

# PHASE INVERSION DURING COMPOUNDING -- THE EFFECT OF VISCOSITY VARIATION WITH TEMPERATURE

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## Abstract

The effect of different rheological and thermal behavior of the components in an immiscible blend, on the evolution of its morphology during compounding was investigated. Phase inversion, where there is a transformation from a morphology of component A dispersed in component B to that of component B dispersed in component A during compounding was shown to occur in blends with a low viscosity minor component. Relative transition temperatures and relative viscosities were systematically varied. The temperature dependence of viscosity of the individual components and its effect on determining phase inversion behavior was explored.

## Introduction

A specific target morphology is often the goal in the compounding of immiscible blends. This morphology has to be achieved while blending two or more components of different rheological and thermal properties. A good understanding of the mechanisms of mixing during compounding in such blends is essential to determine the process conditions. Mixing in the fully molten melt state is relatively well understood [1]. But it has been shown that most of the reduction in size in going from solid pellets of the polymer to the final dispersed phase morphology occurs in the melting regime [2].

This aspect of mixing during the melting/softening regime is not very well understood. It has been observed that in the presence of a low melting point minor component, a phase inversion phenomenon, where the minor component forms the continuous phase, may occur during compounding[3,4]. This interesting behavior has also been shown to occur in systems of similar transition temperatures, with a low viscosity minor component [5]. Our work focuses on elucidating the effects of these two parameters on the compounding behavior; by using model blend systems where the viscosity ratios and relative transition temperatures can be independently varied. The viscosity ratio at a representative shear rate and a single temperature is unlikely to adequately characterize the blend. Hence, rheological measurements have been made in both the solid state and the melt, and these have been

correlated with the observed processing behavior of the blends.

## Experiments

### Materials

The choice of the individual components making up the blend was based on their melting/softening points and their viscosity at the processing temperature and at a representative shear rate in the mixer. In addition to the polycaprolactone/polyethylene system already reported [6]; a series of four polybutylenes from Shell, a polycarbonate from Bayer, and an amorphous copolyester from Eastman Chemical Company were used. The relevant thermophysical properties of the blend components are summarized in Table 1. Different molecular weights of the polybutylenes (PB) and polyethylenes (PE) were used so that the rheology of the blend could be varied without changing the melting/softening temperatures of the components.

### Procedure

Each of the components was dried under vacuum at a temperature below the transition temperature for 40hrs. Different combinations of the components were used to prepare blends of different viscosity ratios and relative transition temperatures. Polybutylene/Polycaprolactone, Polycarbonate/Polyethylene, PETG/Polyethylene blends were investigated. In all these blends the minor phase was kept at 10 wt.%.

A Haake Rheomix 600 batch mixer was used for all the compounding runs. The dried pellets were hand mixed in a tray before being fed into an intensive batch mixer with rotor blades set to rotate at 50 r.p.m. The torque required to drive the polymer mixture at a constant rotor speed was followed as a function of time.

At selected times into compounding, the mixer was stopped and samples were collected. These samples were quenched in liquid nitrogen to preserve the morphology at that time. Methylene chloride was used to selectively dissolve away one of the components and determine the continuous phase. In each of the blend systems mentioned

above, only one of the two components was soluble in methylene chloride.

Rheological measurements were made using an ARES mechanical spectrometer from Rheometrics. In the melt state, a parallel plate fixture was used and the complex viscosity and modulus were measured in a dynamic shear mode. For measuring the rheology in the solid state, a torsional fixture was used. Rectangular coupons of the polymer were compression molded and were sheared under torsion to obtain the complex moduli in the solid state under dynamic shear deformation at low strains. Our aim was to measure the rheology of the polymers across the entire temperature range that a pellet would experience in a typical compounding operation as described above.

## Results

### *PETG/PE Blends*

The magnitude of the complex viscosity as a function of temperature of these components is shown in Fig. 2. The PETG used as a major component in these blends was an amorphous high viscosity component with a  $T_g$  of 80°C. Two different Polyethylenes (PE-A and PE-D) were used as the minor component. The DSC traces on these polyethylenes showed a melting peak close to 100°C. The torque traces of these blends at a mixer set temperature of 180°C are shown in Fig. 1. In the blend with the low viscosity PE, a pronounced region of low torque is observed. Samples collected at this time showed that the PE was the continuous phase. In the blend with PE-A; samples were collected at 30s, 70s and 5min into mixing. The first of these corresponds roughly to the peak torque value. At this time into mixing, PE-A was found to be the continuous phase. At later times, PETG was the continuous phase.

