Investigation of Mixing in the Melting Regime During Polymer Compounding

by

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To my parents.
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ABSTRACT

Morphology evolution in the melting regime during compounding of immiscible polymer blends, where most of the size scale reduction occurs, is studied. Starting from an initial solid pellet mixture of two components, the progression to the final two-phase viscoelastic melt involves an intermediate stage where either one or both the components are melting or softening. Our focus is identifying and quantifying the factors that determine morphologies in the melting regime.

We identify blend systems that exhibit a transformation in morphology from a minor-component continuous phase with dispersed major component domains to that with the major component being the continuous matrix phase, as a function of mixing time. This phenomenon of phase inversion during compounding is demonstrated to occur even in blends with a higher melting point minor component. A low solid modulus and a low melt viscosity are shown to favor the formation of the continuous phase by the minor component. Polycaprolactone/polyethylene, polystyrene/polyethylene, polycarbonate/polyethylene, poly(ethylene-co-cyclohexane dimethylene terephthalate)/polyethylene, and polybutylene/polycaprolactone blends were studied. These model blends were chosen based on the melt viscosity ratio and the relative softening temperatures of the two components. These two parameters were used to develop a two-dimensional framework for summarizing the compounding behavior of blends. For compounding runs with a small amount of the minor component (~10wt.%) at a constant mixer temperature, phase inversion was observed for blend viscosity ratios less than 0.2, irrespective of the relative transition temperatures of the two components. Using a temperature ramping program resulted in the low melting component forming the continuous phase initially. Selective dissolution studies were used to quantify the amount of minor component present in the continuous phase at different mixing times.

A polystyrene/polyethylene blend with a melt viscosity ratio of ~0.001, was used to study the effect of batch size on the time required to form a continuous phase of the
major component, polystyrene. Similar morphological changes were observed during compounding of batch sizes ranging from 12g to 240g. Upon a five-fold increase in batch size the time to phase inversion increased by a factor of 3. This increase was explained by a combination of reduced heat conduction and reduced mechanical energy input to the batch.

To enable studies at different batch sizes in the same mixing bowl, a novel mixing blade with modular elements was designed and constructed. This design was used for both radial and axial scaleup studies. The effect of changing the blade configuration on the time to phase inversion was explained using a specific relative stagger parameter, which is a measure of the effectiveness of stress transfer to the batch.

Flow visualization using a glass window and blend sampling was used to develop a detailed description of the deformation steps leading to phase inversion in a model low-viscosity ratio blend. Intermediate morphologies of flattened pellets, stacks of pellets, fibers and clusters were identified. Based on these observations a micro-structural model was developed to predict the time to phase inversion. The model incorporates a simplified flow-field approximation and calculates the strain in the major component. A strain-based criterion was proposed which in conjunction with the model yielded an explicit expression for the time to phase inversion. Model predictions of the dependence of time to phase inversion on nominal maximum-shear-rate in the mixer, volume fraction of the minor component and blend viscosity ratio were shown to be in excellent agreement with experimental results.

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1. INTRODUCTION

1.1 Polymer Blending

Polymer blends are mixtures of more than one polymer designed to achieve specific improvements in properties or processing behavior. Throughout this thesis, we consider only polymer blends which are mixtures of two polymers that are immiscible under all processing conditions. Due to the long chain nature of polymer molecules entropic contribution to the free energy of mixing is negligible and formation of a miscible polymeric system requires significant negative enthalpy of mixing (1). Following Utracki (2) we refer to miscible or compatibilized mixtures as alloys and distinguish these from the systems studied in this thesis.

Blending is an attractive means for creating new polymeric systems with better performance and processing characteristics than the existing ones. There are significant savings associated with blending as a means to create a new polymeric system to satisfy a need as opposed to the development of a new polymer. Blending can also be used to extend the performance of an expensive resin using a less expensive one provided the properties relevant to the specific application are not sacrificed. Different grades of blends with differing cost, performance and processing characteristics can be easily developed via blending. One of the largest applications of blending is in the toughening of thermoplastics using elastomeric components. An excellent review of the toughening of thermoplastics is given by Kambour (3). More recent work (4-7) has shown the existence of a critical matrix-ligament-thickness in blends that controls the brittle to ductile transition in polymer blends.

The key challenge in every blending operation is achieving a prescribed morphology, in many cases that of the minor component inside a matrix of the major component. This morphology, or the spatial distribution of the two immiscible components in the mixture, is dependent on the intrinsic properties of the components and the thermal and stress histories undergone by them during processing.
Typical processing equipment used for blending has moving blades that convey and deform the material inside a heated chamber. These compounding steps are carried out in continuous processing equipment like screw extruders or batch equipment like the batch intensive mixers. All the compounding experiments described in this thesis were performed in a batch intensive mixer, illustrated schematically in Figure 1.1. It consists of a pair of

![Image of mixer](image)

Figure 1.1: A cross-section of the mixer showing the ram and pellets of a blend as they are fed into a Haake Rheomix 600 mixing bowl and compounded with a pair of roller blades.

counter-rotating blades inside a closed chamber. Material is fed in from the top using the feed chute, under a constant feeding load provided by the ram. A thermocouple makes contact with the batch and records the batch temperature. The drive shaft of the motor is instrumented to measure the torque required to maintain a set rpm of the blades.
Batch mixers provide a convenient means to study the processing behavior of polymer blends using small quantities of material. The flow-field due to two counter-rotating blades in the mixer provides a good approximation to that experienced in a twin screw extruder. The process variables that can be controlled in the batch mixer are the mixing temperature, addition protocol of the blend components and the blade speed. These in turn determine the heating and deformation of the batch and thus the blend morphology at any mixing time. There are two primary modes of energy input to the batch: dissipation in the batch due to deformation (e.g. frictional heating of solid particles or viscous dissipation in the melt) and heat conduction from the walls of the mixing bowl. In a typical compounding run, solid pellets or powder of the two components to be blended are dry mixed and fed into the mixer under a constant load. The mixer is usually preheated to the compounding temperature and the blades are set to rotate at a constant r.p.m. throughout the compounding run.

1.2 Morphological Regimes During Compounding

Based on the material behavior three broad regimes can be identified during compounding of polymer blends. These are:

1. Solids Conveying and Deformation Regime

2. Melting or Softening Regime, and

3. Melt Mixing Regime

Solids conveying corresponds to the very initial stages of compounding, immediately after the batch is fed into the mixer. The blend components, pellets or powder at room temperature, are compacted by the feeding ram and conveyed inside the heated mixing bowl. The shear and compressive forces in the mixing bowl deform the pellets and energy dissipation due to inter-particle friction, friction between the pellets and mixer walls along with heat conduction results in an increase in the temperature of the pellets. The size of the blend components is reduced from the initial feed particle size through abrasion from particle surfaces. Simultaneous energy dissipation due to plastic deformation and contact with the hot mixer walls results in the formation of a melt film which wets the distributed
solids in the batch. Recently, an attempt has been made to quantify frictional energy dissipation and plastic energy dissipation due to bulk deformation of the solid (8).

On formation of a sufficient amount of melt, viscous dissipation in the melt becomes the dominant mode of heating of the unmolten solids in the batch and governs further morphology development. This mode of melting, involving stress and heat transfer to distributed unmolten regions by a viscous melt has been termed dissipative mix-melting (9). The heat for melting is provided primarily by converting the mechanical energy of the rotating blades into dissipation due to deformation in the liquid and solid phases. This is the primary mode of melting in compounding runs with batch mixers and twin-screw extruders.

On complete melting of the two components, further changes in the morphology are governed by a balance of hydrodynamic forces tending to break up the dispersed domains and restoring forces due to interfacial tension and elasticity of the dispersed phase. This fluid flow regime has been the focus of almost all prior work on mixing and dispersion in polymeric formulations. Detailed reviews of the developments in the understanding of dispersive forces in the fluid flow regime were presented by Rallison (10, 11) and Bentley and Leal (12). However, recent work in the area of mixing in immiscible polymer/polymer blends has conclusively demonstrated that the majority of the domain size reduction occurs in the melting regime of the process. These results highlight a serious gap in our understanding of morphology development during polymer compounding.

Scott and Macosko (13) reported model experiments on amorphous blends which probed the initial stages of mixing. They identified a two-orders of magnitude decrease in the domain size of the dispersed phase from the initial 3mm pellets during the melting regime in the compounding of polystyrene/nylon blends. They proposed the formation of sheets and a lace-like structure from the softening pellets to explain the observed morphologies. A schematic of this mode of morphology evolution, the “sheeting mechanism”, is presented in Figure 1.2. Recent work by other researchers in the field has confirmed that the melting/softening regime is critical to morphology development during compounding (14-17). This thesis addresses morphology development in this regime and
Figure 1.2: A schematic of the sheeting mechanism proposed in (13) to explain the rapid decrease in the domain size during initial stages of melting in polymer compounding.

seeks to quantify material and process conditions under which a prolonged melting regime is observed.

1.3 Phase Inversion During Compounding

Blend morphology in the melting regime during compounding depends on the melting rates and rheologies of the blend components. Due to differences in the melting order of the blend components, the intermediate morphologies observed can be very different from the steady state morphology of a two-phase viscoelastic melt. An interesting intermediate morphology that could be formed is that of a continuous phase of the minor component surrounding the unmolten domains of the major component. During compounding of a glassy component with rubbers, Shih (18, 19) found that because the rubbery component softened first during processing, it initially becomes the continuous phase despite being present as the minor component in the blend. After the softening temperature of the glassy (major) component was reached, a phase inversion occurred so that the glassy polymer became the continuous phase with the rubber dispersed inside it. This sequence of morphological changes is illustrated in Figure 1.3.
Despite the established importance of the melting regime and the interesting morphological structures associated with it, very limited work has been done on quantifying the effect of material and process conditions on the duration of this regime. In our investigation, we define phase inversion during compounding as the transformation in blend morphology from that of component A dispersed in component B to that of component B dispersed in component A as a function of processing time. The goal of this thesis is to identify and quantify factors that influence the occurrence of phase inversion during compounding. The effect of material properties, like the solid state modulus and the melt viscosity of the two components is systematically studied. A time to phase inversion is defined and the effect of varying blend composition, mixing conditions (mixer temperature, initial particle size of the components, shear-rate in the mixer) is investigated.

1.4 Overview of the Thesis

Phase inversion during the compounding of blends with a high-melting point low-viscosity minor component is studied in Chapter 2. A model polycaprolactone /
polyethylene (PCL/PE) blend is used to investigate morphology development. Morphological analysis revealed that a low-modulus in the solid state and a low melt viscosity forced the formation of a continuous phase of polyethylene at short mixing times followed by phase inversion. Blends with a higher viscosity polyethylene did not show phase inversion during compounding.

The effect of viscosity ratio of the blend on the occurrence of phase inversion during compounding is systematically studied in Chapter 3. Different blend systems were chosen based on the relative transition temperatures of the two components and the melt viscosity ratios \( \lambda = \eta_{\text{minor}} / \eta_{\text{major}} \) at representative process conditions. A framework based on these two factors is presented to delineate the blends that exhibit phase inversion during compounding. It was found that for blends with a viscosity ratio less than 0.2 an initial continuous phase of the minor component was formed during compounding runs at a constant mixer temperature. Using a ramped temperature program on the mixer resulted in the low-melting component forming the continuous phase initially. In blends exhibiting phase inversion quantitative measures of the minor component present as the continuous phase at different mixing times prior to phase inversion were determined using selective dissolution.

For very low-viscosity ratio systems (\( \lambda \sim 0.001 \)) the effect of batch size on the time to phase inversion is studied in Chapter 4. Similar morphological changes were observed during compounding of polystyrene/polyethylene blends at different batch sizes from 12g to 240g. Based on visual observation of the morphological changes, a constant nominal-maximum-shear-rate scaleup condition was used. Upon a five-fold increase in the batch size, the time to phase inversion is shown to increase by a factor of 3. This change is explained using a combination of reduced specific area and hence heat conduction to the batch and a reduced mechanical energy input under the experimental conditions. A novel modular blade system was designed for use with batch mixers. The design features were exploited to study radial and axial scaleup behavior of low-viscosity ratio blends.

Chapter 5 presents the results from visualization of the deformation of a major component in a low-viscosity minor component during compounding. Based on the
observed morphologies a microscopic model for phase inversion is developed. An explicit expression for the time to phase inversion is derived from the model. Model predictions on the effect of shear-rate, volume fraction of the minor component, viscosity ratio and blade design are shown to agree very well with experimental results mentioned in Chapters 3 and 4.
2. PHASE INVERSION DURING COMPOUNDING WITH A LOW-MELTING MAJOR COMPONENT

2.1 Background

Blending of two or more polymeric materials is widely used to achieve property enhancements more economically than synthesizing a new material. Most of these blends are prepared in large compounding equipment where blending occurs by the use of heat transfer and simultaneous deformation of the components (9). The typical addition protocol for blending using an extruder involves feeding of a mixture of pellets into a conveying section. Further downstream at the kneading block section, most of the melting occurs due to the large stresses imposed on the softening pellets. The sequence of processes undergone by a single component in an extruder from the solids conveying to melting to the fluid flow regime has been well documented (18). Four different regimes have been used to characterize this progression in the compounding of immiscible blends (18):

1. Elastic pellets
2. Deformable pellets
3. Transition material
4. Viscoelastic fluid

These rheologically different regimes are expected in any processing operation starting with solid pellets and ending with a melt. During the compounding of a blend, each component needs to make the transition from a solid pellet to a melt. The presence of a material with different rheological and thermal behavior brings about differences in the melting rates of the components thus leading to a variety of morphologies during compounding of immiscible blends.

The morphology at long mixing times for immiscible polymer blends has been studied extensively (20-24). The size and shape of the minor component is known to affect the mechanical properties of the final blend. For example, Wu (25) has reported a sharp brittle
to ductile transition at a critical particle size and interparticle spacing in rubber toughened nylon blends, when the rubber volume fraction was kept constant. In order to achieve the required final morphology we need to understand the mechanisms of size reduction in polymer compounding.

Investigations of blend morphology at different mixing times has shown that most of the size reduction occurs very early in compounding. These studies have focused the interest of researchers on the melting/softening stage during compounding. Favis (26) reported that very little reduction of phase size occurred after the first 2 minutes of mixing in the compounding of different viscosity ratio polypropylene/polycarbonate blends. Plochocki et al. (27) found that the dispersed phase domain size went through a minimum with increasing mixing energy, indicating that the dispersed phase size does not decrease monotonically with mixing time. Scott and Macosko (13) used selective dissolution studies on early mixing time samples to characterize the morphology of polystyrene/nylon blends. They found that deformation of the nylon proceeded through a “sheeting mechanism”. Similar behavior was observed during compounding in a twin screw extruder (16). Lindt and Ghosh (17) reported the formation of fine lamellar structures by the melting pellets which were then broken up by capillary forces resulting in a reduction of the scale of segregation in the multicomponent blend by a couple of orders of magnitude in a short time.

In spite of the accumulated data on the qualitative behavior of blend systems during the melting/softening regime, there are fundamental questions that still need to be answered. How is the melting of one component affected by the presence of another low melting component? What is the role of rheology of the components in determining their melting rates in a typical compounding operation? Is it possible to predict the morphology evolution during the entire course of a compounding operation with a knowledge of the rheological, thermal properties of the components and the process conditions?

Recent work has begun to address some of these questions. One morphology that is of great practical interest is the formation of the continuous phase by the minor component (< 50 wt.%) in the blend. Shih (18,19,28) and Sundararaj et al. (29) have worked
extensively with systems with a low melting minor component in the blend. It was found that in a compounding run where the temperature was ramped steadily from below the melting point of the minor component, the initial morphology showed that the minor component was the continuous phase. The minor component melted first and covered the pellets of the major component. As the temperature was increased close to the major component melting point, the major component pellets began to get deformed. This was shown to correspond to an increase in the torque required to deform the sample at constant rotor speed. Following deformation, the concentration of the major component in the continuous phase steadily increased until an inversion in the phase continuity was observed, with the major component becoming the continuous phase. This change in morphology as a function of mixing time was termed “inversion of phase continuity” (29) or simply “phase inversion”. Figure 2.1 shows a schematic of this behavior during compounding. This phenomenon was first reported by Shih (19) during the compounding of a polyarylate resin with an ethylene/acrylate rubber as the minor component. Sundararaj et al. (29) reported phase inversion in the compounding of nylon/polystyrene, polystyrene/ethylene-propylene (major/minor component) blends. In each of the above blends the minor component had a much lower melting/softening temperature than the major component. Further, the inversion in phase continuity was clearly seen when a ramped temperature profile starting below the melting point of the minor component was used. Scott and Joung (30) reported on the effect of viscosity ratio on morphology at early mixing times in polystyrene/polyethylene blends. The transition temperatures for both components was close to 100°C. But the polystyrene underwent a glass transition, whereas the polyethylene underwent a melting transition. In the low viscosity ratio blends, polyethylene formed the continuous phase initially. Longer mixing times (>3 min) were required for the polystyrene to form the continuous phase. The time to phase inversion was shown to increase with decreasing viscosity of the minor polyethylene component.
Figure 2.1: Schematic representation of phase inversion during compounding. At short mixing times the minor component is continuous; with continued mixing phase inversion occurs and the major component forms the continuous phase.

This phenomenon has to be distinguished from the existing literature on phase inversion in immiscible liquid/liquid systems, where the progressive addition of one liquid to another enables it to form the continuous phase at a particular volume fraction (31, 32,33). The studies on emulsions of oil and water are an example of such a phase inversion. It was proposed that a "catastrophic inversion" (31) occurred when a close packed arrangement of dispersed phase droplets coalesced, trapping the continuous phase between them. As both phases were liquid; the agitator speed, the relative viscosities and the presence of surfactants was shown to determine the volume fraction at which this inversion occurred. In contrast, phase inversion during compounding may occur even if the final morphology has the minor component as the dispersed phase. While the final morphology may be determined by relative viscosities of the two phases and their volume fractions (34), the morphology at early mixing times is more complex. Differences in transition temperatures and rheology of individual component close to their transition temperature is expected to critically influence the progression to the final morphology.

In this chapter, we discuss the compounding of immiscible blends with a high-melting minor component. The viscosity ratio, defined to be the ratio of the minor component to major component viscosity at a representative shear rate and temperature, is varied by choosing different molecular weight samples of the components. Our goal is to identify whether or not phase inversion occurs in systems with a high-melting minor component and how the process conditions affect the morphology evolution.
2.2 Experimental Procedure

2.2.1 Materials

Polycaprolactones (PCL) from Union Carbide with melting points of 64°C were chosen as the major component. The minor component was one of two polyethylenes (PE) from Eastman Chemical with a melting point close to 100°C. Two different molecular weights of each component were used. The designations of the components and their nomenclature have been specified in Table 2.1. The higher molecular weight samples have been labeled ‘A’ (PCL-A and PE-A). Thus four PCL/PE blends of different viscosity ratios were studied. In all the experiments described in this chapter, PE formed 10% by weight of the blend. The thermal properties of the blend components were determined by a differential scanning calorimetry (DSC) trace. A Perkin-Elmer DSC-7 was used at a scanning rate of 10°C/min. The DSC traces are shown in Figure 2.2.

2.2.2 Rheological Measurements

The rheological behavior at small strains of individual blend components was measured using a Rheometrics ARES mechanical spectrometer. These measurements were made from room temperature to the processing temperatures used in the compounding runs. At room temperature all the components are solid. Rectangular coupons approximately 10mm x 12mm x 1.7mm (LxWxH) were made in a compression mold. These were used with a torsion rectangular fixture in the ARES rheometer to measure the complex shear

<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial Designation</th>
<th>Melt Index at 190°C (g/10min)</th>
<th>Tm(°C) (from DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL-A</td>
<td>Tone P787&lt;sup&gt;1&lt;/sup&gt;</td>
<td>4</td>
<td>64</td>
</tr>
<tr>
<td>PCL-B</td>
<td>Tone P767e&lt;sup&gt;1&lt;/sup&gt;</td>
<td>30</td>
<td>64</td>
</tr>
<tr>
<td>PE-A</td>
<td>Epolene C-14&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.6</td>
<td>98</td>
</tr>
<tr>
<td>PE-D</td>
<td>Epolene C-10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>2250</td>
<td>101</td>
</tr>
</tbody>
</table>

<sup>1</sup> Union Carbide Chemical and Plastics Company Inc.

