to phase separate at certain positions in the product (t_{inj} = 1 sec). A more detailed study of the influence of injection moulding parameters is reported extensively in [6] and will soon be published elsewhere.

3: Kinetics of (spinodal) phase separation

The above mentioned injection moulding experiments show phase separated regions at melt temperatures of 250 °C. If one looks at figure 1, one might think that it is not surprising that phase separation takes place, since we are about 10 °C above the equilibrium cloud point temperature. However, slowly processed samples with a melt temperature of 250 °C do not show phase separation. This is logical if one investigates the phase separation kinetics of the blend. Figure 1 shows the phase behaviour as obtained after very long times at the temperature applied. Figure 5 shows the phase separation kinetics for a SMA/PMMA 20/80 blend with SMA SZ28110. Here one can see that it takes at least 2 minutes for the blend to phase separate at 250 °C. However, the blend is only for a few seconds (0.5s to 4s) at this

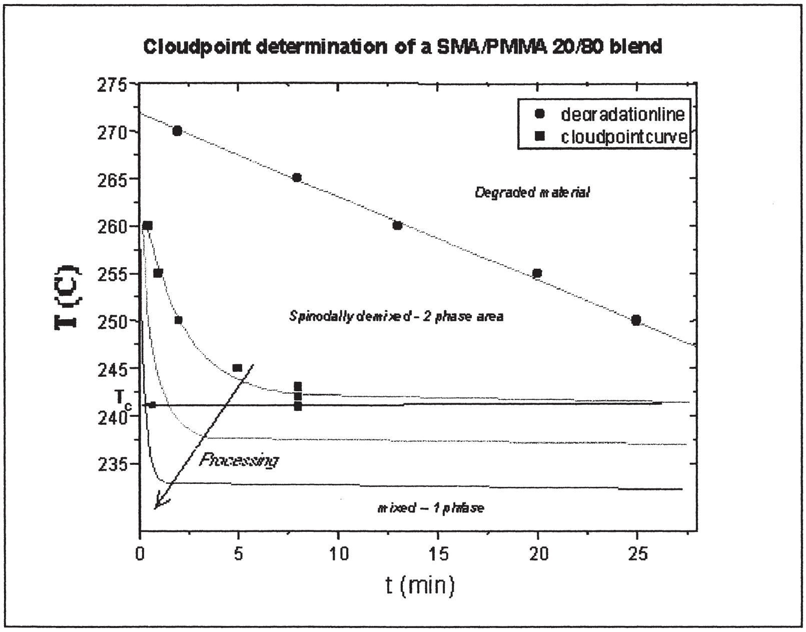


Figure 5: Phase separation kinetics and its expected change with injection moulding processing conditions.

temperature and immediately starts to cool down in the cold mould. So the locally phase separated areas in the products were not caused by the temperature of the melt. It is believed that the deformations imposed to the blend change the phase separation kinetics as is indicated by the arrow in figure 5.

4: Capillary flow experiments

In order to better understand the injection moulding experiments, capillary flow experiments were performed, which, like injection moulding, combine shear, elongation, pressure and friction heating. The experimental set up is explained in figure 6.

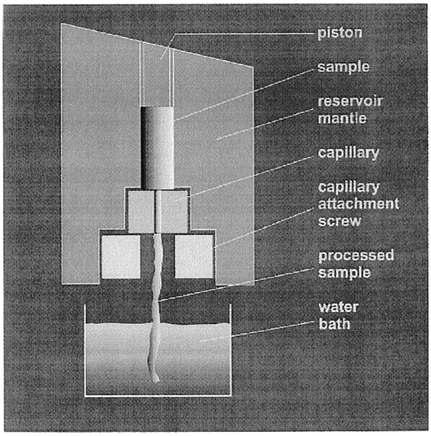


Figure 6: Experimental set up of the capillary flow experiment

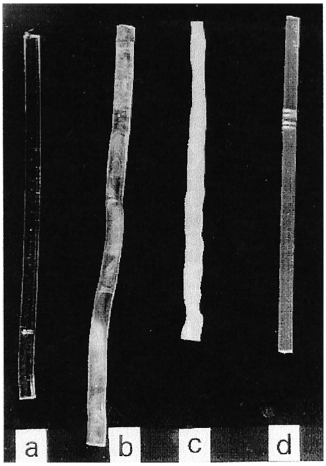


Figure 7: Sample appearance of blends processed with capillary flow

Samples of a SMA/PMMA 20/80 blend with a SMA SZ32080 (Cloud point temperature of 205 °C) were processed with different piston speeds (apparant shear rates) and temperatures. The samples obtained showed 4 typical sample appearances as explained in figure 7.