### *PB/PCL Blends*

Different molecular weights of polybutylene (PB-A through PB-D) were blended with the lower molecular weight Polycaprolactone PCL-B. In this blend system, the minor component (PCL) has a much lower melting point than the major component. A constant mixer set temperature of 180°C was used to compound these blends. At this temperature and a representative shear rate of 100s<sup>-1</sup>, the viscosity ratios in these blends is close to one. The torque traces for these blending runs are shown in Fig. 3. Unlike the behavior of the torque with a low viscosity minor component, there is no low torque region during mixing. Samples were taken at about 45 seconds into mixing corresponding to the drop from feed torque peak. Dissolution studies with methylene chloride indicated that PB was the continuous phase in these samples. Despite the presence of a low melting minor component, the major component was the continuous

phase even at short mixing times. The temperature dependent complex viscosity of PB-A/PCL-B and PB-D/PCL-B blend components is shown in Fig. 4.

### *PC/PE Blends*

In contrast with the above blends, this system has a more viscous major component whose softening temperature (150°C) is far above the melting point of the minor PE component. A mixer set temperature of 180°C was used. The torque traces (Fig. 5) of the low viscosity blend indicate a low torque region coinciding with the PE being the continuous phase. The rheological measurements of these blend components are shown in Fig. 6.

## Discussion

A convenient way to group these different blend systems is shown in Table 2. A representative value of the viscosity ratio and the transition temperatures based on DSC measurements were used to differentiate the blends. The results of the dissolution studies to determine the continuous phase are included. Our understanding of the phase inversion mechanism in compounding has clearly shown the importance of both the relative transition temperature and the viscosity ratio of the components making up the blend. We have previously reported on the importance of considering the relative viscosity ratios in determining phase inversion even in blends with a higher melting point minor phase [6]. We have tried to understand the mechanism of phase inversion by studying the rheology of the components across the entire temperature range of interest in compounding.

Our rheological measurements show the expected sharp drop in the complex viscosity associated with going from a solid to a polymer melt. In a blend of two components of different transition temperatures, the compounding behavior is critically determined by the relative positions of this drop in viscosity of the two components.

As shown by the viscosity curves for the two PEs [Fig. 2], the melting point as measured in a DSC may not be an accurate representation of the relevant transition temperature for processing operations which involve dissipative mix-melting. The lower molecular weight PE, begins to soften at a lower temperature. This coupled with a very low viscosity in the melt state enables the formation of a continuous phase by the PE. An increase in torque due to phase inversion is observed in the blends with PE-D [Fig. 1]. This torque rise is not seen in the blend with the more viscous PE-A.

In the PB/PCL-B blends, despite the presence of a low melting point minor component, a single feed torque peak is observed [Fig. 3]. The comparable melt viscosities of the PCL and PBs [Fig. 4] seems to overshadow the effect

of the low melting point of PCL on the observed processing behavior. Our dissolution studies at different mixing times indicated that PB was the continuous phase. But this does not imply that PCL never formed the continuous phase. Hence these results have been labeled inconclusive in Table 2.

In the PC/PE blends, the low viscosity and the lower melting point of the PEs, favor phase inversion, as was indeed observed by the dissolution studies. In addition, a distinct rise in torque associated with phase inversion is observed in the lower viscosity ratio PC/PE-D blend.

### Conclusions

From the work presented here, the following conclusions can be drawn:

- 1) Phase inversion is likely to occur in the presence of a low viscosity component, even if it has a higher melting point. It is most favored in a system with a low viscosity, low melting point minor component.
- 2) The torque trace alone is not a reliable indicator of the occurrence of phase inversion during compounding. This is shown by the traces from the PETG/PE-A and PC/PE-A blending runs.
- 3) The sharp drop in viscosity, associated with melting of semi-crystalline polymers and the softening of amorphous polymers, is an important factor in determining the morphology evolution during compounding. It has been shown that a combination of low melt viscosity and lower

softening point of PE-D changes the observed processing behavior.

- 4) The relative transition temperatures and the relative viscosities provide a framework under which the compounding behavior can be investigated. This is a first step toward quantifying the parameters determining the mechanisms of mixing during the melting/softening regime.

### Acknowledgments

This work was supported by the Department of Materials Science and Engineering at MIT and the Eastman Chemical Company.