<sup>2</sup> Eastman Chemical Company
modulus and viscosity as a function of temperature and frequency. In the melt state the samples were melt pressed into 25mm disks approximately 2.5mm in thickness. These were then used with a parallel plate fixture in the rheometer and their complex modulus and hence viscosity was measured. Both these sets of measurements were made at low strains to ensure a linear viscoelastic response of the material. With the solid torsion samples the measurement limit was reached when the rectangular coupon became soft and began to flow close to its melting point. When the parallel plate fixtures were used with the melt, very large torque values were needed to deform the disk just above its nominal melting peak as seen in a DSC trace.

### 2.2.3 Compounding Runs

All the compounding runs were performed in a Haake Rheomix 600 batch intensive mixer. In this batch mixer a pair of roller blades are used to transfer mechanical energy to the blend inside a closed, heated metal chamber. The torque required to drive the blades and the temperature of the melt inside the chamber can be measured as a function of mixing time. In all the experiments discussed here the rotor speed was kept constant at 50
r.p.m. Experiments showed that a batch size of 55g resulted in an appropriate volume of material to achieve uniform mixing within the chamber. Before each blending run, solid pellets of both the components were dried at 50°C under vacuum for 36hrs. A mixture of the pellets in the right proportion by weight was then dry blended in a tray. This mixture of dried pellets was fed into a hot mixer under a constant force of 5kg.

2.2.4 Blend Morphology Characterization

To sample the morphology at any mixing time for a particular blend, the rotor blades were stopped and the mixing bowl was opened. A small sample was quickly collected and immediately quenched in liquid nitrogen to freeze the morphology. Methylene chloride was used as a selective solvent to identify the continuous phase. PCL was found to dissolve in methylene chloride while the PE phase was unaffected. Rectangular pieces were cut from the quenched samples. They were then immersed in excess methylene chloride and left undisturbed overnight. If after this exposure to methylene chloride the sample retained its original shape with just a small shrinkage in size, it was concluded that PE was the continuous phase in that sample. If PCL was continuous, most of the sample dissolved and on evaporating the solvent, it formed a thin coating on the walls of the container. The samples that showed an initial PE continuous phase, were examined further in an electron microscope. Fracture surfaces of the blend samples were exposed to a 2% solution of phosphotungstic acid (PTA) for 4 hrs. PTA reacts with surface functional groups as a positive stain and is not expected to directly stain polyolefins (35). These stained samples were then imaged in an ElectroScan Environmental Scanning Microscope ESEM E-3, under both secondary and backscattered electron imaging modes. For comparison, pure PCL and PE surfaces were also imaged after a similar exposure to PTA. At a beam voltage of 25kV, PCL showed significant beam damage on slow scans at high magnifications. Presence of the stain and beam damage of the surface were both used to mark the presence of PCL on the sample surface.

Experiments were designed to investigate the effect of viscosity ratio, mixer set temperature and the use of a ramped temperature program on the continuous phase at different mixing times in each of the four PCL/PE blends.
2.3 Results

Results from differential scanning calorimetry (DSC) of the blend components are shown in Figure 2.2. Although the peak melting temperatures for both the PE s are close to 100°C, PE-D shows a broad peak indicative of a large softening range (Figure 2.2). This was further confirmed by rheological measurements described below. Both the PCLs showed a sharp peak close to 64°C.

Small strain rheology in the linear viscoelastic region was measured at different frequencies and from room temperature to the process temperature for each of the blend components. The magnitude of the complex viscosity measured at 100 rad/s is shown in Figure 2.3, for the four individual components. According to the Cox-Merz rule (36), this is equivalent to the shear viscosity at 100 s⁻¹. This value of shear rate is comparable to that estimated during compounding on the basis of drag flow at the smallest gap between the roller blades and the mixer walls. The discontinuities in the curve represent the change in the measuring mode. The measurements to the left of the break are measurements made on the solid rectangular coupons under torsion. The measurements to the right of the discontinuity are melt measurements on circular disks in a parallel plate fixture. All the curves show the drop of a couple of orders of magnitude in the complex viscosity associated with the melting of the solid polymer. The PCLs show a sharp drop over a small temperature range. The viscosity curves for the PE s show a gradual drop beginning about 20°C below their nominal melting points. In the melt state the viscosities of the PCLs were comparable with that of the PE-A. The viscosity of PE-D, is lower by a couple of orders of magnitude. In addition, the softening of PE-D occurs about 15°C earlier than that of PE-A. The viscosity of the lower molecular weight PE-D was too low to be measured beyond 140°C.
Figure 2.3: Magnitude of complex viscosity under shear measured at $100\text{s}^{-1}$ using a parallel disk fixture in the melt and a torsion fixture in the solid state.

### 2.3.1 Compounding at Constant Mixer Temperature

For the first set of runs the mixer was preheated to $140^\circ\text{C}$. Four different blends each having PE as the minor component (10 wt.%) were investigated. Figure 2.4 shows the torque trace for a typical blending run. The solid pellets are fed under a constant force into a hot mixer with the rotor blades set to rotate at 50 r.p.m. As material is fed into the mixing chamber the torque required to maintain the rotor speed increases. The pellets are softened when they come into contact with the hot mixer walls and this leads to a subsequent reduction in torque. This feed torque peak is typical of such an addition protocol for the compounding of polymers in a batch intensive mixer.

The behavior of the torque traces after the first feed torque peak is qualitatively different for the blends with the low viscosity PE-D component. As shown in Figure 2.5, there is a dip in the torque trace followed by a second peak. This second peak is more
pronounced in the PCL-A/PE-D blend. The torque values at long mixing times (~ 10 min) reach a steady value which is indicative of the viscosity of the two phase viscoelastic melt.

Samples were taken at 45s into mixing, in each of the PCL/PE blends. It was found that PE was the continuous phase in the PCL/PE-D blends, whereas PCL was continuous in the PCL/PE-A blends. Similar samples collected at long mixing times (~6 min) into mixing showed that PCL was the continuous phase in all the blends. Hence there was an inversion in the continuous phase as a function of compounding time in PCL/PE-D blends.

An early mixing time sample from PCL-A/PE-D runs was stained with PTA and imaged using an electron microscope as described in the experimental section. The sample was collected from the high shear region in the mixer, corresponding to the smallest gap between the blades and the mixing bowl. The stained surface of this sample showed a continuous film of PE. Thus a film of PE formed over the still melting pellets of PCL in the high shear regions, leading to the observed low torque values at short mixing times in

![Graph showing torque vs time for PCL/PE-A blends](image)

**Figure 2.4:** Mixer torque as a function of time for PCL/PE-A (90/10) blends compounded at 140°C. PCL was the continuous phase at 45s as well as at long times.
Figure 2.5: Mixer torque as a function of time for PCL/PE-D (90/10) blends compounded at 140°C. PE was the continuous phase at 45s and PCL was continuous at 6 minutes.

PCL-A/PE-D blends.

2.3.2 Effect of Mixer Temperature on Phase Inversion

This phase inversion was investigated further in PCL/PE-D blends by changing the temperature program during compounding. In one set of experiments, a constant mixer temperature, different from 140°C (used in the runs above) was used. The results of compounding runs on the PCL-A/PE-D blends under different mixer set temperatures are shown in Figure 2.6. The steady torques at long mixing times increase with decreasing mixer temperature due to the increasing viscosity of the melts at lower temperatures. In each of these runs, a low torque value immediately following the feed torque was observed. Samples taken at this time into mixing, indicated that PE was the continuous phase. Samples collected after 10 minutes of mixing had spheres of polyethylene about 10μm in diameter inside a polycaprolactone matrix. Hence the second torque peaks
Figure 2.6: Mixer torques as a function of time for different mixer set temperatures for PCL-A/PE-D blend, with 10 wt.% PE-D. Samples were collected at torque minimum immediately after feed torque peak and indicated a continuous PE phase.

observed in the compounding runs in Figure 2.6 correspond to progressive deformation of the higher viscosity PCL, resulting in a continuous phase of PCL. The torque trace for the run at 100°C shows the increased difficulty in feeding the material at low temperatures.

2.3.3 Compounding with Ramped Mixer Temperature

The second set of experiments imposed a ramped temperature program to the mixing bowl. A steady ramping rate heated the mixer blocks from 30°C to 55°C at 5°C/min. The temperature was then maintained at 55°C for 5 minutes and then ramped up to 140°C at the same rate. The torque and temperature traces for PCL-A/PE-D under this temperature ramping program are shown in Figure 2.7. Feeding of the complete batch of pellets was completed only at about 3 minutes after the beginning of the run. A sample collected at 3.5 minutes showed PCL to be the continuous phase. Thus PE did not form a continuous phase at early times after completion of feeding in these ramped temperature runs. The
melt temperature as measured by a thermocouple in contact with the melt inside the mixing chamber shows that due to frictional heating, the blend temperature reaches the melting point of PCL (64°C) even when the mixer walls are held at a constant 55°C.

![Graph showing torque and temperature as functions of time.](image)

Figure 2.7: Torque and temperature as a function of time for ramped temperature runs with PCL-A/PE-D blends with 10 wt.% PE-D.

2.3.4 Compounding in a Cold Mixer

The effect of solid-solid frictional heating was investigated using single component runs in a cold mixer. The mixer walls were kept at 30°C. Four different mixer runs were performed. For each run, 35g of a single component was fed into the cold mixer and the torque and temperature traces were recorded as a function of time. The torque curves are shown in Figure 2.8 and Figure 2.9. The pellets of PCL were approximately spherical in shape with a diameter of about 3mm. PE-A pellets were slightly bigger (~4mm) while PE-D pellets were cylindrical with a height of 3mm and a diameter of 2mm. All these dimensions are bigger than the smallest gap between the roller blades and the mixer walls (1.42mm). There was an initial torque peak as soon as feeding was started in the PE runs
(Figure 2.8). The temperature rose quickly and reached a steady value of 76°C and 40°C for PE-A and PE-D respectively, at 10 minutes. In either case, at 10min, all the polyethylene was ground into a powder. In contrast, it was found that the PCL runs had to be carried out to longer times to see any qualitative changes in the torque trace. As seen from Figure 2.9 a rise in torque was seen at 4.5min with PCL-B and at 10.5min with PCL-A. A sharp rise in temperature coincided with the torque rise. The sample inside the mixer at 20 minutes was found to be a single fused mass of polymer. The thermocouple in contact with the polymer measured 69°C and 56°C at 10 minutes for PCL-A and PCL-B respectively.

Figure 2.8: Mixer torque as a function of time for PE runs at a mixer temperature of 30°C.
Figure 2.9: Mixer torque as a function of time for PCL runs at a mixer temperature of 30°C.

2.4 Discussion

The most surprising finding from early morphology studies reported here, is the formation of the continuous phase by PE in PCL/PE-D blends. PE has a higher melting point than the PCL as seen from the DSC trace (Figure 2.2). This system is the first reported instance of a high melting minor component forming the continuous phase during a compounding run (37). Earlier observations have shown that the presence of a low melting minor component could result in an inversion in phase continuity with compounding time (19, 28, 29). Most previous work with blends showing phase inversion relied on temperature ramping to study morphology before and after phase inversion. Initial low temperatures forced the melting of the low melting point minor component leading to a continuous phase of the minor component. As the temperature was increased above the major component melting point a phase inversion occurred. In addition, Scott and Joung (30) reported phase inversion in blends even when a constant mixer
temperature was used throughout the compounding run. The formation of the continuous phase by the polyethylene was aided by its low melt viscosity and the fact that polystyrene had to go through a glass to rubber transition to form a viscous melt.

In our studies both components are semi-crystalline and undergo melting transitions. Both show nearly three orders of magnitude drop in complex viscosity due to melting. But PE-D shows the drop in viscosity at a much lower temperature (~85°C, Figure 2.3) than the higher molecular weight PE-A. This temperature is also lower than the melting peak calculated from the DSC trace. For understanding the rheological behavior during compounding, this softening temperature is a better characteristic of the material than the DSC peak. In addition PE-D pellets are also the softest in the solid state. A comparison of the G' values is given Table 2.2. Plochocki and coworkers (27) have suggested that the abrasion of the pellets at early mixing times could lead to more stretching and breaking away of the lower elasticity pellets. They suggest that that the elasticity ratio might be more relevant at early dispersion times, to characterize the morphology. Due to a lower modulus, it is easier for the PE-D pellets to get stretched when subjected to shear at pellet-pellet, and pellet-mixer wall contacts. In addition, due to heat transfer from the walls, melting of the pellets occurs simultaneously. The PE-D pellets on shearing and melting form a very low viscosity liquid. It is known that low viscosity liquids tend to encapsulate higher viscosity components and to segregate to the high shear regions (38, 39). This has also been shown to occur during processing with a low viscosity component

<table>
<thead>
<tr>
<th>Component</th>
<th>Viscosity (Pa-s)</th>
<th>G' (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL-A</td>
<td>3060</td>
<td>160</td>
</tr>
<tr>
<td>PCL-B</td>
<td>623</td>
<td>217</td>
</tr>
<tr>
<td>PE-A</td>
<td>1050</td>
<td>108</td>
</tr>
<tr>
<td>PE-D</td>
<td>12</td>
<td>29</td>
</tr>
</tbody>
</table>
in a polymer blend (30). The preferential shearing of PE-D pellets in the solid state enables them to melt completely before all the PCL has melted, and hence form the continuous phase at early mixing times. PE-A pellets, on the other hand, require much larger forces for deformation. This is evident from their larger moduli and the torque values from the cold mixer runs (Figure 2.8). A low modulus in the solid state is required for effective grinding of the minor component pellets, thereby increasing their surface area. This increases the probability of these pellets coming in contact with the hot regions in the mixer. At the onset of melting, a low melt viscosity favors flow of the melt and the attendant coalescence and encapsulation of the still melting major component pellets results in a continuous phase of the minor component. As shown in this study, this can happen even if the minor component has a higher melting point. If melting proceeds without significant grinding or stretching in the solid state, the low melting component is expected to form the continuous phase first. This is the likely reason for the absence of phase inversion in PCL/PE-A blends. The cold mixer runs help decouple the effects of deformation in the solid state from that in the melt. In the run with the polyethylenes the final temperature is well below their melting points and the hence deformation of the pellets results in a powdery mass. But the frictional heating due to deformation of the polycaprolactones causes the temperature to reach their (lower) melting points and hence a fused mass of polymer is obtained at the end of the run.

Table 2.3. Viscosity and elasticity ratios for the different blends.

<table>
<thead>
<tr>
<th>Major/Minor Component</th>
<th>Viscosity Ratio</th>
<th>Elasticity Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_{\text{minor}} / \eta_{\text{major}}$</td>
<td>$G'<em>{\text{minor}} / G'</em>{\text{major}}$</td>
</tr>
<tr>
<td>PCL-A/PE-A</td>
<td>0.34</td>
<td>0.67</td>
</tr>
<tr>
<td>PCL-B/PE-A</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>PCL-A/PE-D</td>
<td>0.004</td>
<td>0.18</td>
</tr>
<tr>
<td>PCL-B/PE-D</td>
<td>0.02</td>
<td>0.13</td>
</tr>
</tbody>
</table>
At early mixing times the pellets of both components in the blend undergo large deformations and are simultaneously melting inside a hot mixer. After a given mixing time, the component with a larger molten fraction will form the continuous phase provided there is enough of it to form a continuous network through the blend. For a hexagonal closed packed arrangement of monodisperse spheres the maximum packing volume fraction is 0.74. But with a distribution of spheres of different radii, closer packing can be achieved (2), hence reducing the minimum volume fraction required by a component to form a continuous network in the blend. At a fixed concentration, the minor component will form the continuous phase initially if a large fraction of it melts before the melting of the major component. This is aided by having a low-melting minor component. But in our studies with PCL/PE-D blends, we have seen that even in the presence of a high-melting-point minor component, a suitable combination of low modulus in the solid state and a very low melt viscosity might bring about a continuous phase of the minor component. In each of the runs the long time morphology was one of dispersed PE particles inside PCL. This phase inversion in PCL/PE-D blends occurred with a corresponding rise in torque due to the deforming pellets of PCL, as seen from Figure 2.5 and Figure 2.6. Decreasing the mixer set temperature decreases the rate of melting of the components during the blending run. Phase inversion was seen to occur even when the melting rate was thus decreased, for the PCL-A/PE-D blend (Figure 2.6). The qualitative nature of the torque curves did not change, although at lower temperatures, longer times were required for the feeding torque peak and the second torque peak associated with phase inversion. Each of these curves shows an initial low torque value corresponding to the low viscosity PE component being the continuous phase. With further mixing the higher viscosity PCL component is deformed to form the continuous phase. This deformation of the higher viscosity component results in the second torque peaks seen in Figure 2.6. It was found necessary to hold the temperature below the melting point of PE to prevent it from forming the continuous phase. This is evident from the temperature ramping run in Figure 2.7, where the low melting PCL component formed the continuous phase after completion of feeding. This result is consistent with observations of Sundararaj and coworkers (29), where temperature ramping resulted in a continuous phase of the low melting component.
Scott and Joung (30) reported a viscosity ratio of about 0.1, below which a qualitative difference in torque traces was observed corresponding to phase inversion. The viscosity ratios of the PCL/PE-A blends (Table 2.3) are above this value. In these blends, samples collected at 45s had a continuous PCL phase. It is unlikely that the PE formed a continuous phase before 45s into mixing. The higher modulus and hence higher deformation energies required to stretch PE-A pellets (Figure 2.8), along with the higher softening temperature of 100°C from Figure 2.3, partially justify this conclusion.

For blends whose components have similar melt rheologies and melting/softening points, empirical relations have been proposed to determine the minimum volume fraction of a component required to form a continuous phase. Melt viscosity ratios (34, 40, 41) or torque ratios (42) have been used to predict the volume fraction at which there is a change in the continuous phase from one component to the other. These criteria are applicable for long mixing time samples where a steady temperature distribution exists in the blend. But these have been shown to be unsatisfactory in predicting the point of phase inversion as it occurs during compounding (30, 43). The melt viscosity ratio at 140°C and 100s⁻¹ for the blends studied in this work are given in Table 2.3. Application of the following relation (34):

\[
\frac{\phi_{PE}}{\phi_{PCL}} = \frac{\eta_{PE}}{\eta_{PCL}}
\]

(2-1)

where \(\eta\) represents the viscosities and \(\phi\) the volume fractions, indicates that PE should form the continuous phase at long mixing times in PCL/PE-D blends. This is in contrast with the experimental findings, where all the blends the long mixing time samples showed the major PCL phase to be continuous. The prediction of the point of inversion is theoretically quite intractable for the complex thermal and flow histories experienced in the batch mixer. A possible approach using an isothermal simplified flow-field approximation is developed in Chapter 5.
2.5 Conclusions

We have investigated the morphology at different mixing times in the compounding of immiscible blends with a high melting minor component. It was shown that a low modulus in the solid state and a very low melt viscosity enabled the minor component to form the continuous phase at short mixing times, in PCL/PE-D blends. The softening temperatures from rheological measurements were observed to be a better indicator of processing behavior than the peak values calculated from a DSC trace. Contrary to previous understanding of the phenomenon, phase inversion was shown to occur even in blends in which the major component had a lower melting point. The occurrence of phase inversion was shown to be determined by the temperature protocol used during compounding. A slowly ramped temperature protocol prevented the high melting minor component from forming the continuous phase at early mixing times, thus preventing phase inversion during compounding.
3. VISCOSITY RATIO AND TRANSITION TEMPERATURE EFFECTS

3.1 Introduction

The physical properties of a blend of immiscible polymers are strongly dependent on the phase domain structure of the components in the blend. In blends with a small amount of one component (~10 wt.%) the final morphology is usually one of the minor component dispersed in a continuous phase of the major component. This is achieved by compounding, where the required size reduction is brought about by the simultaneous use of mechanical and thermal energy. Dissipative mix melting (9), where stress transfer to the polymer inside a closed heated chamber takes place, is the primary means of achieving this size reduction in twin-screw extruders and batch intensive mixers.