Sample **a** is a fully mixed transparant sample, sample **d** is slightly demixed hazy sample, sample **c** is a further demixed opaque sample, while sample **b** is a combination of transparant material with cloudy material circeled around it. The capillary experiments are discussed in detail in a recent article [7, 8]. Using these visual sample appearances a phase diagram as a function of piston speed applied could be created as shown in figures 8, 9 and 10.

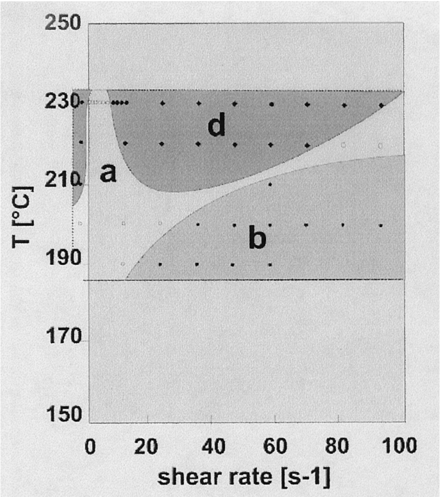


Figure 8: Complex change of phase behaviour with piston speed in a capillary exper.

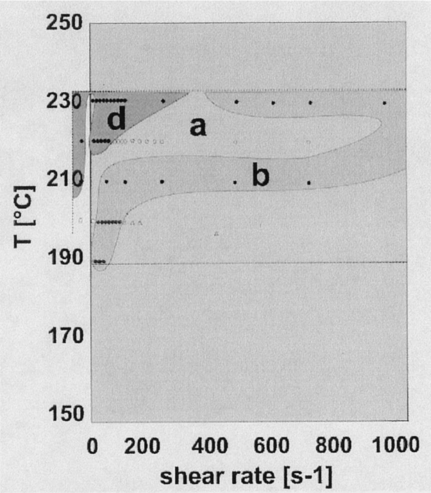


Figure 9: Figure 8 continued for higher Piston speeds

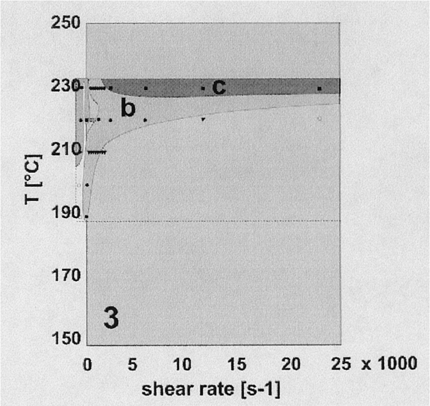


Figure 10: Figure 8 and 9 continued for higher Piston speeds.

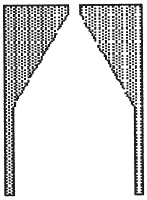


Figure 11: A 1/1 capillary (1 mm length, 1 mm diameter)

From figure 8, 9 and 10 one can see that the phase behaviour changes in a complex way showing both deformation induced mixing and redemixing.

5: Capillary flow using a short capillary (uniaxial elongation)

If one reduces the length of the capillary used, the shear contribution to the deformation is reduced enormously, resulting in mainly uniaxial elongation (in combination with pressure).

If one performs similar experiments as in section 4 with the capillary as shown in figure 11, on a 20/80 SMA/PMMA blend with SMA SZ28110, one obtains the result shown in figure 12.