### References

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(Keywords: Phase inversion, immiscible blends, viscosity ratio, compounding)

**Table 1: Thermophysical Properties of Blend Components**

Material	Viscosity (180°C and 100s-1) Pa-s	Transition Temperature -- °C (from DSC measurements)
PE - A	1100	98
PE - D	12 <sup>a</sup>	100
PETG	6328	80
PB - A	845	116
PB - B	832	111
PB - C	324	110
PB - D	136	108
PCL - B	335	64
PC	7698	140

<sup>a</sup> at 140°C

**Table 2: Summary of processing behavior of model blend systems**

	$T_{\text{major}} < T_{\text{minor}}$	$T_{\text{major}} \sim T_{\text{minor}}$	$T_{\text{major}} > T_{\text{minor}}$
$\lambda^1 \ll 1$	PCL / PE-D <sup>2</sup> PETG/PE		PC / PE-A PC / PE-D
$\lambda \sim 1$	PCL / PE-A <sup>2</sup>		PB / PCL-B
$\lambda \gg 1$			

<sup>1</sup> $\lambda = \eta_{\text{minor}} / \eta_{\text{major}}$ ; with the viscosities measured at representative process conditions; (<sup>2</sup>Ref. [6])

▒ Indicates Phase Inversion occurs; □ Indicates inconclusive result

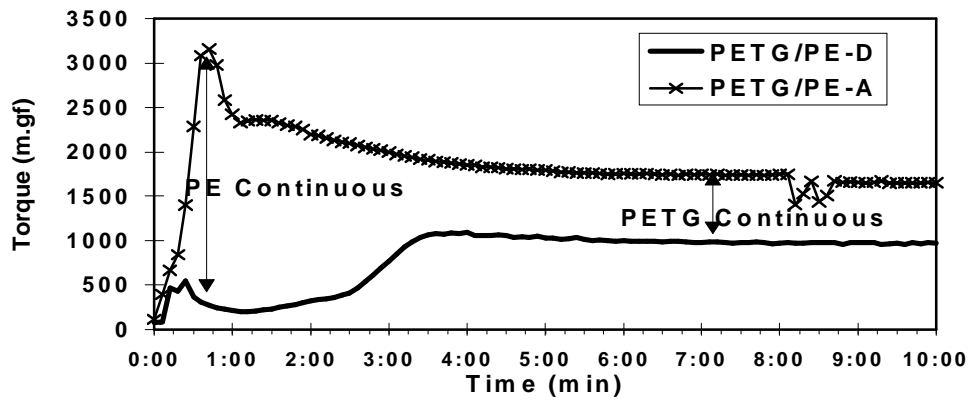


Figure 1: Mixer torque Curves for PETG/PE blends at 180°C

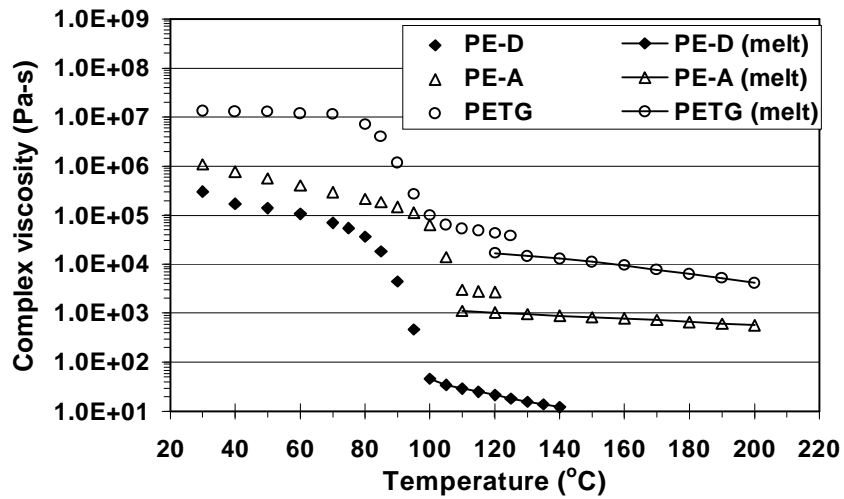


Figure 2: Complex viscosities of blend components in PETG/PE blends at  $100s^{-1}$