Initial work with immiscible blends has concentrated on the effects of material and process conditions on the final morphology for a given set of components. It has been shown that the melt viscosity of a component is a good measure of its tendency to form the continuous matrix phase in a blend (20-24). Lower-viscosity components tend to form the continuous phase at a much lower volume fraction than higher-viscosity ones (34). Viscous and interfacial forces have been used to explain the size and size distribution of droplets of the dispersed phase in the blend (25). Later work (13, 17, 26) has shown that most of this size-scale reduction occurs very early in the melting regime. Scott and Macosko (13) presented results of mixing in the melting regime of a polystyrene/nylon blend. They described a “sheeting mechanism” for the size-scale reduction of the nylon. Favis (26) reported that very little size reduction occurred after 2 minutes of mixing in the compounding of polypropylene/polycarbonate blends. These investigations have prompted an interest in the melting/softening regime in the compounding of immiscible blends.

The presence of a second component of different thermal and rheological properties changes the melting or softening rate of the major component. This may result in
differences in morphology evolution with mixing time. For some combinations of process and material conditions, an intermediate morphology where the minor component is present as the continuous phase encapsulating unmolten particles of the major phase, has been shown to occur (16, 18, 19, 30, 44, Chapter 2). With continued mixing and deformation of the major component, an inversion of phase continuity occurs with the major component now forming the matrix. This phenomenon has been termed “phase inversion” and was first reported by Shih et al. (18), during the compounding of a polyarylate and ethylene/acrylate (80/20) blend. Subsequent investigations (16, 44) showed the occurrence of phase inversion in blends with a lower-melting-point minor component, especially when a slowly increasing temperature program was used. The presence of a low-viscosity component was also shown to result in phase inversion in polystyrene/polyethylene blends with a viscosity ratio below 0.1 (30). The viscosity ratio was defined as the minor component to major component melt-viscosity-ratio at representative process conditions. In Chapter 2, phase inversion was shown to occur even when the minor component had a higher melting point. In our studies with polycaprolactone/polyethylene blends, we showed that a low modulus in the solid state along with a low melt viscosity result in a continuous phase of the minor component at short mixing times. These results led to the following key questions that are addressed in this chapter. Is the viscosity ratio a reliable indicator for the occurrence of phase inversion in a blend? How does the process temperature affect morphology evolution at early mixing times? Does the nature of the major component—amorphous or semicrystalline—determine the process time required for it to form the continuous phase? Is there a framework to analyze the accumulated work on phase inversion during compounding in blends with a low concentration of the minor component? What is the role of viscous dissipation in the melt on the rate of morphology evolution?

Different model systems were chosen to answer these questions. The minor component was fixed at 10 wt.% in all the blends. Compounding runs were carried out in a batch intensive mixer and continuous-phase evolution was studied as a function of mixing time. Our goal was to investigate the influence of two parameters: the relative transition temperatures of blend components, and their viscosity ratio at the process
temperature and a representative shear rate. Process conditions were varied by choosing a constant temperature or a slowly ramped temperature for the mixer.

3.2 Experiments

Blend components for the model systems were selected on the basis of their softening temperatures and their viscosities at representative process temperatures and shear rates. Polycarbonate (PC) from Miles Inc., polybutylenes (PB-A and PB-D) from Shell Oil Company, and an amorphous copolyester (PETG) from Eastman Chemical Company were used as the major component in different blends. Polyethylene (PE-A and PE-D) from Eastman Chemical Company and polycaprolactone (PCL-B) from Union Carbide Corporation were used as the minor components. The relevant commercial designations and material properties are summarized in Table 3.1. Results from the following blend systems (major/minor component) are presented here: PC/PE, PETG/PE, and PB/PCL.

Differential scanning calorimetry (DSC) was used to determine the glass transition

Table 3.1: Blend components used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial Designation</th>
<th>Viscosity Pa-s (180°C and 100s⁻¹)</th>
<th>Transition Temperature (from DSC) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-A</td>
<td>Epolene C-14 ¹</td>
<td>1100</td>
<td>98 (T_m)</td>
</tr>
<tr>
<td>PE-D</td>
<td>Epolene C-10 ¹</td>
<td>12⁸</td>
<td>100 (T_n)</td>
</tr>
<tr>
<td>PCL-B</td>
<td>Tone P 767e²</td>
<td>335</td>
<td>64 (T_m)</td>
</tr>
<tr>
<td>PC</td>
<td>Makrolon CD-2005 ³</td>
<td>7698</td>
<td>140 (T_L)</td>
</tr>
<tr>
<td>PETG</td>
<td>PETG Copolyester 6763 ¹</td>
<td>6328</td>
<td>80 (T_g)</td>
</tr>
<tr>
<td>PB-A</td>
<td>Polybutylene 0110 ⁴</td>
<td>845</td>
<td>116 (T_m)</td>
</tr>
<tr>
<td>PB-D</td>
<td>Polybutylene 0800 ⁴</td>
<td>136</td>
<td>108 (T_n)</td>
</tr>
</tbody>
</table>

⁸ measured at 140°C and 100rad/s
¹ Eastman Chemical Company
² Union Carbide Corporation
³ Miles Incorporated
⁴ Shell Oil Company
temperature of the amorphous components and the melting temperature of the semicrystalline components. A scan rate of 10°C/min was selected on a Perkin-Elmer DSC-7. The results are included in Table 3.1. Rheological measurements on the individual components were obtained from an ARES mechanical spectrometer under a dynamic strain mode. Measurements in the melt-state of the components were made using 25mm disks in a parallel-plate fixture. For solid-state measurements, rectangular coupons of the samples were deformed under torsion. Typical results are shown in Figure 3.1. Each component’s viscosity curve has two regions separated by a discontinuity close to its melting or softening temperature. Solid-state measurements under torsion are shown to the left of the discontinuity and melt measurements are shown to the right, at higher temperatures. A complete description of small-strain rheology of blend components from room temperature to the process temperature was thus obtained.

The compounding runs were carried out in a Haake Rheomix 600 batch intensive mixer. For each blend, the batch size for good intermixing between the two halves of the mixing chamber was first determined. Batch sizes of 50g for PB/PCL, 60g for PC/PE and 70g for PETG/PE blends were used. Prior to blending, the components were dried overnight at 50°C under vacuum. The dried pellets in the right proportion (10 wt.% of the minor component) were hand mixed in a tray. The batch was then added to the mixer, which had been preheated to the desired temperature, under a constant force of 5kg. The torque trace and the melt temperature were recorded as a function of mixing time. The rotor speed was kept constant at 50 r.p.m. in all the blending runs reported here.

In order to investigate the morphology, the batch mixer was stopped at a particular mixing time, and a sample was quickly collected and quenched in liquid nitrogen. One of the components was then selectively dissolved in a suitable solvent. Methylene chloride was used to dissolve the major component in PC/PE and PETG/PE blends and the minor component in PB/PCL blends; hexane was used to dissolve PE-D in PC/PE-D blends. The dissolution was carried out in excess solvent in a beaker left undisturbed overnight. A Soxhlet extraction apparatus (13) was used to determine the weight loss of the sample on dissolution. This gave a quantitative value for the amount of the soluble component.
present in the continuous phase. The emphasis was on contrasting the early mixing time morphologies with the final morphology achieved after about 10 minutes of compounding.

3.3 Results

Results from the compounding runs and the measurement of component rheologies for each of the three different blend systems are presented in detail below. The complex viscosity of the blend components, measured at 100 rad/s is reported in Table 3.1. By the Cox-Merz rule (36), this was taken to represent the steady-shear viscosity of the blend components at 100 s⁻¹. This shear rate calculated assuming pure drag flow between the roller blades and mixing bowl walls, was taken to be representative of the maximum shear rate experienced by the polymer batch inside the mixer. The viscosity ratio, λ, was defined as the ratio of the melt viscosity of the minor component to that of the major component at the process temperature and 100 s⁻¹. The ratio of the real part of the shear modulus of the minor component to that of the major component was defined as the elasticity ratio. These values for the different blend systems are reported in Table 3.2.

3.3.1 Effect of Transition Temperature—PC/PE Blends

This system is representative of blends with a lower-melting-point minor component. The major component in these blends was polycarbonate with a Tg of 140°C. The minor component (PE) had a lower melting point (~100°C). Two different molecular weights of

<table>
<thead>
<tr>
<th>Blend (Major / Minor)</th>
<th>Viscosity Ratio, λ, at process temperature, 100s⁻¹</th>
<th>G' Ratio (minor/major) at 30°C, 100 rad/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC / PE-A</td>
<td>0.14</td>
<td>0.083</td>
</tr>
<tr>
<td>PC / PE-D</td>
<td>~0.002</td>
<td>0.023</td>
</tr>
<tr>
<td>PETG / PE-A</td>
<td>0.17</td>
<td>0.081</td>
</tr>
<tr>
<td>PETG / PE-D</td>
<td>~0.001</td>
<td>0.022</td>
</tr>
<tr>
<td>PB-A / PCL - B</td>
<td>0.4</td>
<td>0.904</td>
</tr>
<tr>
<td>PB-D / PCL-B</td>
<td>2.5</td>
<td>0.868</td>
</tr>
</tbody>
</table>
PE (PE-A and PE-D) were used. The complex-viscosity measurements on these blend components are shown in Figure 3.1. The melt viscosities of the polyethylenes are lower than that of the polycarbonate. The viscosity ratio at 180\degree C and 100 s\(^{-1}\) was 0.14 and 0.002 for PC/PE-A and PC/PE-D blends, respectively. Earlier work (28, 44) has shown that phase inversion during compounding can occur when a lower-melting-point minor component is used.

The mixing torque as a function of time for compounding these blends at a constant mixer temperature of 180\degree C is shown in Figure 3.2. Only the lower-viscosity-polyethylene blend shows a pronounced low-torque region. But early mixing time samples from both blends indicated that PE was the continuous phase. After 15 minutes of mixing, PC was found to be the continuous phase in both blends. Thus, phase inversion during compounding occurred in this system of blends with a lower-melting-point minor component. Samples were collected at 3, 4, and 5 minutes into mixing in the PC/PE-D

Figure 3.1: Magnitude of complex viscosity in the melt and solid state at 100 rad/s as a function of temperature for PC, PE-A and PE-D.
blend. The PE phase was then selectively extracted using hexane in a Soxhlet apparatus. PE formed 10 wt.% of the initial mixture of pellets. The ratio of the amount of PE which is continuous to the total blend weight is represented as a percentage in Table 3.3. These sampling times straddle the second torque peak shown in Figure 3.2, and indicate the progressive incorporation of the PE into the previously dispersed PC, thus bringing about phase inversion.

![Figure 3.2](image)

Figure 3.2: Torque traces for compounding runs at 180°C for PC/PE (90/10) blends: PC/PE-A and PC/PE-D. The continuous phase at different times and the viscosity ratios are indicated.

### 3.3.2 Effect of Viscosity Ratio—PETG/PE Blends

The major component in these blends (PETG) has a lower softening temperature, as measured by DSC, but a higher viscosity than PE, the minor component. This is similar to the polycaprolactone/polyethylene blend reported in Chapter 2 but has an amorphous major component. As seen from the rheology data in Figure 3.3, the PE s show a sharp
drop in the viscosity due to melting while the glass to rubber transition of PETG occurs over a larger temperature range.

![Graph showing the magnitude of complex viscosity as a function of temperature for PETG, PE-A, and PE-D.]

Figure 3.3: Magnitude of complex viscosity in the melt and solid state at 100 rad/s as a function of temperature for PETG, PE-A, and PE-D.

The torque trace (Figure 3.4) indicated a low-torque region only with the lower-viscosity PE blend. However, dissolution with methylene chloride showed that PE was the continuous phase at early mixing times in both blends. The difference in torque traces is explained by the viscosity ratios (minor/major) in the two blends. From Table 3.2, these are 0.17 for the PETG/PE-A blend and ~0.001 for the PETG/PE-D blend. The much lower viscosity of PE-D decreases the viscous dissipation (30) and delays the softening of PETG, resulting in the low-torque values.

As an additional means to study dispersion of the minor component at early mixing times, a small amount of carbon black was premixed into the PE phase, to color it, before compounding with PETG. Samples collected at early mixing times during the
compounding of this carbon-black-filled PE with PETG provided a visual contrast between the two components. Figure 3.5 shows this contrast in samples after different mixing times. In the shortest-mixing-time sample with the PETG/PE-D blend (Figure 3.5a) collected at 30s, the individual pellets of PETG are clearly visible. The molten carbon-black-mixed PE forms a continuous phase encapsulating the clear PETG pellets. This picture provides direct evidence for the formation of the continuous phase by a component comprising 10 wt.% of the blend. In addition, due to the low viscosity of PE-D, the mixing torque corresponding to this stage in mixing has a low value (Figure 3.4). With continued mixing, individual pellets of PETG are no longer visible (Figure 3.5b) and after ~ 4 minutes of mixing, the sample visually shows a uniform dispersion of the carbon black (Figure 3.5c). In contrast, a sample collected at 41s into mixing with the PETG/PE-A blend did not show undeformed pellets of PETG (Figure 3.5d). In this blend, which has a higher-viscosity minor component, the deformation of both components proceeded simultaneously.

Table 3.3: Quantitative description of the amount of minor component that is continuous obtained by selective dissolution.

<table>
<thead>
<tr>
<th>Blend (Major/Minor Component)</th>
<th>Elapsed Mixing Time before Sampling (min : sec)</th>
<th>(wt. of minor component which is continuous / Total blend weight) X 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/PE-D</td>
<td>3 : 00</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>4 : 00</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>5 : 00</td>
<td>0.9</td>
</tr>
<tr>
<td>PB-A/PCL-B</td>
<td>0 : 30</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0 : 50</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>1 : 10</td>
<td>3.4</td>
</tr>
<tr>
<td>PB-D/PCL-B</td>
<td>0 : 25</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>0 : 40</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>0 : 55</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Figure 3.4: Torque traces for compounding runs at 180°C for PETG/PE (90/10) blends. The continuous phase at different times and the viscosity ratios are indicated.

Figure 3.5(a)
Figure 3.5: Photographs of samples with PETG/PE compounding runs at 180°C. Carbon black was premixed into PE. Torque curves are shown in Figure 3.4. (5a) 30s sample from PETG/PE-D blend; (5b) 1min 15s sample from PETG/PE-D blend; (5c) 3min 45s sample from PETG/PE-D blend; (5d) 41s sample from PETG/PE-A blend. The small tick marks are 1mm apart.

Figure 3.6: Magnitude of complex viscosity in the melt and solid state at 100 rad/s as a function of temperature for PB-A, PB-D and PCL-B.
3.3.3 Effect of Temperature Program—PB/PCL Blends

In addition to the components' transition temperatures and rheologies, the process temperature history is an important factor affecting morphology evolution. We studied the effect of two different temperature programs on the compounding behavior of PB/PCL-B blends. In these blends, the major component (PB) has a higher melting point, but the viscosity ratios are also higher: 0.4 for PB-A/PCL-B and 2.5 for PB-D/PCL-B blends. The temperature dependence of the complex viscosity of these components is shown in Figure 3.6.

![Figure 3.6](image)

Figure 3.6: Temperature dependence of the complex viscosity of PB components.

The first temperature program used a constant mixer temperature of 180°C during compounding. The torque traces for these runs are shown in Figure 3.7. Unlike the traces shown
above with PE-D, there is no low-torque region preceding a second torque peak for these runs. Samples were collected at 30, 50 and 70s into mixing for PB-A/PCL-B; and at 25, 40 and 55s into mixing for PB-D/PCL-B blends. Small cubes cut from these samples were exposed to excess methylene chloride to dissolve away the PCL. The Soxhlet apparatus was also used to determine the weight loss of each sample when exposed to methylene chloride. Methylene chloride has no effect on polybutylene; thus the weight loss corresponds to the amount of PCL which is continuous. The ratio of this weight loss to the total blend weight is reported in Table 3.3 for different-mixing-time samples. These results indicate that in the earliest sample, almost all the PCL was continuous. After extraction of PCL, the samples remained as a single fused mass, indicating that PB had begun to melt and fuse even at such short mixing times. These results show that both components melt at similar rates, leading to an initially co-continuous morphology.

![Graph: Torque and melt temperature traces for compounding with a ramped temperature program for PB-A/PCL-B(90/10) blend. The continuous phase at different sampling times is indicated.](image)

Figure 3.8: Torque and melt temperature traces for compounding with a ramped temperature program for PB-A/PCL-B(90/10) blend. The continuous phase at different sampling times is indicated.

A second temperature program heated the mixer from 60°C to 180°C at a constant rate of 5°C/min. Multiple runs were performed with this temperature program and the blend was sampled at 2, 3, and 6 minutes into mixing. The melt temperature was 90°C, 95°C, and 113°C respectively,
as measured by the melt thermocouple. The torque trace in Figure 3.8 shows a second peak at about 4 minutes into mixing. The 2- and 3-minute samples, on exposure to methylene chloride and dissolution of PCL, revealed individual deformed pellets of PB. Hence, the molten continuous phase at these early mixing times was PCL. In contrast, the 6-minute sample remained a fused mass even after exposure to methylene chloride, indicating that melting and fusion of PB had begun.

3.4 Discussion

When two immiscible polymers are compounded in a batch mixer, morphology evolution is controlled by the process conditions and their interaction with component rheologies. At a constant weight fraction of the minor component and a constant mixer temperature, the melting/softening temperatures of the components and their rheology in the solid and melt states are expected to govern the observed processing behavior. We have focused our attention on the amount of the minor component which is continuous at different mixing times to characterize the processing behavior.

The results from the PC/PE, PETG/PE, and PB/PCL-B blends can be analyzed in a twodimensional framework as outlined in Table 3.4. As seen from the above experiments, the melt viscosity is an important factor affecting the processing behavior. Although the melt viscosity does not incorporate all the rheological information that is relevant to the compounding of immiscible blends, it provides an easily accessible means of classifying the different blends. The other parameter in our study was the relative transition temperatures of the two components. The results of compounding in the presence of a lower-melting-point minor component are quite distinct from those with a higher-melting-point minor component. The common feature of interest in all the blends we studied was the morphology at short mixing times. We have shown that, under certain conditions, the minor component can form the continuous phase initially, followed by a phase inversion with continued mixing. The blends showing such a behavior have been highlighted by the hashes in Table 3.4.

Additional blend systems studied in our group and by other researchers, at a constant mixer temperature are also included in the table. Most of the prior work looking at phase inversion during compounding involved the use of a ramped temperature profile to obtain an initial
Table 3.4: Summary of processing behavior of immiscible blends at a constant mixer temperature: major/minor components with viscosity ratio, \( \lambda \), in parentheses. Blends showing phase inversion during compounding are highlighted by the hashes.