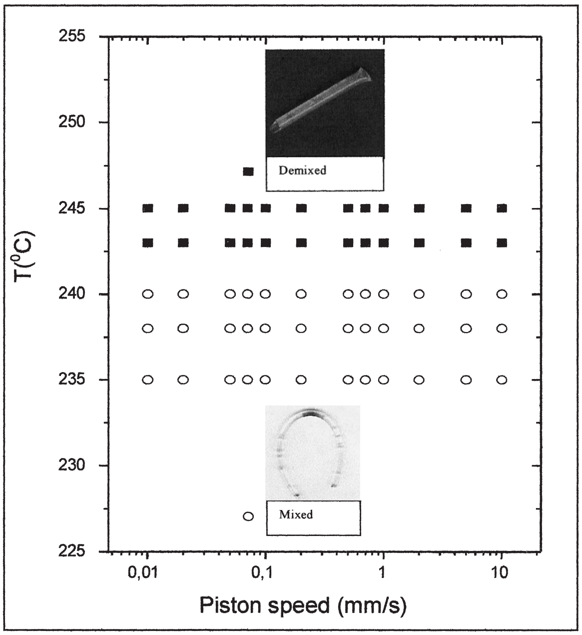
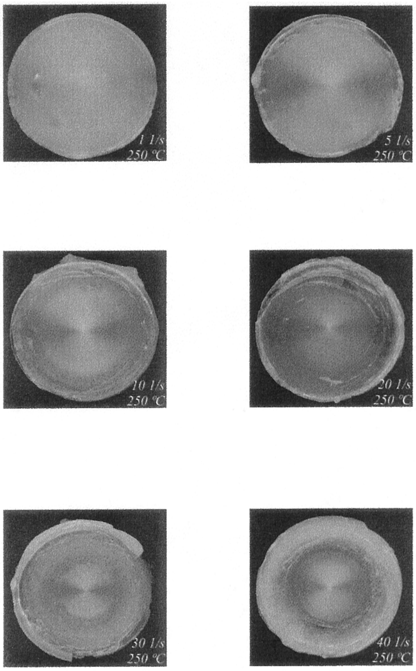


Figure 12: Influence of uniaxial elongational flow on blend phase behaviour.

Figure 12 shows that the phase boundaries of the blend did not change with the deformations applied. This might indicate that the combination of uniaxial elongational flow with pressure does not change the phase boundaries. However, there is another difference between the capillary experiments in section 4 and the experiments mentioned above. The time during which the blend is exposed to the deformations is very different in the two kinds of experiments. For the same piston speed the material is deformed 30 times longer in the capillary of section 4 compared to the capillary of figure 11. It is expected that the time, during which the material was deformed, was to short during this experiment to cause any change of phase behaviour. So, like in the injection moulding experiments, phase separation kinetics have to be taken into account to understand the seeming contradiction between experiments in section 4 and the ones explained above.

6: Parallel plate rheometer experiments

The 20/80 SMA/PMMA with SMA SZ28110 was also sheared in a parallel plate rheometer to investigate the influence of only shear without any other deformations. The shear rate increases with the radius within the samples form 0 s^{-1} to maximum. One can observe a transparant region at intermediate shear rates which scales with shear rate applied. Figure 13 shows some samples obtained after shearing and quenching the materials.



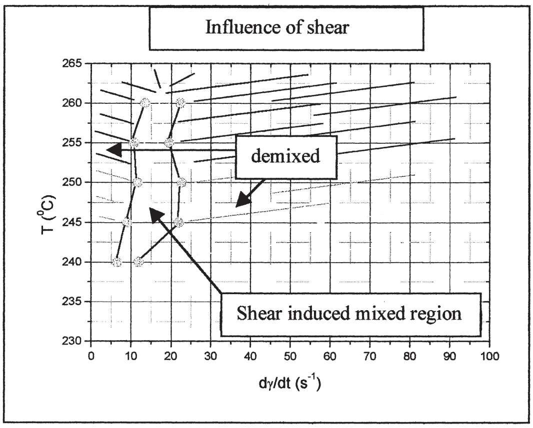


Figure 13: Sheared samples of a 20/80 SMA/PMMA blend with SMA SZ28110.

Figure 14: Shear induced phase diagram of a 20/80 SMA/PMMA with SMA SZ28110.

A diagram as shown in figure 14 could be constructed showing shear induced mixing and redemixing.

CONCLUSIONS

From the above mentioned experiments one can draw the following conclusions:

- Injection moulding does change polymer blend phase behaviour.

- Phase separation kinetics are important to understand the injection moulding experiments and the kinetics are probably influenced by the deformations caused by the injection moulding proces.
- Capillary flow causes a complex change of polymer blend phase behaviour showing both deformation induced mixing and redemixing.
- Short capillaries, causing almost only uniaxial elongation in combination with pressure, cause no change to polymer blend phase behaviour. This is probably due to the short time the deformation is imposed to the material: it is expected that elongation is a main parameter causing changes in polymer blend phase behaviour.
- Parallel plate rheometer experiments show that applying only shear causes a complex change of phase behaviour showing both shear induced mixing and redemixing.

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