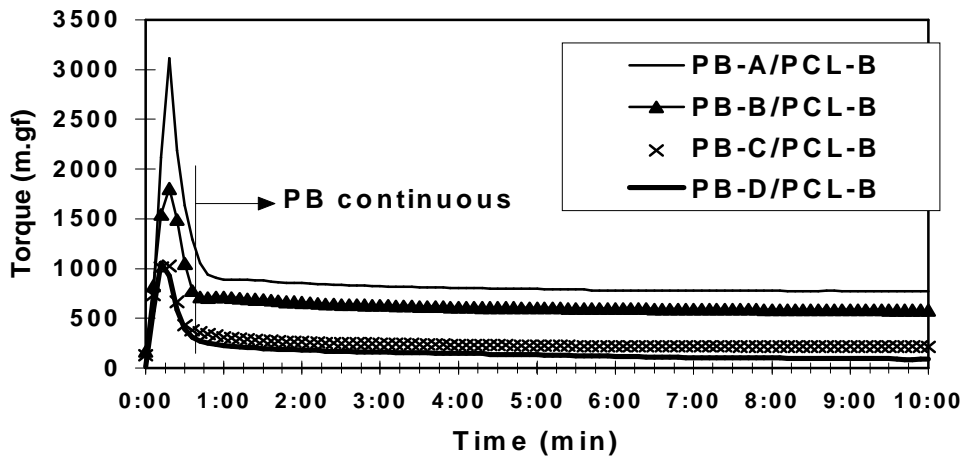


Figure 3: Torque traces for PB/PCL-B blends at a mixer set temperature of 180°C

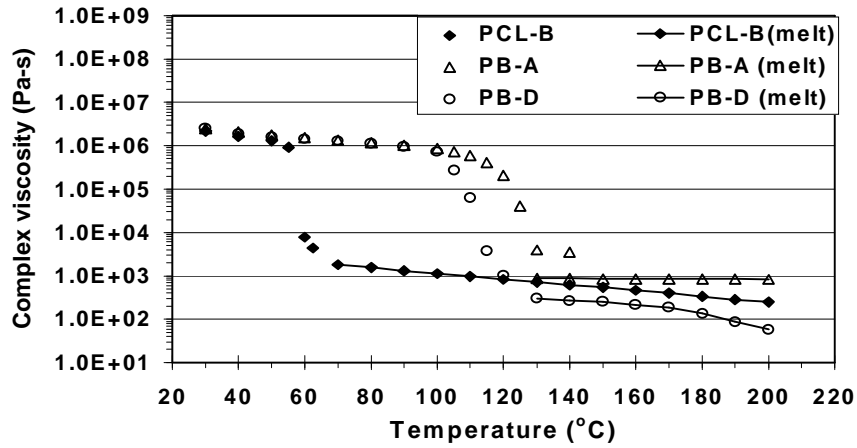


Figure 4: Complex viscosities of blend components in PB/PCL-B blends at 100s<sup>-1</sup>

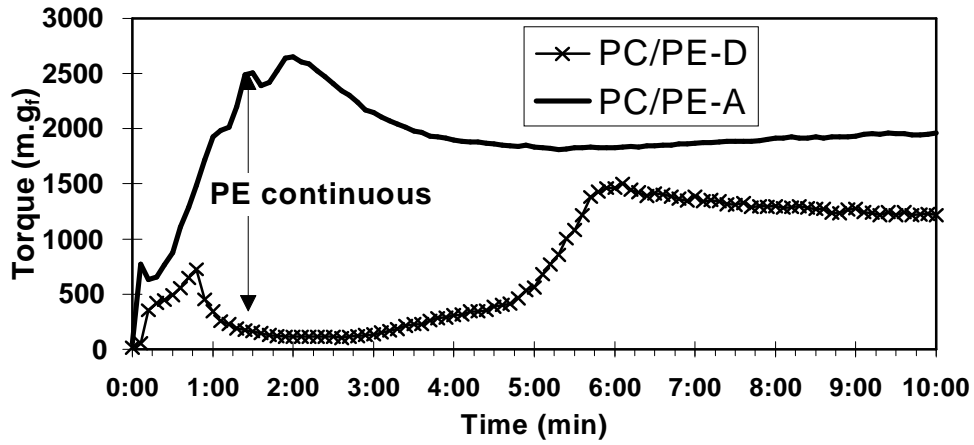


Figure 5: Torque trace for PC/PE blends at a mixer set temperature of 180°C

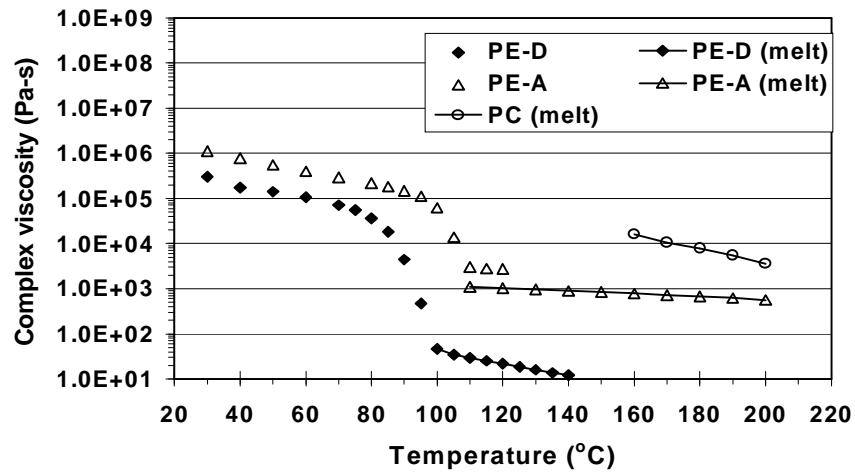


Figure 6: Complex viscosities of blend components in PC/PE blends at 100s<sup>-1</sup>