<table>
<thead>
<tr>
<th>( \lambda )</th>
<th>( T_{\text{major}} &lt; T_{\text{minor}} )</th>
<th>( T_{\text{major}} \sim T_{\text{minor}} )</th>
<th>( T_{\text{major}} &gt; T_{\text{minor}} )</th>
</tr>
</thead>
</table>
| \( \lambda \ll 1 \) | PCL-A / PE-D\(^2\) (0.004)  
PCL-B / PE-D\(^2\) (0.02)  
PETG / PE-A (0.17)  
PETG / PE-D (0.001) | PS / PE\(^3\)  
(0.003 - 0.2) | PC / PE-A (0.14)  
PC / PE-D (-0.002)  
PAR / E-EA-GMA\(^4\) (0.05)  
PA / PS\(^4\) (0.3) |
| \( \lambda \sim 1 \) | PCL-A / PE-A\(^2\) (0.34)  
PCL-B / PE-A\(^2\) (1.7) | PS / PE\(^3\)  
(0.7) | PB-A / PCL-B (0.4)  
PB-D / PCL-B (2.5) |
| \( \lambda >> 1 \) |

\(^1\lambda = \eta_{\text{minor}} / \eta_{\text{major}}\); with the viscosities measured at representative process conditions  
\(^2\)From reference (Chapter 2), 10 wt.% minor component  
\(^3\)From reference (30), < 8 wt.% minor component  
\(^4\)From reference (29), 20 wt.% minor component

Continuous phase of the low-melting minor component. There has been no systematic attempt to categorize blends based on their short-mixing-time morphology. We present here, a new framework based on the melt viscosity ratio and relative transition temperatures of the blend components. Using this framework we can quantify the viscosity ratios and transition temperature differences of an blend for which an initially continuous phase of the minor component will be formed during compounding at a constant process temperature. Phase inversion during compounding is seen to be favored in a blend with a low-viscosity, lower-melting-point minor component. The ability of the minor component to form an initial continuous phase is decreased as its viscosity or softening temperature is increased relative to that of the major component.

The earliest reported instance of phase inversion was in a polyarylate/ethylene acrylate blend (28). The rubbery ethylene acrylate formed the continuous phase, encapsulating the major phase. The melting point of the minor rubbery phase was 80°C compared with a \( T_g \) of 180°C for the polyarylate. Moreover, a slowly ramped temperature program was used to delineate the different
regimes in compounding and the phase inversion that occurred at the softening point of the polyarylate. Later work by Sundararaj et al. (44) included non-reactive systems where the minor component had a lower softening temperature. Blends of nylon/polystyrene are an example of such a system. It was reported that on using a temperature ramping program during compounding, the lower-softening-point minor component initially formed the continuous phase. Further evidence of this conclusion is provided by the results of compounding runs with PC/PE blends in this study. These runs were performed at a constant mixer temperature, yet PE formed the continuous phase initially. The effect of this phase inversion is most pronounced on the torque curve of the PC/PE-D blend, with a viscosity ratio of about ~0.002. As seen from Table 3.3, selective extraction in the Soxhlet apparatus shows that, initially, PE coats the pellets of PC and delays the softening of PC. The amount of PE which is continuous as a fraction of the total blend weight is reduced from 9.5% at 3 minutes to nearly zero at 5 minutes. The second torque peak is thus related to a morphological transformation in which the higher-viscosity PC becomes the continuous phase by progressively incorporating the PE phase. Due to the low thermal conductivity of polymers, viscous dissipation in the melt is a primary means of providing heat for the softening and melting of the polymer. If a low-viscosity film forms on the pellets, viscous dissipation is reduced, delaying the softening of PC pellets. Quantification of this effect is presented below. Moreover, the presence of a low-viscosity melt minimizes exposure of the rest of the batch to the high shear regions of the mixer. This contributes to a further delay in the softening of the pellets. With PC/PE-D blends, it is seen that nearly 5 minutes of mixing is required before the PC pellets show sufficient deformation to form the continuous phase. The second torque peak has often been taken to indicate occurrence of phase inversion in a blend. As the torque curve of the PC/PE-A blend (viscosity ratio of 0.14) shows, this is not always the case, and sampling at different times is the only reliable way of determining the morphology. Our results confirm that phase inversion occurs in the presence of a low-melting-point minor component, even when a constant mixer temperature is used during compounding.

The results of PETG/PE blends provide further evidence for the occurrence of phase inversion in blends with a low-viscosity high-melting minor component. In the PCL/PE blend system (Chapter 2), with a viscosity ratio of 0.02, the second torque peak associated with phase inversion was seen at 1 minute into mixing (45). With the PETG/PE-D blend this peak occurs at 3.5
minutes into mixing. This is explained by the slower softening rate of the amorphous major phase compared to a semicrystalline major phase. Similar behavior was observed by Shih (28) in compounding runs with polyarylate/ethylene acrylate and HDPE/rubber blends. Another interesting result from these PETG/PE blends is that, at the earliest sampling time, PE was the continuous phase in the higher viscosity ratio (0.17) PETG/PE-A blend. Once again, the torque curve did not indicate a second peak corresponding to phase inversion.

With the addition protocol used in these runs, where a mixture of pellets of the two components are added to the hot mixer, compaction of these pellets and their deformation in the solid state is another parameter to be considered. Table 3.2 lists the ratios of the real components of dynamic shear moduli of the blends at 30°C. Plochocki et al. (27) have reported on the tendency of the lower elasticity component to be stretched and broken at early mixing times. It is seen that in PC/PE and PETG/PE blends the minor component has a much lower modulus than the major component. This would cause preferential deformation of the minor component in the solid state and its passage through the high shear, narrow gap regions of the mixer. The elasticity ratios of the PB/PCL-B blends are close to one; hence, we do not expect differences in their deformation in the solid state.

Due to the compaction and deformation of pellets on feeding them into the mixer under a constant force, it is possible that, even at low volume fractions of the minor component, a continuous phase might result as indicated by the dissolution studies. In all the blend systems studied here, the minor component was present at 10 wt.%, which is approximately 12 vol.%. The minimum unoccupied volume in a packing of monodisperse spheres is 26%. Lyngaae-Jorgensen et al. (46) have experimentally observed minimum volume fractions of the minor phase close to the critical percolation threshold of 15.6%, in the final blend of two immiscible polymers. They also found that the percolation threshold decreases when different-sized spherical domains or elongated domains are present. Figure 3.5a shows how a 10 wt.% component could form a continuous phase by encapsulating the unmolten pellets of the major phase.

If the melt viscosities of the blend components are closely matched, viscous dissipation contributing to the melting of pellets does not vary with the composition of the melt. Therefore, compounding of a mixture of pellets at a constant temperature above the melting points of the
two components, will result in the simultaneous softening of the unmolten pellets of both the major and the minor component. Thus, the melt in the mixer will contain enough of the major component to prevent its complete encapsulation by the molten minor component. The initial morphology will not have a continuous phase comprised completely of the minor component, indicating the absence of phase inversion during compounding. The absence of phase inversion is experimentally more difficult to establish than its occurrence. Here, we have collected three short-mixing-time samples starting at 10s after the feeding was completed, and investigated the continuous phase in them. If in all three samples the major component was the continuous phase, it was concluded that phase inversion did not occur in that run. This method was especially useful with the PB/PCL-B blends. PB-A/PCL-B and PB-D/PCL-B have viscosity ratios of 0.4 and 2.5, respectively. Scott and Joung (30) reported that only a single torque peak associated with feeding was observed during compounding when the viscosity ratio was greater than 0.1. The torque traces of PB/PCL-B (Figure 3.7) agree with that conclusion. But, as seen above in PC/PE-A and PETG/PE-A blends this is not indicative of the absence of phase inversion. Dissolution studies with early-mixing-time samples provided conclusive evidence that PB was continuous even at 10s after feeding was completed. Also, the results of Soxhlet extraction reported in Table 3.3 show that, even with all the PCL continuous, enough of the PB has begun melting to hold the post-extraction samples together.

In order to determine the effects of process temperature history, a ramped temperature program was used. The results of the ramped temperature program indicate that the lower-melting-point minor component formed the continuous phase first. Hence, phase inversion was forced in the PB-A/PCL-B system with a suitable choice of temperature program. This is in agreement with earlier observations using a slowly increasing temperature (28, 44), which indicated that the lower-melting-point component will form the continuous phase initially.

A global energy balance can be used to separate out the effects of mechanical energy input through shaft work and energy input through heat conduction from the walls. Following the analysis outlined in Scott and Joung (30), writing an energy conservation equation for the entire batch we obtain:
\[ m C_p \frac{dT_{\text{melt}}}{dt} = \Gamma \cdot \omega + hA(T_{\text{wall}} - T_{\text{melt}}) \]  \hspace{1cm} (3-1) 

where \( m \) is the mass of the batch, \( C_p \) is the average specific heat, \( \Gamma \) is the motor torque, \( \omega \) is the drive-shaft speed and \( h \) is the heat transfer coefficient between the mixing bowl and the polymer batch. In this model the batch is approximated to be a lumped system without any internal temperature gradients. The first term on the right is the mechanical energy input and the second term represents the heat transfer from the walls of the mixer. Rearranging the terms to compute the ratio of heat conduction to mechanical energy dissipation yields:

\[ \frac{hA(T_{\text{wall}} - T_{\text{melt}})}{\Gamma \cdot \omega} = \frac{m C_p \frac{dT_{\text{melt}}}{dt}}{\Gamma \cdot \omega} - 1 \]  \hspace{1cm} (3-2) 

At long mixing times when the melt attains a steady temperature this ratio becomes -1. At any mixing time the above ratio gives the relative importance of heat conduction to viscous dissipation in the melt. Using the temperature and torque data recorded during a typical compounding run, the first term on the right was calculated. The specific heat of the blend was taken to be a mass-weighted average of the component specific heats. For each blend component the temperature dependent specific heat was calculated from the experimental data compiled by van Krevelen (47).

On feeding cold pellets into the hot mixer the melt thermocouple initially showed a decrease in temperature. But after the batch was completely fed, the temperature monotonically increased to the mixer set temperature. This portion of the melt temperature data was fitted with a polynomial, whose time derivative was then used in equation 3-2. Thus the ratio of heat conduction to viscous dissipation was obtained as a function of mixing time and melt temperature for different blends. It should be noted that the heat transfer coefficient calculated as described above is not a constant but is a function of the mixing time.

The temperature dependence of this ratio for PC/PE and PETG/PE blends is shown in Figure 3.9. The mixing times corresponding to the melt temperatures are also indicated in the figures. As seen from Figure 3.9a, the formation of a low-viscosity melt reduces viscous dissipation and delays the rise in melt temperature in the PC/PE-D blend. The melt temperature reaches 180°C at 5 minutes with PC/PE-D as compared with 2 minutes in the PC/PE-A blend. Thus in the low torque region of Figure 3.2, heat conduction is the dominant mode of energy input to the blend.
This results in much longer times to heat and soften the dispersed PC pellets thus delaying phase inversion until about 6 minutes into mixing. In contrast, in the higher viscosity ratio PC/PE-A blend, the above ratio is smaller indicating a larger contribution of the viscous dissipation term to the energy input. Similar behavior is observed with the PETG/PE blend. The low torque region seen in the compounding of PETG/PE-D (Figure 3.4) corresponds to a higher value of the above ratio. Thus viscous dissipation critically affects the softening of the PETG pellets and can change the observed processing behavior dramatically. The presence of a low-viscosity melt delays the softening of unmolten pellets and the above ratio quantifies this effect. We propose that the formation of the initial melt is governed by the relative solid-state moduli of the components and further progression in the rate of morphology evolution is governed by the viscous energy dissipated in the melt.

![Graph showing melt temperature vs. hA(ΔT)/(Γo)](Figure 3.9 (a))
Figure 3.9: Ratio of energy input through heat conduction to viscous dissipation calculated using equation 3-2, as a function of the melt temperature. The mixing time in minutes corresponding to the melt temperature is shown next to the markers, for each blend. (a) PC/PE blends. (b) PETG/PE blends.

The above results highlight the interplay between the process temperature and material rheology in determining the melting rates and, hence, the morphology evolution in different blends. When the solid-state moduli are comparable, deformation of both components occurs simultaneously; if, in addition, the melt viscosities are comparable, we obtain an initial cocontinuous morphology. This is seen from the compounding runs of PB/PCL-B blends. In such a blend with a viscosity ratio above 0.2, the melting of the higher-melting-point component can be delayed by using a programmed temperature to heat the mixer during compounding. As shown in Figure 3.8, this results in the lower-melting-point PCL-B forming the continuous phase initially. In contrast, lower modulus in the solid state and a lower melting point aid the formation of the continuous phase by PE-A in PC/PE-A blends. Even when the major component softening
temperature is reduced below the melting point of PE, as in PETG/PE-A blends, the amorphous nature, and hence slower progression to the rubbery state of PETG delays its formation of the continuous phase in PETG/PE-A blends. It has been shown that a very-low-viscosity minor component delays the softening of the major component to longer mixing times and this effect can be quantified using the ratio of heat conduction to mechanical energy input.

3.5 Conclusions

We have presented a new framework for analyzing the processing behavior of immiscible blends with a small fraction of the minor component. The transition temperatures and melt viscosity ratios were used to differentiate the blends. This new framework enables the quantification of material and process conditions for which certain morphological changes are seen. It was shown that phase inversion, where an intermediate morphology of a continuous phase of the minor component encapsulating all the major component pellets is observed, is most likely in blends with a low-viscosity, lower-softening-temperature minor component. Earlier work with phase inversion was also summarized in the new framework. While it is not comprehensive, the framework does provide a convenient means to delineate the effects of two important parameters in the compounding of immiscible blends. When the mixer is held at a constant temperature, above the melting points of the two components, we have shown that phase inversion occurs when the viscosity ratio is less than about 0.2. The highest-viscosity-ratio system which showed phase inversion in our studies was PETG/PE-A at 0.17, whereas PB-A/PCL-B at 0.4 did not. In addition, pronounced low-torque regions before phase inversion were observed only when the blend viscosity ratio was ~0.001. Hence, the torque trace alone is not a reliable indicator for the occurrence of phase inversion. Sampling and selective dissolution are necessary for the determination of the continuous phase after different mixing times. In the blends showing a prolonged low-torque region, PC/PE-D for example, we have shown that the second torque peak corresponds to the progressive incorporation of the minor component into the more-viscous major component. At low-viscosity ratios, an amorphous major component required a longer time to form the continuous phase than a semicrystalline one. We have also shown that the use of a slowly ramped temperature program results in the low-melting-point component forming the continuous phase initially. This is in agreement with earlier results in the literature and offers an
additional means to control the morphology by a suitable choice of the temperature program. Calculations on the relative energy input showed that viscous heating is primarily responsible for the melting or softening of the pellets in the batch. Thus, phase inversion occurs at shorter mixing times when a higher-viscosity minor component is used.
4. SCALEUP OF PHASE INVERSION DURING COMPOUNDING

4.1 Introduction

Typical compounding conditions for the manufacture of new polymer blends are initially optimized in laboratory scale equipment. Based on the understanding gained from laboratory studies, the process must be scaled up to development and then production size. Successful scaleup of the process is a challenging problem which must be overcome in order to commercialize a new blend.

Scaleup approaches in the literature can be broadly classified into formulation-specific rules and process-analysis-based rules. In the former approach, most commonly used in an industrial setting, a given formulation is compounded in different equipment and the process conditions required to achieve the same "quality" at each scale are determined. Empirical techniques like Design of Experiments are often used in the collection and analysis of process data (48, 49). This approach involves extensive experimental work to identify suitable processing windows and the results are limited to the particular formulation being studied. As opposed to this empirical approach, process analysis models based on unit operations can be developed to identify and quantify the controlling geometric parameters and operating conditions. For example, compounding in plasticating single-screw extruders has been analyzed in terms of solids conveying, melting, and melt conveying regimes (50-52). Such analyses result in rules that quantify the effect of scaleup on extruder performance in the different unit operations. This requires accurate modeling of the material behavior and the flow field in the extruder. Reasonable success has been achieved in modeling the processing of neat resins in single screw extruders. The modeling of material behavior during processing in batch intensive mixers and twin screw extruders is much more difficult due to the complex nature of the flow field. However these are used extensively in the compounding of polymer blends because they are effective dissipative mixing devices. Thus, there is a crucial need to understand the scaleup of compounding behavior in these mixing devices.

In contrast to the two approaches outlined above, our focus in this work is on scaleup that maintains the same mechanism of morphology evolution in the compounding of polymer blends.
This approach emphasizes the progression of the morphological transformation, rather than a particular formulation or type of compounding equipment. We have chosen different blends that show a transformation in morphology from one of the minor component forming the continuous phase to that of the major component forming the continuous phase with continued mixing. This transformation has been termed phase inversion during compounding (19, 28, 29, 45). The goal was to identify the geometric parameters (blade design, minimum gap, etc.) and operating conditions (rotor speed, mixer temperature, etc.) that affect the compounding of these blends on scaleup. Since a mechanism of morphology evolution is studied, the results are expected to be valid for a variety of blend systems that exhibit the above phenomenon during compounding. Based on our understanding of the morphological changes we seek to explain the observed scaleup behavior.

Batch intensive mixers have been extensively used in the rubber industry for compounding. A complete three-dimensional analysis of the flow field inside a batch mixer is difficult and has been achieved only for isothermal conditions. Experimental work with rubbers has shown that for dispersive mixing the critical parameters are the tip clearance, rotor speed, and the mixing time (53). Dispersive mixing models for the breakup of carbon black agglomerates in batch mixers have been proposed based on the agglomerate cohesive strength and the shear stress in the narrow-gap regions of the mixer (54, 55). The scaleup criterion based on the above analysis requires a constant shear-rate to be maintained in the tip region of the blades.

Unfortunately, at present there is no comprehensive mathematical model that describes the complex sequence of steps leading to phase inversion during compounding. Thus the effect of varying some process conditions, like blade design or batch size, while keeping others like the composition constant are best studied experimentally. The above analyses suggest the importance of shear rate in the tip region of the mixer for dispersive mixing. Visual observations using a glass window during compounding in our polystyrene/polyethylene blend showed that the deformation of the polystyrene pellets proceeded by repeated passage through the high shear regions at the blade tips. Therefore, we chose to use a constant nominal maximum-shear-rate condition in our studies on scaleup. This parameter, $\dot{\gamma}_{\text{max,nominal}}$, was calculated assuming pure drag flow between the blades and the mixing bowl.
\[ \dot{\gamma}_{\text{max,nominal}} = \frac{\pi D_{\text{blade}} N}{H} \]  

(4-1)

where \( D_{\text{blade}} \) is the blade diameter, \( N \) is the rotor drive shaft speed in rotations per second and \( H \) is the minimum gap between the blades and mixer wall.

For this work, we chose a low-viscosity-ratio polystyrene/polyethylene (major/minor component) blend for which the mechanism of morphology development during compounding in a batch mixer is very well understood (30). The viscosity ratio is defined as the ratio of the viscosity of the minor component to that of the major component at the mixer temperature and a representative shear rate of 100s\(^{-1}\). The effect of this viscosity ratio, composition of the blend and the mixer temperature on morphology development has been extensively studied. For viscosity ratios less than 0.1 an initial low mixer torque region was observed, corresponding to a continuous phase of polyethylene with polystyrene dispersed in it. Formation of a continuous phase of a low-viscosity polyethylene melt reduced viscous dissipation and hence delayed the heating of polystyrene pellets. Continued mixing resulted in the softening, deformation, and coalescence of the polystyrene domains. This was accompanied by a rise in the mixer torque required to deform the higher viscosity polystyrene. In a polycarbonate/polyethylene system with a viscosity ratio of 0.001 (\( \eta_{\text{PE}} / \eta_{\text{PC}} \)) we have shown that this torque rise corresponds to the gradual incorporation of the minor component into the major component (56). Thus phase inversion during compounding has been shown to predominate in the compounding of low-viscosity-ratio systems. Moreover, in these systems our visual observation of blend morphology at different mixing times (Chapter 5) has identified the deformation behavior of the major component leading to phase inversion. Studies have also detailed the morphological changes which these blends undergo in a steady shear flow (57).

Building on the accumulated understanding of phase inversion in immiscible blends (Chapter 2 and 3), in this work we present results from the scaleup behavior of blends with a viscosity ratio of \(-0.001\) during compounding in batch mixers. The key questions we sought to answer were: Does the mechanism of morphology development remain the same for different batch sizes? How can we study multiple batch sizes and blade designs quickly and efficiently while retaining geometric similarity in blade design? Can we predict the time to phase inversion upon scaleup?
Detailed studies of the effects of scaleup and changes in equipment configuration require access to equipment at different size scales with alterable geometries. It is also desirable to have the capability for maintaining geometric similarity or providing for specific changes in geometric characteristics upon scaleup. Processing small samples is often important in research environments where quantities of new materials may be quite limited.

In order to achieve these goals, a novel blade design for batch intensive mixers has been developed and constructed. This modular design is described in greater detail in the experimental section. The batch size can be varied by using different numbers of elements with a single mixing bowl. For example, batch sizes from 8cm³ to 64cm³ can be studied in a single mixing bowl using our design. The modular nature of the blades either preserves geometric similarity or provides for controlled variation at different batch sizes. Another great advantage of the modular blades is the ability to configure different blade designs with minimum effort. By specifying different arrangements of the elements we can use the same blades to study the effect of the blade configuration on any interesting processing phenomena. Although blade designs with modular elements in batch mixers have been reported in the literature (58, 59), we have not seen any application that exploited their modular nature for scaleup studies. Our design brings some of the flexibility enjoyed in twin screw extruders to the batch intensive mixer.

4.2 Experiments

4.2.1 Materials Characterization and Experimental Protocol

Polystyrene from BASF was the major component and polyethylene from Eastman Chemical Company was the minor component in the blend. A summary of the relevant properties is shown in Table 4.1. Rheological measurements on the blend components were made using an ARES mechanical spectrometer from Rheometric Scientific. Disks for use with a parallel plate fixture and rectangular coupons for use with a torsion fixture were compression molded from dried pellets of polystyrene and polyethylene. The complex moduli and viscosity of the components under dynamic shear strain within the linear viscoelastic limit were then measured. The Cox-Merz (36) rule was used to correlate these with steady-shear viscosity of the components under a representative shear rate inside the mixer. A summary of the temperature dependent viscosity of two of the components used here is presented in Figure 4.1. These curves were measured at
100 s\(^{-1}\), which was calculated assuming pure drag flow in the minimum gap between the blades and the mixing bowl. By using the torsion fixture for solid state measurements and the parallel plates for the melt measurement, a description of the small-strain material behavior over the entire temperature range encountered during processing was obtained. The softening temperatures obtained from these measurements are the relevant temperatures for describing material behavior in a compounding operation as opposed to differential scanning calorimetry (DSC) measurements. Rheological measurements show that polystyrene softens at a higher temperature (120\(^\circ\)C) than polyethylene (90\(^\circ\)C) although DSC measurements indicated a melting peak for the polyethylene close to the \(T_g\) of polystyrene.

<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial Designation</th>
<th>Viscosity (180(^\circ)C, 100s(^{-1})) Pa-s</th>
<th>Viscosity Ratio (180(^\circ)C, 100s(^{-1}))</th>
<th>Transition Temperature ((^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS(^1)</td>
<td>BASF 1424</td>
<td>716</td>
<td>-</td>
<td>100 ((T_g))</td>
</tr>
<tr>
<td>PE-C(^2)</td>
<td>Epolene C-13</td>
<td>41</td>
<td>0.05</td>
<td>89 ((T_m))</td>
</tr>
<tr>
<td>PE-D(^2)</td>
<td>Epolene C-10</td>
<td>3.3</td>
<td>0.005</td>
<td>104 ((T_m))</td>
</tr>
<tr>
<td>PE-E(^2)</td>
<td>Epolene C-15</td>
<td>1.9</td>
<td>0.003</td>
<td>101 ((T_m))</td>
</tr>
</tbody>
</table>

\(^1\)BASF Corporation  
\(^2\)Eastman Chemical Company

In a typical compounding run, a mixture of dried pellets of the two components in the correct proportion was hand-mixed in a tray. This mixture was then added to a mixer preheated to the compounding temperature with a given blade configuration mounted onto the shafts. A constant degree of fill corresponding to 70% of the total available mixing volume was used for all the runs. For example, with roller blades in the small mixing bowl, a batch size of 49g was used for the polystyrene/polyethylene blend. This degree of fill provided good material exchange between the two halves of the mixing bowl. The melt temperature and the torque required to drive the rotors were recorded as a function of mixing time. Compounding runs were done at mixer set temperatures of 160, 180, and 200\(^\circ\)C. In addition, three different blend compositions (2, 4, and 7.8 wt.% of polyethylene) were studied.
Pellets of polystyrene were cylinders of 2.5mm diameter and 3mm height. Polyethylene pellets were spherical with an average diameter of 2.5mm. These dimensions are larger than the minimum gap between the blades and the mixer wall.

![Graph showing complex viscosity vs. temperature for PE-D and PS](image)

Figure 4.1: Small strain rheological measurements of the complex viscosity of the blend components.

### 4.2.2 Equipment

Two different mixing bowls with available mixing volumes of 120cm³ and 720cm³ (without the blades) were used for the different compounding runs. The small mixer was a Haake Rheomix 600 and the large mixer was a REE-6 Brabender Prep Mixer. A rotor speed of 50 r.p.m. was used for the compounding runs in the small mixer. To achieve the same nominal maximum-shear-rate in the large mixer, the drive shaft was run at 29 rpm. This follows from Eq. 4-1 using the blade and
mixing bowl dimensions given in Table 4.2. Our initial compounding runs were performed using roller blades.

Using the dimensions of the two sets of roller blades and mixing bowls, different geometric parameters of interest were calculated and these are summarized in Table 4.2. The minimum gap in the large mixer was 1.5mm compared with 1.4mm in the small mixer. The mixing blades are not directly heated but they provide additional area for the conduction of heat to or from the batch. For this reason, both the area of the mixing bowl and the area of the blades in contact with the batch were measured. On scaleup to a large mixer the specific area, defined as the ratio of area to the volume, decreases. For the two mixing bowls used here the specific area, neglecting the blade surface area, decreased from 1.2cm\(^{-1}\) to 0.7cm\(^{-1}\) on scaleup. Upon including the area of the blades this value decreases from 2.6cm\(^{-1}\) in the small mixer to 1.6cm\(^{-1}\) in the large mixer. In either case, the specific area of the large mixing bowl is about 60% of the small mixing bowl specific area.

<table>
<thead>
<tr>
<th>Table 4.2. Roller Blades: comparison of the two batch mixers.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mixer Capacity</strong></td>
</tr>
<tr>
<td>Mixer Capacity</td>
</tr>
<tr>
<td><strong>Blade Dimensions</strong></td>
</tr>
<tr>
<td><strong>Mixing Bowl Dimensions</strong></td>
</tr>
<tr>
<td>Minimum gap between blades and mixing bowl</td>
</tr>
<tr>
<td>Surface Area of Mixing Bowl</td>
</tr>
<tr>
<td>Minimum gap between blades and mixing bowl</td>
</tr>
<tr>
<td><strong>Surface Area of Mixing Bowl</strong></td>
</tr>
<tr>
<td><strong>Surface Area of Blades</strong></td>
</tr>
<tr>
<td><strong>Specific Area (without blades)</strong></td>
</tr>
<tr>
<td><strong>Specific Area (including the blades)</strong></td>
</tr>
</tbody>
</table>
4.3 Novel Modular Triangular Blades

Novel mixing blades with modular elements were designed for the batch intensive mixer. The new blade design consists of triangular elements that are mounted onto a central shaft using a keyway and key. A photograph of the components of the new blades used with the small mixing bowl is shown in Figure 4.2a. For comparison, roller blades used with the same mixing bowl are shown in Figure 4.2b. The central shafts were machined out of stainless steel to within 0.0005in tolerance in order to mate with the gearbox on the mixer. The triangles were machined out of aluminum and were 0.23in thick. The flat tips of the triangle were approximately 0.125in wide. The small roller blades have the same tip width. The dimensions of the triangle were chosen such that the smallest clearance between the triangles and the mixer bowl walls was 1.4mm. The same clearance is present when roller blades are used with the small mixing bowl. By mounting different numbers of triangles on the shafts the available mixer volume could be varied from 8cm$^3$ to 64cm$^3$. The unused portion of the mixing bowl was filled with spacer blocks like the one shown in Figure 4.2. Three different batch sizes corresponding to 2, 4, and 6 triangles on each shaft were studied in the small mixer. The geometric parameters of interest for these blade designs are summarized in Table 4.3. The built-up blades corresponding to these batch sizes are shown in Figure 4.3.

<table>
<thead>
<tr>
<th>Batch Size</th>
<th>2 Triangles</th>
<th>4 Triangles</th>
<th>6 Triangles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing Volume</td>
<td>12 g</td>
<td>23 g</td>
<td>35 g</td>
</tr>
<tr>
<td>16 cm$^3$</td>
<td>32 cm$^3$</td>
<td>48 cm$^3$</td>
<td></td>
</tr>
<tr>
<td>Surface Area of Mixing Bowl</td>
<td>18 cm$^2$</td>
<td>37 cm$^2$</td>
<td>55 cm$^2$</td>
</tr>
<tr>
<td>Surface Area of Blades</td>
<td>21 cm$^2$</td>
<td>42 cm$^2$</td>
<td>63 cm$^2$</td>
</tr>
<tr>
<td>Specific Area (including the blades)</td>
<td>2.45 cm$^{-1}$</td>
<td>2.45 cm$^{-1}$</td>
<td>2.45 cm$^{-1}$</td>
</tr>
</tbody>
</table>
Figure 4.2: Elements of the new blade design (a). Roller blades used in the same mixing bowl are shown for comparison (b).

Figure 4.3: Blade designs used for compounding runs at three different batch sizes. In the case of 2 or 4 elements, the spacer blocks used were longer than those shown here in order to completely fill the space unoccupied by the triangles. The small tick marks on the ruler are 1mm apart.
Table 4.4. Triangular Blades: comparison of the process parameters corresponding to the compounding runs in the small and large mixers.

<table>
<thead>
<tr>
<th></th>
<th>Small Mixer</th>
<th>Large Mixer</th>
<th>Ratio (Large / Small)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Batch Size</strong></td>
<td>35 g</td>
<td>300 g</td>
<td>8.6</td>
</tr>
<tr>
<td><strong>Blade Diameter</strong></td>
<td>3.64 cm</td>
<td>6.70 cm</td>
<td>1.8</td>
</tr>
<tr>
<td><strong>Minimum Gap</strong></td>
<td>1.4 mm</td>
<td>1.5 mm</td>
<td>1.1</td>
</tr>
<tr>
<td><strong>Rotor Speed</strong></td>
<td>50 r.p.m.</td>
<td>29 r.p.m.</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Specific Area</strong></td>
<td>2.45 cm(^{-1})</td>
<td>1.30 cm(^{-1})</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Two sets of blades, one set for each of the two mixing bowls, were made and the important parameters of these blades are compared in Table 4.4. The specific area of the triangular blades decreased from 2.45 cm\(^{-1}\) in the small mixer to 1.3 cm\(^{-1}\) in the large mixer. The blade design used for these scaleup runs between mixing bowls was the aligned configuration, shown in Figure 4.4a.

The modular design allows for great flexibility in the final blade configuration. A keyway machined into the shaft and each of the triangular elements was used with a key to assemble the elements onto the shaft. The keyway on the triangles was machined at three different positions relative to the tip. In this way, the stagger between succeeding triangular elements could be varied. Multiple configurations with six elements on each shaft were studied. Configurations were chosen to provide very different flow fields inside the mixer. Four of the configurations used in this study are shown in Figure 4.4.

In the aligned configuration, there is no stagger between succeeding elements and visual observation through the feed chute showed negligible axial motion of the batch. There was good material exchange between the two halves of the mixing bowl because the blades were rotated at different speeds with the slower one rotating at two-thirds the set rpm. It is anticipated that with this configuration all material elements in the batch have
similar deformation histories and are confined to a small axial region throughout the mixing process. In the symmetric conveying configuration of the blades the triangles were mounted symmetrically on the two shafts. On each shaft the triangles were mounted such that the rotation of the blades caused material flow away from the central region of the mixing bowl. This is seen from studying the arrangement in Figure 4.4b and observing that the blades counter rotate inside the mixing bowl. As opposed to this, the asymmetric conveying configuration forces material flow in opposite directions. From Figure 4.4c, as seen from the spacer block end, the top shaft rotates counter-clockwise and the bottom shaft rotates clockwise. This rotation causes material to be pushed to the fifth element from the spacer block by the top blade and the second element from the spacer block by the bottom blade. In the “star” configuration (Figure 4.4d), the relative arrangement of the elements was an axially scaled version of those used for the 2 and 4 triangle designs. Each of the above designs had differing number of staggered elements; ranging from none in the aligned configurations to five in the asymmetric configuration.

The results from the compounding runs with the different blade designs are presented below. The measured torque was used to calculate the specific power input:

\[ \dot{w}(t) = \frac{\Gamma(t) \omega}{m} \]  

(4-2)

where \( \Gamma \) is the torque, \( \omega \) the drive shaft speed and \( m \) is the batch size. This quantifies the specific mechanical energy input and facilitates direct comparison of the compounding runs across different mixing conditions.

Figure 4.4(a)
Figure 4.4: Different configurations of six-triangular-element blade designs used in this study. Each design has a different relative stagger: (a) zero, (b) four, (c) five, and (d) one. The small tick marks on the ruler are 1mm apart.

4.4 Results

4.4.1 Radial Scaleup with Roller Blades

The specific power input at constant drive shaft speed for the compounding runs of different PS/PE blends at 180°C is shown in Figure 4.5a & b. The viscosity ratio of the blend was the process variable in these runs. The blend composition was fixed at 7.8wt.% of polyethylene. Similar compounding runs were performed in the two mixing bowls. It was found that feeding of the batch took about 20s in the smaller mixer and about 100s in
the large mixer. Each blending run showed a low torque region when polyethylene was continuous and a second torque peak associated with phase inversion to a polystyrene continuous phase. The mixing time at which the second torque peak was observed was labeled the time to phase inversion, based on detailed studies of morphology as a function of time in this blend (30). Given the complex nature of morphological transformations accompanying phase inversion, this provides a simple means to identify similar times in the processing history of the blends in the two mixers. It is seen that lowering the viscosity ratio increases the time to phase inversion in both the mixers. For a given blend, longer mixing times are required to achieve phase inversion in the large mixer. For the PS/PE-D blend phase inversion occurred at 22.5 minutes in the large mixer and at 8 minutes in the small mixer. The times to phase inversion for the different blending runs are indicated in the figure.

![Graph showing specific power input vs time for different blends](image.png)

Figure 4.5(a)
Figure 4.5: Compounding runs at 180°C and 7.8 wt.% PE using roller blades in the (a) small mixer and (b) large mixer. The melt viscosity ratio ($\eta_{PE} / \eta_{PS}$) at 180°C and 100s$^{-1}$ is indicated in the legend. The time to phase inversion (in minutes) is indicated for each run.

The second process parameter that was varied was the blend composition. Three different concentrations of PE-D (2, 4, and 7.8wt.%) were compounded with PS and the times to phase inversion were compared. These results are shown in Figure 4.6. The viscosity ratio for this blend was 0.005. At very low concentrations it is unlikely that PE forms all of the continuous phase. But the torque traces showed a low torque region following the completion of feeding, indicating that the presence of a low-viscosity melt has a lubricating effect on the blend. This minimizes the exposure of polystyrene pellets to the high shear regions and delays their deformation, and the consequent torque rise, to longer mixing times. The observed times to phase inversion varied from 3.5 to 8 minutes in the small mixer and from 12 to 22.5 minutes in the large mixer.

For the above PS/PE-D blend at a composition of 7.8 wt.% PE-D, the effect of varying the mixer set temperature was also investigated. Three different mixer
temperatures of 160, 180, and 200°C were used. Progression to a blend with a polystyrene matrix required longer mixing times as the mixer temperature was lowered (Figure 4.7). The mixing times increased from 11.5 minutes at 200°C to 57 minutes at 160°C for the compounding runs in the large mixing bowl.

Figure 4.6(a)
Figure 4.6: Effect of weight fraction of the low-viscosity minor component, PE-D, on the time to phase inversion in PS/PE-D blends with a viscosity ratio of 0.005. Compounding runs at 180°C with roller blades in the (a) small mixer and (b) large mixer. The time to phase inversion in minutes is indicated for each run.

The observed times to phase inversion and the specific work input until phase inversion for the runs described above are summarized in Table 4.5. The specific work input until phase inversion was calculated by integrating eq. 4-2:

\[
w(t_{p,I}) = \int_{0}^{t_{p,I}} \frac{\Gamma(t)\omega}{m} dt \quad (4-3)
\]

Under the constant nominal maximum-shear-rate condition, it is seen that the times to phase inversion in the large mixer were nearly 3 times the corresponding mixing times in the small mixer. The specific work input until phase inversion increased by 70% on scaleup to the large mixer.
Figure 4.7: Effect of varying the mixer temperature on the time to phase inversion in PS/PE-D (92.2/7.8) blends with a viscosity ratio of 0.005. Compounding runs using roller
blades in the (a) small mixer and (b) large mixer are shown. The time to phase inversion in minutes is indicated for each run.

Table 4.5: Variation in the time to phase inversion, $t_{P,I}$, and the specific work input until phase inversion on scaleup to a large mixer using roller blades.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>$t_{P,I}$ Small Mixer (min)</th>
<th>$t_{P,I}$ Large Mixer (min)</th>
<th>Ratio of Times to Phase Inversion (Large/Small Mixer)</th>
<th>Ratio of Specific Work (Large/Small Mixer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity Ratio ($\eta_{PE}/\eta_{PS}$)</td>
<td>0.05</td>
<td>3</td>
<td>7.5</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>8</td>
<td>22.5</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>10.5</td>
<td>35</td>
<td>3.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Volume Fraction of PE-D (wt.%)</td>
<td>2.0</td>
<td>3.5</td>
<td>12</td>
<td>3.4</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>5</td>
<td>16.5</td>
<td>3.3</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>8</td>
<td>22.5</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td>Mixer Temperature ($^\circ$C)</td>
<td>160</td>
<td>15</td>
<td>57</td>
<td>3.8</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>8</td>
<td>22.5</td>
<td>2.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4</td>
<td>11.5</td>
<td>2.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

4.4.2 Radial Scaleup with Modular Triangular Blades

Similar to the mixing runs with the roller blades, the effect of volume fraction of PE-D and the mixer temperature on the time to phase inversion in the two mixing bowls was studied. The aligned blade configuration was used for all the compounding runs. For the compounding runs at different volume fractions of PE-D, a mixer temperature of 180$^\circ$C was used. For the runs where the mixer temperature was varied, 7.8wt.% of polyethylene (PE-D) was used. The torque traces for these blending runs with triangular blades were qualitatively similar to the corresponding ones with roller blades which have been shown previously. The time to phase inversion for each run and specific work input until phase inversion are compiled in Table 4.6. The times to phase inversion on radial scaleup with
triangular blades increased by a factor of about 2.7 and the specific work input until phase inversion scaled by a factor of 2.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>( t_{p, L} ) Small Mixer (min)</th>
<th>( t_{p, L} ) Large Mixer (min)</th>
<th>Ratio of Times to Phase Inversion (Large/Small) Mixer</th>
<th>Ratio of Specific Work (Large/Small) Mixer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Fraction of PE-D (wt.%)</td>
<td>2.0</td>
<td>4.5</td>
<td>11</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>6</td>
<td>15</td>
<td>2.5</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>7.8</td>
<td>8</td>
<td>21.5</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td>Mixer Temperature (°C)</td>
<td>160</td>
<td>20.5</td>
<td>56</td>
<td>2.7</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>8</td>
<td>21.5</td>
<td>2.7</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>4</td>
<td>12.5</td>
<td>3.1</td>
<td>2.3</td>
</tr>
</tbody>
</table>

4.4.3 Effect of Blade Configuration on Compounding Behavior

The primary advantage of the modular blades is the ability to use the same mixing bowl to obtain different batch sizes and blade configurations. Control of relative stagger of the triangular elements influences the effectiveness of the blades in deforming the polystyrene phase and thus changes the time to phase inversion. To investigate the magnitude of this effect on the time to phase inversion four different blade configurations were used at a batch size of 35g (six triangles on each shaft in the small mixing bowl). A relative stagger parameter is defined as the number of successive elements on a shaft that are staggered with respect to one another:

\[
\text{relative stagger} = \text{number of successive staggered elements (on each shaft)}
\]  

(4-4)
For example, from Figure 4.4d, in the star configuration where the third and fourth elements are staggered the relative stagger is one. In contrast, for the asymmetric configuration the relative stagger is five.

A comparison of the specific power input for the compounding of a 92.2/7.8 PS/PE-D \((\lambda = 0.005)\) blend at 180\(^\circ\)C is shown in Figure 4.8. The times to the phase inversion are also indicated in the figure. The highest steady-state power input was observed with the aligned configuration in which there is no stagger between the elements. This configuration also showed the shortest time to phase inversion. Increasing the number of staggered elements decreased the steady state power input and resulted in longer times to phase inversion. The longest time to phase inversion was observed with the asymmetric configuration with a relative stagger of five. This indicates staggering the elements reduces the stress transfer to the batch by providing flow paths for the material to escape the high shear nip regions. For example, with the star configuration, this occurs at the 60\(^\circ\) stagger between the third and fourth triangular elements.
4.4.4 Effect of Axial Scaleup using Triangular Blades

![Graph showing specific power input over time for different configurations.](image)

Figure 4.8: Specific power input for different configurations of six elements on each shaft during the compounding of a 92.2/7.8 polystyrene/polyethylene blend ($\lambda = 0.005$) at 180°C. The configurations used are those shown in Figure 4.4 above. The time to phase inversion peak in minutes is included in the legend.

By changing the number of elements on each shaft different batch sizes in the same mixing bowl can be achieved. These compounding runs correspond to axial scaleup. Different batch sizes were investigated in the small mixing bowl by using 2, 4, and 6 elements on each shaft. The batch sizes varied from 12g to 35g. In these runs the specific area of the various designs varied less than 5% from 2.45 cm$^{-1}$.

Batch sizes of 12, 23, and 35g corresponding to 2, 4, and 6 triangular elements on each shaft were used. The built-up blades are shown in Figure 4.3. The relative stagger for the three designs was kept constant at one. This configuration allows for some axial convection of the material due to the presence of staggered elements. The specific power
input for compounding of a 7.8 wt.% polyethylene blend at 180°C is shown in Figure 4.9 for the different batch sizes.

Figure 4.9: Compounding runs with PS/PE-D (92.2/7.8) blends (λ = 0.005) at three different batch sizes at 180°C using the star configuration. A similar run using roller blades and a batch size of 49g is included for comparison. The time to phase inversion in minutes is included in the legend.

The results of the compounding runs reported in the previous section indicate that increasing the relative stagger increases the time to phase inversion at constant batch size. To better capture the effect of relative stagger on the deformation of the material a specific relative stagger parameter is defined:

\[
\text{specific relative stagger} = \frac{\text{relative stagger}}{\text{mass of the batch}}
\]  

(4-5)

Thus, for the three batch sizes used this specific relative stagger decreases upon increasing the batch size from 12 to 35g. The observed times to phase inversion for the compounding
runs at 180°C have been plotted against this specific relative stagger parameter in Figure 4.10. Results for three different compositions of PE are shown. It is observed that the times to phase inversion increased with specific relative stagger almost linearly. Similar trends were observed with the compounding runs at 200°C. This data shows that scaling to larger batch sizes while maintaining the relative stagger results in shorter times to phase inversion. At a larger batch size a smaller fraction of the material can avoid the high shear regions at the staggered elements. This suggests that scaleup at constant specific relative stagger is more likely to maintain a constant time to phase inversion.

![Graph showing the variation of time to phase inversion with specific relative stagger](image)

Figure 4.10: Variation of the time to phase inversion with the specific relative stagger parameter. Results from compounding runs of the PS/PE-D ($\lambda = 0.005$) blend at 180°C and different weight fractions of PE are shown.

### 4.5 Discussion

In this work we have studied a series of polystyrene/polyethylene blends that exhibit phase inversion during compounding. A low solid modulus and a low melt viscosity force the formation of a continuous phase by the minor-component polyethylene at short mixing times. The unsoftened polystyrene pellets are coated with and conveyed in the low-viscosity melt, which delays their heating and deformation. Our visual observations of the intermediate morphology in the compounding of such blends showed that the major component pellets are effectively prevented from deformation by the low-viscosity melt.
Reduced viscous dissipation due to a lubricating effect of the polyethylene leads to very long mixing times for the polystyrene to reach its softening temperature and be deformed on passage through the narrow-gap high-shear regions in the mixer. Various intermediate morphologies of flattened pellets, clusters of the major component, and fiber pulling from these clusters were observed en route to the formation of the continuous phase by the major component (Chapter 5). Each compounding run showed a distinct torque peak associated with this transformation and we have studied the mixing time corresponding to this peak under different batch sizes and blade designs.

We have investigated batch sizes from 12g to 240g with different blade designs in the various compounding runs mentioned above. At every scale, we observed the phase inversion mechanism of morphology development consisting of an initially continuous polyethylene melt with dispersed polystyrene pellets that transformed to a continuous phase of polystyrene with dispersed polyethylene domains. Over the process range investigated here the mechanism of morphology development is independent of the scale of mixing. For systems with a strong propensity for phase inversion (56) such as the one studied here, it is expected that phase inversion during compounding is a scale independent phenomenon with the kinetics of transformation determined by the rate of softening of the major component under the specific process conditions. Scaleup rules or process models should account for this feature in order to accurately predict the time to phase inversion.

During compounding in a batch mixer work input through the shafts and heat conduction from the walls of the mixer are the two modes of energy input into the material. A global energy balance for the batch can be written as:

$$\rho C_p \frac{dT}{dt} = \frac{\Gamma \cdot \omega}{V} + h \left[ \frac{A}{V} \right] (T_{wall} - T)$$  (4-6)

where $\rho$ is the density, $V$ is the volume, $C_p$ is the average specific heat, $T$ is the melt temperature, $\Gamma$ is the torque, $\omega$ is the drive shaft speed and $h$ is an average heat transfer coefficient. The formation of an initial low-viscosity melt of polyethylene reduces viscous heating and heat conduction from the walls dominates in the low torque regions of Figure
4.5. The large mixer has a lower specific area and this should delay the heating of the dispersed polystyrene pellets, thus delaying phase inversion. Moreover under the conditions used here, the large mixer was run at 29 r.p.m. compared to 50 r.p.m. on the small mixer to keep the nominal maximum-shear-rate constant. This results in a reduced contribution from the mechanical energy input term on scaleup. This is easily seen from a comparison of the specific power input traces for the two mixing bowls in Figure 4.5. The specific power input in the polyethylene continuous region for PS/PE-D blend in the large mixer is nearly a third of the corresponding value in the small mixer.

However, the reduced mechanical energy input alone does not account for the increase in the time to phase inversion in the large mixer. We compounded the PS/PE-D blend at 50 r.p.m. in the large mixer. This resulted in a specific power input nearly equal to that observed in the small mixer, in the polyethylene continuous region. Despite this the time to phase inversion was found to be 15 min in the large mixer, nearly twice as long as the time required in the small mixer.

Rearranging Eq. 4-6, we can quantify the relative importance of the two energy input terms:

$$\frac{hA \Delta T}{\Gamma \cdot \omega} = \frac{mC_P}{\Gamma \cdot \omega} \frac{dT}{dt} - I$$

(4-7)

This representation avoids the direct computation of the heat transfer coefficient. The value of the above ratio equals -1 at steady-state when the material temperature becomes constant. The evolution of this ratio with mixing time for the compounding runs with roller blades is shown in Figure 4.11. The corresponding times to phase inversion in the small and large mixing bowls are indicated. In both mixing bowls the ratio has a large positive value in the region corresponding to the polyethylene continuous phase. This indicates that in the compounding of low-viscosity-ratio blends the heat conduction term dominates the viscous dissipation energy input. On scaleup to a large mixer, with geometrically similar blades, the specific area of the mixer decreases. With roller blades, the specific area decreases by a factor of 1.6 (2.6 cm\(^{-1}\) to 1.6 cm\(^{-1}\)) and for triangular blades the specific area decreases by a factor of 1.9 (2.45 cm\(^{-1}\) to 1.3 cm\(^{-1}\)). The observed times to
phase inversion on scaleup using roller blades increased on average by a factor of 3 (Table 4.5). Using triangular blades the time to phase inversion increased by a factor of 2.6 (Table 4.6). Thus the decrease in the specific area alone cannot explain the change in the time to phase inversion.

![Graph showing HAT/Theta over time for Small Roller Blades and Large Roller Blades](image)

**Figure 4.11:** Relative importance of heat conduction to mechanical energy input as a function of mixing time when the low-viscosity polyethylene forms the continuous phase. The curves were calculated using the torque and melt temperature data for a 92.2/7.8 PS/PE-D ($\lambda = 0.005$) blend compounded at 180° C using roller blades.

Both the reduced mechanical energy input due to the scaleup condition used in this study, and the decrease in specific area contribute to the observed increases in the time to phase inversion in the large mixer. However, it is clear that energy input to the material does not completely determine the time to phase inversion. If it did, then the time to phase inversion for a particular blend would always occur at the same temperature. Numerous studies, including this work, have shown that this is not the case (30, 44, 56). The specific work input to phase inversion is not independent of scale either. In fact, this quantity on average increases by a factor of 1.7 on scaleup using roller blades and by a factor of 1.9 using triangular blades. Nevertheless, analysis of the energy input is a good first step in
identifying the crucial parameters that determine the time to phase inversion. It makes a strong case for considering the specific area of the mixer as an important parameter in analyzing compounding of low-viscosity-ratio blends. An analysis of the microstructural changes which occur during compounding is necessary to predict the time to phase inversion, and this is the focus of a separate manuscript (Chapter 5).

A significant accomplishment of this work is the design of a blade system that is flexible and provides for multiple batch sizes in a single mixing bowl. In addition, blade element shapes other than triangles may be used to expand the collection of blade configurations available. Although our focus was on the compounding of blends exhibiting phase inversion during compounding we can easily extend the use of the modular blades to the study of any other process of interest in batch mixers.

Our experiments on axial scaleup in the same mixing bowl illustrate the flexibility and ease of use of the novel blade design for scaleup studies. The specific area for the different blade designs changes by less than 5%. The primary factor determining the time to phase inversion is the nature of material flow paths inside the mixer. Blade designs that allow for leakage flows that avoid the high shear tip regions are shown to reduce the stress transfer to the batch resulting in longer times to phase inversion. We have used a relative stagger parameter to identify different blade designs according to their effectiveness in bringing about phase inversion. This has direct application to the kneading block sections of twin-screw extruders. Using a parameter similar to the relative stagger parameter introduced here we can quantify the effect of stagger in the kneading block section on the screw length to achieve phase inversion. Our results indicate that, for a given length of the kneading section, decreasing the number of staggered elements increases their effectiveness in achieving phase inversion.

There are a number of similarities in the designs of the two kinds of blades used here. The nearly triangular cross-section of the roller blades was the motivating factor in the design of the modular blades. The roller blades are designed so that material is moved from the ends to the center of the mixing bowl providing good axial mixing of the batch. In our aligned configuration with the triangular blades, there is virtually no axial
movement of the batch. This was confirmed by visual observation of the batch movement through the feed chute. Each material element is confined to a small axial length and is deformed by repeated passage through the high-shear region. However, in both these designs there are no flow paths that avoid the high shear region. As outlined above, repeated passage of the polystyrene pellets through the high-shear region is critical to their deformation leading to phase inversion. The tip length and minimum gap for the triangular blades were machined to be the same as those of the roller blades. We would therefore expect similar times to phase inversion on using the roller blades or the triangular blades in the aligned configuration under the constant nominal maximum-shear-rate condition. A comparison of the corresponding entries in Table 4.5 and Table 4.6 shows that this is indeed the case. For the compounding of a 7.8wt.% PS/PE-D blend at 180°C, we obtain identical times to phase inversion in the small mixing bowl (8 min) and in the large mixing bowl the results from the two blade designs differ by one minute (22.5 min with roller blades and 21.5 min with triangular blades). This highlights the importance of the narrow-gap high-shear region in determining the time to phase inversion. Any model of this phenomenon as it is observed in batch mixing operations has to account for the time between successive passages through this region (Chapter 5) in a similar manner to models currently used for the dispersion of carbon black agglomerates into rubber matrices (60).

4.6 Conclusions

This work has investigated the scaleup behavior of phase inversion during compounding, commonly observed with low-viscosity-ratio blends. The compounding runs were performed in two different size mixing bowls with a model polystyrene/polyethylene blend. Each run was characterized by a time to phase inversion, corresponding to the formation of the continuous phase by the higher-viscosity polystyrene. The same mechanism of morphology development was observed over different batch sizes from 12g to 240g and under different mixing conditions. Over the range of parameters studied the occurrence of phase inversion was shown to be independent of scale and blade configuration with the kinetics of the transformation being determined by the specific process conditions.
On scaleup to the large mixer using roller blades the time to phase inversion increased by a factor of 3. Similar experiments with triangular blades resulted in an increase in the time to phase inversion by a factor of 2.6. The change in the time to phase inversion is influenced by a combination of the decreased specific area and a reduced mechanical energy input under the scaleup condition we used. Corresponding runs with roller blades and aligned triangular blades showed similar times to phase inversion, justifying the importance of the high-shear regions in determining the mixing time.

A notable feature of this work is the successful design and use of modular blades for scaleup studies in batch mixers. The flexibility of the design was exploited to study the effect of different blade configurations on the compounding behavior in the same mixing bowl. Axial scaleup runs using different elements in the same mixing bowl illustrated the importance of material flow paths in determining the time to phase inversion. For all these runs, the specific area remained essentially constant. The observed differences in the time to phase inversion were explained by introducing a specific relative stagger parameter. Increasing the specific relative stagger reduced the stress transfer to the batch, resulting in longer times to phase inversion. These results indicate that in twin-screw extrusion, increasing the stagger for a given kneading block section will increase the screw length required to achieve phase inversion.
5. VISUALIZATION AND MICROSCOPIC MODEL OF PHASE INVERSION

5.1 Introduction

Phase inversion during compounding, the subject of this investigation, is a mechanism of morphological change in the melting regime. Prior experimental work in batch mixers and twin screw extruders has identified different blend systems in which phase inversion occurs. In these blends there was a transformation from a major component dispersed in the minor component to a morphology of the major component forming the continuous phase as a function of mixing time (19, 28, 30, 44, 45). The melt viscosity ratio (minor component to major component viscosity under the process conditions), the volume fraction of the minor component, the mixer temperature program and the initial particle size have all been shown to influence the time to phase inversion (28, 30, 44). A two-dimensional framework based on the melt viscosity ratio and the transition temperatures of the blend components has been presented to summarize the existing results of blends that exhibit this phenomenon (56). Recent work in our laboratory has focused on scaleup of the compounding of blends exhibiting phase inversion (Chapter 4, 61).

From the accumulated experimental data a number of conclusions can now be drawn on the occurrence of this interesting phenomenon. For compounding in batch mixers, at a constant temperature above the softening temperatures of the two components, phase inversion has been shown to occur preferentially in blends with a melt viscosity ratio below 0.2 (61). The time to phase inversion has been reported to increase with increasing amount of the low-viscosity minor component in the blend. Increasing the mixer temperature decreases the time required to achieve a continuous phase of the major component (30).

Despite these observations, there are very few results that identify the individual morphologies en route to the formation of the continuous phase by the major component. A sheeting mechanism (13) has been proposed to describe the deformation and size scale reduction of the pellets during compounding. This mechanism has been used to explain the occurrence of phase inversion in blends with a low melting point minor component (29).
In such blends, it has been proposed that an initial melt of the minor component is formed. Deformation of the dispersed major component pellets proceeds by heating, softening and tearing away of the outer layers until a critical concentration of the major component in the melt is reached. At this mixing time the major component domains coalesce encapsulating the minor component thus bringing about an inversion in the phase continuity. A more detailed description of deformation of the major component pellets inside a lower viscosity melt is the subject of a recent investigation in our laboratory (57). Isothermal steady-shear conditions were used to study the deformation of dispersed polystyrene pellets in a polystyrene/polyethylene disk and the intermediate morphologies at different strains were identified. In contrast, our interest in this chapter is on phase inversion as it occurs during compounding in batch intensive mixers. Our focus is to identify the sequence of deformation steps of the major component dispersed inside a low-viscosity melt of the minor component (viscosity ratio, \( \lambda \sim 0.001 \)) as observed in a batch mixing operation. By using low-viscosity ratio blends and low mixing temperatures we achieved very long times to phase inversion. This enabled identification of the individual stages of deformation of the major component. These studies form the basis for the development of a model to predict the time to phase inversion.

Although a large number of studies have identified the different parameters that govern morphology development during compounding, theoretical description and modeling of the phenomenon has lagged far behind. Analysis of non-isothermal, large deformation flows in multiphase systems is a very difficult problem. Nevertheless, simplified models can be formulated with assumptions based on experimental observation of the flow-field and morphology development in batch mixers. Therefore our goals in this chapter are two-fold: to identify the sequence of deformation steps undergone by a major component leading to phase inversion in batch mixers and to develop a morphological model based on these observations to predict the time to phase inversion.

Our modeling effort for the flow-field identifies the narrow-gap high-stress regions as a defining feature of all blade designs used in batch mixers. Material transport through the high-stress region exerts large stresses on the batch causing effective dispersive mixing. The larger space between the rotors and the mixer wall act as an extensive mixing section,
bringing about good distributive mixing. For the compounding of carbon black agglomerates into polymeric matrices Manas-Zloczower et. al. (54, 55) provide a mathematical model for dispersive mixing in batch mixers. Their model consists of three sub-models:

1. The overall flow pattern in the mixer was modeled as a well-mixed region associated with the volume space between the rotors and a steady recycling stream over the high shear region.

2. A structural model of the carbon black agglomerates describing the magnitude of the cohesive forces holding the aggregates together.

3. The hydrodynamic behavior of the agglomerate on passage through the high-stress regions resulting in a viscous force tending to breakup the agglomerates.

The above model was used to determine the agglomerate size distribution as a function of mixing time and process conditions. Our observations of morphology development during phase inversion indicate an analogous process. Thus, we adapt the formalism of this approach to the problem of describing the deformation of the major component surrounded by a low-viscosity blend on repeated passage through the high-stress regions.

5.2 Visual Observation of Phase Inversion During Compounding

5.2.1 Experiments

Deformation of the major component in a low-viscosity ratio blend was investigated using a model system consisting of a poly(ethylene-co-cyclohexane dimethylene terephthalate), PETG, as the major component and polyethylene, PE, as the minor component. Previous work in our laboratory showed that this system is representative of many blends which undergo phase inversion during compounding. The major component PETG was an amorphous co-polyester with a T₆ of 80°C and the minor component was a PE wax with a melting peak at 100°C. The melt viscosity ratio (ηₑ / ηₑₑ at 100s⁻¹ and 120°C) was 0.001. The blend was compounded in a Haake Rheomix 600 batch mixer using roller blades. The concentration of polyethylene in the blend was fixed at 5wt.%. A batch size of 70g corresponding to 70% degree of fill was used to provide good
intermixing between the two halves of the mixing bowl. A modified front plate with a glass window was used for process visualization. The torque required to compound the batch at a constant rotor shaft speed of 50 r.p.m. and the melt temperature were monitored and these are shown in Figure 5.1. At different mixing times the motor was stopped and a small amount of the blend was withdrawn from the central mixing zone. These samples were air cooled and photographed to show the deformation of the PETG domains. These results are shown in Figure 5.2. A series of such experiments at different mixing temperatures were carried out and the salient features of the deformation of the PETG pellets are summarized below. In an earlier study with the same blend, using selective dissolution it was shown that the low-torque region during compounding corresponds to a continuous phase of polyethylene (56).

![Graph showing Torque and Melt Temperature over time](image)

Figure 5.1: Torque and Melt Temperature from the compounding of a PETG/PE (95/5) blend at 120°C in a batch mixer using roller blades. The blend viscosity ratio was 0.001. The dips in the torque curve correspond to the times when the mixer was stopped and the sample was quickly collected. These samples are shown in Figure 5.2.

### 5.2.2 Summary of Morphological Changes

The following morphological changes leading to phase inversion were observed:
1. A melt film of PE coated all the undeformed pellets of PETG. This occurred between 30s and 2 minutes into mixing, the longer times corresponding to the lower mixer temperature runs.

2. PETG pellets were conveyed by the melt in the mixing chamber and occasionally underwent shearing at the smallest gap region between the blades and the mixing bowl.

3. A central column of packed PETG pellets was formed between the two chambers of the mixing bowl. The blades were seen to slip past this column, simultaneously compacting and exerting shearing forces on it.

4. The pellets of PETG were flattened into pancake-shaped disks, by successive passages through the nip region (Figure 5.2 b,c). The initial 3mm high cylindrical pellets were reduced to ~ 1mm thick disks.

5. At this dimension, the individual pellets could not be deformed any further as their thickness was less than the minimum gap in the mixer. Further deformation required a packing of multiple disks to form a stack which could then be deformed as a whole.

6. Formation of the stacked pile of PETG disks required the draining away of the intervening PE film. At lower mixer temperatures, this took longer and individual PETG disks could be identified even after 45 minutes of mixing at 120°C (Figure 5.2c).

7. Thin fibers were drawn from the one of the corners of the PETG stacks, which were then broken off (Figure 5.2 c-e). At this stage of mixing the blend began to turn opaque, indicating the presence of very small domains of PETG.

Continued mixing resulted in an almost entirely fibrous blend (a “sugar-candy” texture) and the fibers began to fuse to form a single continuous phase (Figure 5.2f). Homogenization of the blend required the tearing away of clumps of material and passage through the nip region. Further direct visual observation through the glass window was not possible beyond this stage in mixing.
Figure 5.2(a) 10 Minutes

(b) 25 Minutes

(c) 45 Minutes
Figure 5.2: Blend samples from the compounding run shown in Figure 5.1, were collected and air-cooled. The corresponding times are indicated. The major component PETG is clearly visible whereas the molten polyethylene forms a thin coating on the PETG pellets.

Similar compounding runs at different mixer temperatures showed qualitatively the same behavior of the major component leading to phase inversion. The notable differences were in the rate of progression through the different morphological regimes and these observations are listed below.
1. At lower mixer temperature there was a greater degree of homogeneity in the blend dispersion at any given time. Only one particular morphology—slightly deformed PETG pellets or flattened PETG disks or fibrous PETG strands—was observed at a certain mixing time.

2. Agglomeration of PETG disks to form stacks that could be deformed further was facilitated at higher temperature. It appeared that the higher temperatures resulted in greater probability that the collision of two PETG disks would result in their confluence.

3. This sequence of events was completed in shorter mixing times at higher temperatures, thus reducing the time to phase inversion.

4. At the highest temperatures studied here, 160 and 180°C, the fibrous morphology of PETG could not be separately identified. It is possible that at the higher temperatures, greater viscous flow aided the deformation and coalescence of fused PETG clumps, without the need for an intermediate fibrous stage.

It was seen that by reducing the mixer temperature, the different deformation steps required for the transformation of PETG pellets dispersed in molten PE to a continuous melt of PETG, could be clearly identified. The primary steps for phase inversion to occur are the deformation and coalescence of PETG pellets. These take place in a cyclical manner: deformation of softening pellets into disks, agglomeration of these disks into stacks accompanied by drainage of the low-viscosity film; deformation of these stacks as a unit, drawing and tearing away of fibers, formation of clumps of fibrous material and further homogenization till a continuous matrix of PETG is formed. A similar cycle of deformation of the dispersed major component, drainage and rupture of the intervening film of the minor component, and coalescence of the major component domains was observed in model experiments under isothermal, steady-shear flow in a PS/PE disk (57).

The above exposition identifies typical morphological changes en route to phase inversion during compounding. These observations form the basis for a theoretical model of this phenomenon. A simplified representation of the above sequence of events is used to obtain an expression predicting the time to phase inversion during compounding.
Predictions of the model are compared to experimental data from compounding runs with low-viscosity ratio blends in batch mixers (Chapter 4).

5.3 Modeling of Phase Inversion During Compounding in Batch Mixers

During compounding in a batch mixer the material periodically passes over the narrow-gap high-stress region between the blades and the mixing bowl. This is a characteristic feature of all blade designs used in batch intensive mixers. Different blade designs differ in the length of the high-stress region and the nature of the flow field in the large gap between the two blades. For example, roller blades have three narrow-width tip regions on each blade and move the material to the central portion of the mixer from the ends. For a complete description of flow in the mixer the three-dimensional time-dependent field equations must be solved. Early attempts using finite elements were restricted to modeling the 2-d flow in the mixer ignoring the axial flow (62, 63). More recently the full three-dimensional isothermal flow for a power law fluid has been simulated by using a number of sequential geometries to represent a complete mixing cycle (64, 65). These simulations are computationally intensive and require the use of supercomputers. In contrast to this approach, White et. al. (66-68) have proposed the use of lubrication approximation to simplify the mixer flow-field. This approach has been used to model Newtonian (66, 67) and non-Newtonian, non-isothermal flow (68) of a fully filled batch intensive mixer. The authors use an integral method in the solution procedure and represent the flow-field in terms of the axial, tangential and inter-rotor flux in the mixer.

A significant simplification of the flow-field can be achieved by lumping the large gap regions into a single well-mixed region and focusing on the small gap regions as the source of most of the dispersive mixing (9, 54). This assumes that good material redistribution occurs between successive passages through the high-stress region. By lumping the large clearances in the mixer into a single region, the rate determining step in the compounding operation is assumed to be material passage through the high-stress region. This simplifying assumption confines the deformation of the material to the high-stress regions interspersed with homogenizing flow in the well-mixed region. Our visual studies of phase
inversion indicate that the deformation of the dispersed major component pellets proceeds via periodic passage through the high-stress region, consistent with this conceptual picture.

In addition to the flow-field, the model requires a description of material deformation in the flow-field of the mixer. From our visualization experiments it is clear that the low-viscosity minor component forms the continuous phase at short mixing times. The major component is dispersed as individual domains whose repeated deformation and coalescence leads to phase inversion. Therefore we develop a description of the deformation of the major component encapsulated by a lower viscosity minor component on passage through the high-stress regions of the mixer. The model approximates the different steps leading to phase inversion as observed in our visualization experiments. Thus the focus of the model is twofold: representation of the flow field in the batch mixer and description of the deformation of the major component on repeated passage through the high-stress regions in the mixer.

5.3.1 Idealization of the Batch Mixer Operation

The batch mixer is modeled as a low-shear well-mixed region with a small amount of recirculating flow over the high-stress narrow-gap regions. This is illustrated schematically in Figure 5.3. The flow rate over the high-stress regions is calculated assuming pure drag flow between the blade tip and the mixer wall. Combining the flow-rate over each blade tip, the total flow-rate over the wings of the two blades is (55):

\[ Q = Q_{\text{left}} + Q_{\text{right}} = m_l \frac{\pi D_{\text{blade}} N_l H}{2} L_{\text{blade}} + m_r \frac{\pi D_{\text{blade}} N_r H}{2} L_{\text{blade}} \] (5-1)

where \( m_l, m_r \) are the number of wings of the blades; \( D_{\text{blade}}, L_{\text{blade}} \) are the largest diameter and the length of each blade; \( N_r, N_l \) are the rotational speeds (in rotations per second) of the right and left blades, and \( H \) is the minimum gap between the blades and the mixer wall. When the blades are rotated with a friction factor of \( 2/3 \) (i.e. \( N_r = (2/3) N_l \)) and for roller blades where the number of wings on each blade is three (\( m_l = m_r = 3 \)) the above equation simplifies to:
\[ Q = \frac{5\pi D_{blade} N_1 H L_{blade}}{2} \quad (5-2) \]

For a batch of volume \( V \), the average time between successive passes over a high-stress region can then be defined as:

\[ \bar{t} = \frac{V}{Q} = \frac{2V}{5\pi D_{blade} N H L_{blade}} \quad (5-3) \]

where the subscript on the blade speed has been dropped. There are no material properties involved in the calculation of \( \bar{t} \). Therefore, for all dispersive mixing operations in the mixer where passage through the high-stress region is critical, \( \bar{t} \) is the relevant time scale for the process.

Figure 5.3: Schematic of the batch mixer considered as a well-mixed volume \( V \), and a re-circulating flow over the high-stress region \( Q \).

Extension of the analysis to the specific phenomenon of phase inversion requires a description of the deformation of the major component during a single-pass through the high-stress region. Since the flow-field in the high-stress region is a combination of both shear and extensional flow, simple shear flow and planar extensional flow are both considered.
5.3.2 Description of Material Deformation—Simple Shear Flow

Consider a stratified layer-morphology with the major component encapsulated by the minor component film as shown schematically in Figure 5.4. Flow in the high-stress region has been approximated as the two-dimensional flow between infinite parallel plates with the top plate moving at the peripheral velocity of the blade tip. Neglecting pressure gradients in the flow direction and assuming creeping flow, the steady x-direction momentum equation reduces to:

\[
\frac{d\tau_{yx}}{dy} = 0
\]  \hspace{1cm} (5-4)

For generalized Newtonian liquids the constant-shear-stress condition yields a linear velocity profile in each layer. No-slip conditions at the bounding walls and at the interfaces between the layers along with the constant-shear-stress condition can be used to solve for the velocity profile in each layer. The shear-rates can then be calculated from the velocity profiles in the minor and major component layers and are:

\[
\dot{\gamma}_{\text{minor}} = \dot{\gamma}_{\text{nom}} \frac{\eta_{\text{major}}}{(\phi_{\text{major}} \eta_{\text{minor}} + \phi_{\text{minor}} \eta_{\text{major}})} \]  \hspace{1cm} (5-5)

\[
\dot{\gamma}_{\text{major}} = \dot{\gamma}_{\text{nom}} \frac{\eta_{\text{minor}}}{(\phi_{\text{major}} \eta_{\text{minor}} + \phi_{\text{minor}} \eta_{\text{major}})} \]  \hspace{1cm} (5-6)

Figure 5.4: Schematic of the deformation of the major component on passage through the narrow-gap high-stress region of the mixer. Pure drag flow with a constant shear stress across the gap is assumed.
where $\dot{\gamma}_{nom} = \sqrt{H}$ is the nominal velocity gradient and the $\varphi$’s are volume fractions of the major and minor components. For a given length of the high shear region, $L_{hs}$, the average residence time in the high-stress region is $2L_{hs}/v$. Therefore, the average strain accumulated by the major component during a single passage through the high-stress region is:

$$\bar{\gamma}_{major,\, one\,-\,pass} = \frac{\eta_{minor}}{\left(\varphi_{major} \eta_{minor} + \varphi_{minor} \eta_{major}\right)} \frac{2L_{hs}}{H} \tag{5-7}$$

Defining a viscosity ratio $\lambda = \frac{\eta_{minor}}{\eta_{major}}$ and rewriting the volume fraction of the minor component $\varphi_{minor}$ as $\varphi$ in the above equation we obtain:

$$\bar{\gamma}_{major,\, one\,-\,pass} = \frac{\lambda}{\left(1 - \varphi\right)\lambda + \varphi} \frac{2L_{hs}}{H} \tag{5-8}$$

5.3.3 Material Deformation—Planar Extensional Flow

Planar extensional flow has been chosen to approximate the material response to elongational components in the high-stress region of the mixer. From Figure 5.2, the presence of flattened disks and fibers being pulled from these domains indicates the presence of significant elongational components in the flow inside the mixer. A schematic of the flow between two parallel plates under planar extension is shown in Figure 5.5. Under the assumption of affine deformation, the velocity profile in each component is the same and is given by:

$$v_x = \dot{\varepsilon} x \quad and \quad v_y = -\dot{\varepsilon} y \tag{5-9}$$

where $\dot{\varepsilon}$ is the rate of extension. Under these conditions, both components undergo equal rates of extension. The average strain undergone by the major component can be written as:

$$\bar{\varepsilon}_{major,\, one\,-\,pass} = \left(\frac{H_{max} - H}{H}\right) \tag{5-10}$$
where $H_{\text{max}}$ is the maximum gap between the blades and the mixer wall. This is an approximate representation of the extensional strain experienced by the major component due a squeezing flow which changes the gap between the blades and the mixer from $H_{\text{max}}$ to $H$. In contrast to eq. 5-8, the strain in the major component under planar extensional flow is thus independent of the volume fraction of the minor component and the viscosity ratio of the blend. Implications of this result to the predictions obtained from the model are discussed further under model validation.

Figure 5.5: Schematic of the planar extensional approximation to the flow-field in the high-stress regions of the mixer.

5.3.4 Strain Distribution Function for the Batch Volume

The strain undergone by the major component is assumed to accumulate over a number of passes through the high-stress region. With this assumption, at any mixing time we can compute a strain distribution function for the major component if we know the distribution function for the number of passes through the high-stress region. When the high-stress region is a small fraction of the total batch volume it has been shown (54) that the probability, $p_k(t)$, that a given particle has made $k$ passes through the high-stress region is well approximated by a Poisson distribution:

$$p_k(t) = \frac{(\frac{t}{\bar{t}})^k}{k!} \exp\left(-\frac{t}{\bar{t}}\right)$$  \hspace{1cm} (5-11)
This is also the volume fraction of the batch that has undergone \( k \) passes at any given time \( t \). From the above distribution the volume fraction of the batch that has undergone exactly \( k \) passes is a maximum at \( k = \frac{t}{t'} \).

### 5.3.5 Strain Based Criterion for Phase Inversion

Deformation of the major component and drainage of the intervening film of the low-viscosity minor component are crucial to the coalescence of the major component domains bringing about phase inversion. The visualization studies mentioned above highlight the various modes of deformation of the PETG pellets leading to phase inversion. Recent work in our laboratory on phase inversion under isothermal steady-shear conditions in a polystyrene/polyethylene disk (57) used a strain measure to characterize the progression to a PS continuous phase blend.

These experimental results suggest a criterion for phase inversion based on the strain imparted to the major component. In our model we propose that phase inversion occurs at a critical strain \( \gamma_c \), in the major component. This requires \( n_c = \frac{\gamma_c}{\gamma_{\text{one-pass}}} \) passes through the high-stress regions. From eq. 5-11, the volume fraction of the batch that has undergone \( n_c \) passes at a given mixing time can be calculated. This is a maximum when \( \frac{t}{t'} = n_c \). Moreover at this mixing time, approximately half the batch has made \( n_c \) passes through a high-stress region. Using this mixing time as our estimate for the time to phase inversion and substituting from eqns. 5-3 and 5-8 (for the shear strain), we obtain:

\[
 t_{P.I.} = \frac{\bar{\gamma}_c}{\bar{\gamma}_{\text{one-pass}}} \bar{t} = \frac{\bar{\gamma}_c \left[(1 - \varphi) \lambda + \varphi\right]}{\lambda L_{\text{ns}}} \frac{V}{5\pi D_{\text{blade}} N L_{\text{blade}}} \quad (5-12)
\]

The analogous expression for time to phase inversion using the extensional strain, eq. 5-10 is:

\[
 t_{P.I.} = \frac{\bar{\gamma}_c}{\bar{\varepsilon}_{\text{one-pass}}} \bar{t} = \frac{\bar{\gamma}_c}{H_{\text{max}} - H} \frac{2 V}{5\pi D_{\text{blade}} N L_{\text{blade}}} \quad (5-13)
\]
This extensional-strain expression for the time to phase inversion does not depend on the volume fraction of the minor component or the blend viscosity ratio. The actual flow-field has both shear and extensional components. Therefore, the experimentally observed times to phase inversion should be explained by a combination of the above two equations.

These are the first reported expressions for computing the time to phase inversion during compounding in batch mixers. In the derivation above, isothermal conditions were assumed and a simplified representation of the flow was used. In addition, the blend components were assumed to be Newtonian liquids and a single strain measure was used to calculate the time to phase inversion. Use of this expression to predict the time to phase inversion should account for these limitations. With this caveat, the model predictions are compared to results from compounding of different low viscosity ratio polystyrene/polyethylene blends reported in the previous chapters.

5.4 Model Validation

5.4.1 Compounding Experiments

Compounding experiments were performed in two different mixing bowls. The melt viscosity ratio of the blend was varied by choosing different polyethylenes in the PS/PE blends (Chapter 4). In all the blends the melt viscosity ratio \( \lambda = \eta_{PE} / \eta_{PS} \) at the mixer temperature was below 0.05. Blend composition was also varied for one blend (PS/PE-D with \( \lambda = 0.005 \)). Every compounding run was characterized by the time to phase inversion—the time required to form a continuous phase of polystyrene. Our initial runs used roller blades to compound a PS/PE (7.8wt.% polyethylene) blend with a viscosity ratio of 0.005 at 180°C in two different mixing bowls. A constant nominal maximum-shear-rate condition was used to calculate the rotor speed for each mixing bowl.

5.4.2 Effect of Scaleup on \( t_{PI} \)

Using the blade specifications in Table 5.1 we can compute \( \tilde{t} \) for the two mixing bowls. From eq. 5-3 we have:

\[
\tilde{t}_{\text{small-mixer}} = 3.1 \text{ s} ; \quad \tilde{t}_{\text{large-mixer}} = 7.6 \text{ s} = 2.45 \times \tilde{t}_{\text{small-mixer}} \quad (5-14)
\]
<table>
<thead>
<tr>
<th>Mixer Capacity</th>
<th>Small Mixer</th>
<th>Large Mixer</th>
<th>Ratio (Large / Small)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>69 cm³</td>
<td>350 cm³</td>
<td>5</td>
</tr>
<tr>
<td>Blade Diameter</td>
<td>3.64 cm dia.</td>
<td>6.70 cm dia.</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>4.67 cm long</td>
<td>8.40 cm long</td>
<td>1.8</td>
</tr>
<tr>
<td>Mixing Bowl Dimensions</td>
<td>3.92 cm dia.</td>
<td>7.00 cm dia.</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>4.76 cm long</td>
<td>8.60 cm long</td>
<td>1.8</td>
</tr>
<tr>
<td>Minimum gap between blades and mixing bowl</td>
<td>1.4 mm</td>
<td>1.5 mm</td>
<td>1.1</td>
</tr>
<tr>
<td>Length of high-stress region, $L_h$</td>
<td>0.32 cm</td>
<td>0.32 cm</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Thus the average time between passes through a high-stress region is larger by a factor of 2.45 in the large mixer. The experimentally determined time to phase inversion for this blend increased from 8 min in the small mixer to 22.5 min in the large mixer; an increase by a factor of 2.8. This close an agreement using the above model indicates that the idealization of the flow-field into a well-mixed region and a recirculating stream through the high-stress region is valid. Therefore for any other blade design and mixing bowl the calculation of $\bar{t}$ should provide a good estimate for the increase in the time to phase inversion on scaleup. Further evidence of this conclusion is provided from results of the time to phase inversion using modular blades of different lengths in the same mixing bowl. For these blades, described in Chapter 4, the batch volume was increased by adding additional elements along the axis of the blade shaft. This does not change the value of $\bar{t}$, and the observed times to phase inversion were constant, neglecting the effect of blade configuration.

### 5.4.3 Effect of Shear Rate on $t_{P.I.}$

Our visualization studies illustrate that flow through the high-stress regions critically influence morphology development. The nominal shear-rate $\dot{\gamma}_{nom}$, is a measure of the rate of deformation in the high-stress regions. Rewriting eq. 5-12 to include this term we have:

$$t_{P.I.} = \frac{\bar{\gamma}_c \left[ (1-\varphi)\lambda + \varphi \right]}{\lambda L_{hs} H} \frac{V}{5\dot{\gamma}_{nom}}$$  \hspace{1cm} (5-15)
This equation predicts that the time to phase inversion is inversely proportional to the nominal maximum-shear-rate in the mixer. A similar dependence is predicted from the extensional flow expression, eq. 5-13. Compounding runs were done with the above PS/PE blend at 180°C and different rotor speeds. For each run the time to phase inversion and the corresponding nominal maximum-shear-rate were calculated. These results are plotted in Figure 5.4. The two sets of data correspond to runs in the two mixing bowls. For each mixing bowl, the data were fit to a curve of the form $t_{P.I.} = \frac{A}{\gamma_{nom}}$, where $A$ is a constant. As seen from Figure 5.4, experimental data did indeed show the functional

![Graph showing time to phase inversion vs shear rate for Large and Small Rollers](image)

Figure 5.6: Variation in the time to phase inversion during compounding of a PS/PE-D (92.2/7.8) blend with a viscosity ratio of 0.005 using roller blades in two different mixing bowls. The mixer temperature was kept constant at 180°C and different shear-rates were achieved using different rotor speeds.

dependence derived in the above model.

5.4.4 Effect of $\phi$ and $\lambda$ on $t_{P.I.}$

For compounding of blends with a viscosity ratio $\sim 0.001$ and with low minor component concentrations ($<10$ vol.%) eq. 5-12 simplifies to:
\[ t_{P.I.} = \frac{\tilde{V}}{\lambda L_{hs} H} \frac{V}{\tilde{\gamma}_{nom}} \]  

(5-16)

In the derivation of the above equation the flow in the nip regions was assumed to be pure drag flow. This neglects the effect of extensional components in the wedge-flow approaching the nip. Our experimental observations (Figure 5.2) indicate the presence of highly elongated domains (flattened disks, fibers pulled from these disks) en route to phase inversion. Thus extensional flow is also important in determining the morphological changes leading to phase inversion. In our derivation above, the effects of shear and extensional components were considered separately. In the actual flow-field shear and elongational strains occur simultaneously and the time to phase inversion will be determined by a combination of the two effects. The shear equation (eq. 5-12) predicts a (-1) power dependence on \( \lambda \) and a (+1) power dependence on \( \phi \). In contrast, the extensional flow equation (eq. 5-13) indicates that \( t_{P.I.} \) is independent of these two factors. Therefore we expect:

\[ t_{P.I.} \propto \phi^n \text{ where } 0 \leq n \leq 1 \]

\[ t_{P.I.} \propto \lambda^m \text{ where } -1 \leq m \leq 0 \]  

(5-17)

To test these predictions, PS/PE blends with different concentration of PE and melt viscosity ratio of 0.005 were compounded at 180°C and the observed times to phase inversion are plotted in Figure 5.7. A curve fit through the experimental data indicated that the functional dependence was \( \sim \phi^{0.47} \) in the large mixer and \( \sim \phi^{0.61} \) in the small mixer.

To test the effect of viscosity ratio on the time to phase inversion, three different PS/PE blends were used. In each blend the PE concentration was fixed at 7.8wt.% (9.7vol.%). The observed times to phase inversion for compounding in two different mixing bowls with roller blades are shown in Figure 5.8. The best curve fit through each data set showed a less than inverse dependence of \( t_{P.I.} \) on the viscosity ratio (\( \sim \lambda^{-0.53} \) in the large mixer and \( \sim \lambda^{-0.44} \) in the small mixer). Therefore, the model predictions are in agreement with the experimental observations on the dependence of \( t_{P.I.} \) on \( \phi \) and \( \lambda \).
Figure 5.7: Observed times to phase inversion during compounding of different PS/PE-D blend compositions at 180°C using roller blades in two different mixers. The observed dependence on the volume fraction of PE-D is also indicated.

Figure 5.8: Observed dependence of the time to phase inversion on the melt viscosity ratio during compounding of a PS/PE-D (92.2/.78) blend at 180°C in two different mixers.
5.4.5 Model Limitations and Extension

The above approach while providing explicit expressions for the time to phase inversion has a number of aspects that need to be further explored and refined. The model as developed above is an isothermal one. Chapters 3 and 4 present compounding runs with low-viscosity ratio blends that show a pronounced low-torque region corresponding to a continuous phase of the minor component. The temperature rise in these blends was shown to be determined primarily by heat conduction from the walls, due to the reduced viscous dissipation in the melt. For such blends with a slow rate of heating, an isothermal assumption is a good first approximation for calculating the time to phase inversion. Hence, greater divergence of model predictions from experimental results is expected for lower volume fractions of the minor component, higher viscosity ratios and higher rotor speeds.

As the volume fraction of the minor component is decreased blend viscosity and hence viscous dissipation increases. This results in faster heating of the dispersed major component domains and a further reduction in the time to phase inversion. Similar increase in the viscous dissipation is observed at higher viscosity ratios corresponding to a higher viscosity of the minor component. If these effects are taken into account, a stronger than linear dependence on the volume fraction of the minor component and a stronger than inverse dependence on the viscosity ratio are predicted. This is in contrast to experimental observations of $t_{p,i} \sim \lambda^{-0.5} \phi^{0.5}$. Therefore a modification to the model to account for non-isothermal effects was not pursued.

We have introduced a critical strain to phase inversion, $\bar{\gamma}_c$, as a single unknown parameter that corresponds to the time at which phase inversion occurs. The values of $\bar{\gamma}_c$ under different compounding runs with PS/PE blends as evaluated from eq. 5-12 are listed in Table 5.2. Conceptually, $\bar{\gamma}_c$ represents the amount of strain that adjoining major component pellets need to undergo before the intervening film of the minor component can be drained and coalescence can occur. In our analysis, we assumed a constant value for $\bar{\gamma}_c$. This could be thought to represent the critical strain at a reference temperature above the $T_c$ of the major component. Extension of the above modeling approach requires
an investigation of the dependence of $\bar{\gamma}_c$ on different process parameters. From the existing literature on coalescence, it is expected that $\bar{\gamma}_c$ increases with the volume fraction of the minor component as the film thickness between neighboring major component domains increases. This, along with the deformation of major component under shear, would predict a greater than linear dependence of the time to phase inversion on $\phi$.

In order to extend the model to predict actual values of the time to phase inversion, good estimates of $\bar{\gamma}_c$ under different conditions are required. An example of a technique to obtain this data would be the isothermal steady-shear experiments in a PS/PE disk as performed by Lazo and Scott (57). Similar experiments need to be carried out at different temperatures and volume fractions of the minor component.

Table 5.2: Calculated values of the critical strain to phase inversion $\bar{\gamma}_c$ using eq. 5-12 and experimentally observed times to phase inversion during compounding of PS/PE blends using roller blades in two different mixers.

<table>
<thead>
<tr>
<th>BLEND</th>
<th>VOLUME FRACTION</th>
<th>SMALL MIXER</th>
<th>LARGE MIXER</th>
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</thead>
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<tr>
<td>PS / PE-D ($\lambda = 0.005$)</td>
<td>2.52</td>
<td>50</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>37</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>9.7</td>
<td>26</td>
<td>37</td>
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<table>
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<tr>
<td>0.05</td>
<td>71</td>
<td>88</td>
</tr>
<tr>
<td>PS / PE (7.8wt.% PE)</td>
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<td>26</td>
</tr>
<tr>
<td></td>
<td>0.003</td>
<td>22</td>
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<table>
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<td>15</td>
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<td>68</td>
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<td>37</td>
</tr>
<tr>
<td>98</td>
<td>-</td>
<td>37</td>
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<tr>
<td>PS / PE-D</td>
<td>117</td>
<td>43</td>
</tr>
<tr>
<td>(7.8wt.% PE, $\lambda = 0.005$)</td>
<td>140</td>
<td>41</td>
</tr>
<tr>
<td>152</td>
<td>-</td>
<td>37</td>
</tr>
<tr>
<td>188</td>
<td>-</td>
<td>41</td>
</tr>
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</table>
5.5 Conclusions

Using a model PETG/PE blend we have identified the sequence of steps in the deformation of the major component during compounding in batch mixers leading to phase inversion. A cyclical process of size scale reduction was observed. The pellets were flattened into disks, which then clustered together to form stacks that could be deformed in the narrow-gap regions of the mixers. Fibers were pulled from the ends of the deformed clusters resulting in a large decrease in the size scale of the major component. Continued fiber pulling and homogenization led to a continuous phase by the major component.

A simplified model of this process was developed. The flow-field in the mixer was idealized as a well-mixed region with a recirculating flow through the high-stress regions. Deformation of the major component pellets on passage through the high-stress regions was calculated assuming a multi-layer pure drag flow and extensional flow. These two aspects of the model were combined with a strain-based criterion for phase inversion. An explicit expression for the time to phase inversion was derived with a single unknown, the critical strain to phase inversion.

The model predictions were found to be in excellent agreement with the observed scaleup of the time to phase inversion between two different mixing bowls. The model correctly predicted the inverse power dependence of the time to phase inversion on the maximum nominal-shear-rate in the mixer. A combination of shear and extensional flow, as evident from our visualization studies, was used to explain the observed dependence of $t_{PL}$ on $\phi$ and $\lambda$. Limitations of the model as developed here and possible extension based on a better understanding of the variation of $\bar{\gamma}_c$ with process conditions was discussed.

5.6 Nomenclature

<table>
<thead>
<tr>
<th>English Symbols</th>
<th>Mathematical Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>number of passes through the high-stress region</td>
</tr>
<tr>
<td>$m_l$, $m_r$</td>
<td>number of wings on the left and right rotors in the batch mixer</td>
</tr>
<tr>
<td>$n_c$</td>
<td>number of passes to accumulate the critical strain, $\bar{\gamma}_c$</td>
</tr>
<tr>
<td>$p_k$</td>
<td>Poisson distribution function representing the number of passes through a high-stress region</td>
</tr>
</tbody>
</table>
\( \bar{i} \) 
average time between successive passes through a high-stress region in the batch mixer

\( t_{p,l} \) 
time to phase inversion during compounding

\( v \) 
peripheral velocity at blade tip

\( D_{blade} \) 
outer blade diameter

\( H, H_{max} \) 
minimum and maximum gap between the blades and the mixer wall

\( L_{blade} \) 
length of the blade

\( L_{hs} \) 
length of the high-stress region (blade tip width)

\( N_l, N_r \) 
left blade rotational speed in rotations per second

\( N_r \) 
right blade rotational speed in rotations per second

\( Q \) 
flow rate in the high-stress region

\( V \) 
batch volume

Greek Symbols

\( \dot{\varepsilon} \) 
rate of extension under planar extensional flow

\( \bar{\varepsilon}_{\text{one-pass}} \) 
average extensional strain in a single pass through the high-stress region

\( \phi, \phi \) 
volume fraction of the minor component in the blend

\( \dot{\gamma}_{\text{nom}} \) 
nominal maximum-shear-rate in the gap (\( v / H \))

\( \dot{\gamma}_{\text{major}} \) 
shear-rate in the major component layer

\( \bar{\gamma}_{\text{major, one-pass}} \) 
average strain in the major component in a single pass through the high-stress region

\( \dot{\gamma}_c \) 
critical strain required for phase inversion

\( \eta_{\text{minor}}, \eta_{\text{major}}, \eta \) 
melt viscosity of the components at representative process conditions

\( \lambda \) 
melt viscosity ratio (\( = \eta_{\text{minor}} / \eta_{\text{major}} \))

\( \tau_{yx} \) 
shear-stress in the gap
6. CONCLUSIONS

This thesis investigated morphology development in the melting regime during compounding of immiscible polymer blends. Blend systems that show an intermediate morphology of a continuous phase of the minor component with the major component dispersed in it have been studied. A transformation to a continuous phase of the major component with further mixing was shown to occur and different aspects of this phenomenon of "phase inversion during compounding" were investigated. The main contributions of this work are:

1. First demonstration that phase inversion during compounding can occur in a blend with higher-melting point minor component. The PCL/PE blends mentioned in Chapter 2 were the first example of such a system.

2. Developed a two-dimensional framework based on blend viscosity ratio and transition temperatures of blend components to identify and categorize systems that show phase inversion during compounding. This framework, presented in Chapter 3, is the first attempt to consolidate processing behavior based on morphology evolution during compounding.

3. Proved the occurrence of the same mechanism of morphology development during compounding of low-viscosity-ratio blends in batch sizes from 12g to 240g.

4. Designed and built a novel modular blade design for investigating compounding behavior at different size scales in batch mixers.

5. Exploited the design features to study both axial and radial scaleup of batch sizes and introduced a specific relative stagger parameter to differentiate processing behavior with different blade configurations.

6. Developed the first microstructural model for phase inversion based on a detailed description of deformation steps leading to it. The model presented in Chapter 5 includes the derivation of an explicit expression to predict the time to phase inversion during compounding.
Prior understanding of the phase inversion mechanism was limited to blend systems with a higher-melting-point major component. The melting points of the two components alone were believed to influence the melting order during compounding. Chapter 2 introduces a blend system where we observed phase inversion in a blend with a lower-melting-point major component. This system illustrates that in addition to the melting points of the two components, component rheologies critically determine the continuous phase at short mixing times during compounding.

The small-strain rheological behavior of the blend components was measured from room temperature to the process temperature and a combination of lower shear modulus in the solid state and a lower viscosity in the melt state was shown to favor the formation of a continuous phase. For blend systems with a shear modulus ratio close to 0.1, simultaneous deformation of both components leading to an initial co-continuous morphology was observed. Chapter 3 identifies a PB/PCL system with a $G'$ ratio of 0.1 that exhibited a co-continuous morphology at short mixing times, due to simultaneous deformation of the two components. For blends with a low-modulus minor component (PE-D minor-component blends in Chapters 3 and 4) the initial melt and hence a continuous phase of the minor component encapsulating all the major component domains was observed. Further, a low-melt-viscosity was shown to reduce viscous dissipation and hence heating and deformation of the major component, delaying inversion in phase continuity of the blend. For compounding runs at a constant mixer temperature phase inversion was shown to occur in blends with a viscosity ratio ($\eta_{\text{minor}}/\eta_{\text{major}}$) less than 0.2. Use of temperature ramping during compounding resulted in an initial continuous phase of the lower-melting-point component. In blends with a viscosity ratio of ~0.001, the lower energy dissipation could be directly observed as a reduced torque value during compounding. During the compounding of these blends, a rise in torque was shown by selective dissolution to correspond to the deformation and the coalescence of the major component domains and the progressive encapsulation of the minor component. Our investigations have shown that a low-melt-viscosity ratio and a lower melting point of the minor component favor the occurrence of phase inversion during compounding.
The same mechanism of formation of an initial continuous of the minor component, followed by heating, softening of the major component domains leading to an inversion in phase continuity was shown to occur at batch sizes from 12g to 240g using different blade designs in two batch mixers. As the emphasis was on the mechanism of morphology development, we chose a representative low-viscosity ratio PS/PE system for our studies. The results are thus expected to be applicable to a wide variety of formulations. Phase inversion was shown to occur at all size scales with the kinetics of the transformation determined by the mixing bowl size and the blade design. The ratio of energy input due to heat conduction to that due to viscous dissipation was quantified and the heat conduction term was shown to be the dominant energy input term during compounding. The energy input to achieve phase inversion does not remain constant and hence an energy based criterion for phase inversion will not be a valid criterion.

To facilitate compounding runs at different mixer capacities using the same mixing bowl, a novel modular blade design was conceived and constructed. The flexibility of the design allows for easy access to multiple batch volumes and the potential to study the effect of different blade configurations on any compounding phenomenon of interest. Our studies on the time to phase inversion using different configurations were summarized using a specific-relative-stagger parameter that quantifies the effectiveness of stress transfer per unit mass of the batch. Increasing the specific relative stagger was shown to reduce the stress transfer and hence increase the time to phase inversion.

Our visualization studies using a glass window on the batch mixer showed periodic deformation of the batch on passage through the high-stress tip regions in the mixer. Using a representative low-viscosity-ratio PETG/PE system, different stages of deformation: disks, stacks of flattened disks, fibers and clusters of fibers; of the major component leading to phase inversion were identified. Based on these observations a model to predict the time to phase inversion was developed and presented in Chapter 5. Using a strain-based criterion for phase inversion and a simplified flow-field in the mixer, deformation of the major component in a melt of the minor component was computed. Model predictions of the increase in the time to phase inversion on scaleup are shown to agree with experimental observations of Chapter 4. In addition, the correct dependence of
the time to phase inversion on the nominal-shear-rate in the mixer, the volume fraction of the minor component and melt-viscosity-ratio of the blend was predicted. This is the first reported model that incorporates an approximation to the detailed morphological changes leading to phase inversion during compounding.

6.1 Significance of Results

Polymer blending requires a thorough understanding of the individual regimes of material behavior in order to achieve target morphologies. The focus of this thesis has been the melting regime which is the dominant regime influencing morphology development. The mechanisms of morphology development in this regime are critically determined by the complete rheological behavior of the blend components from room temperature solid-state behavior through the melting/softening temperature to the fully molten state. Chapters 2 and 3 outline the compounding behavior of different model blends and quantify the effect of solid-state moduli and melt viscosity differences on the evolution of the continuous phase. The framework presented in Chapter 3 is a useful starting point for the design of compounding operations to achieve target morphologies. As blend components were chosen based on their transition temperatures and rheologies, the conclusions from our compounding studies are applicable to a broad variety of immiscible blends. For a compounding technologist, these blend systems provide a valuable insight into the material properties that determine the extent of and the morphologies in, the melting regime.

By controlling the relative melting rates of blend components, different morphologies of the major component en route to phase inversion as shown in Chapter 3 and 5, can be achieved. Compounding operations can be designed to stop the mixing en route to phase inversion giving rise to interesting intermediate morphologies: for example a lacy structure of the major component for use in filtration applications. Based on the understanding of phase inversion developed in this thesis, processes that exploit phase inversion to create otherwise inaccessible morphologies can be designed.

Modeling of compounding operations is a challenging problem due to the three-dimensional flow-field and complex material behavior during compounding. Present day
modeling efforts often have to balance sophistication of treatment of the flow-field and material behavior against the computational cost. Because of this, modeling approaches that simplify the phenomena of interest and identify key material and flow characteristics are very valuable. The approach outlined in Chapter 5, indicates the power of judicious selection of simplifying assumptions in building an understanding of a complex mechanism of morphology development. The calculation of a time-scale for mixing and identification of a deformation parameter (major component strain) are expected to be more broadly applicable to any compounding operation. For example, the approach can be extended to continuous compounding equipment like twin-screw extruders. As opposed to a macroscopic energy and momentum balance approach to modeling, the use of a strain-measure incorporates a description of the microscopic details of compounding operations. As the goal of compounding operations is usually the achievement of a certain dispersion in the blend, a microscopic modeling and analysis approach is more useful for the quantification of mixing and comparison of mixing across different equipment or process conditions.

A recurrent challenge in the processing of new blends is the need to prescribe scaleup rules for bringing them into mass production. For specialty blends with expensive components, there is a strong need for mixing devices that can be scaled to larger sizes in small increments. The new blade design for batch mixers introduced in Chapter 4 provides an easy and flexible means to investigate batch sizes from 8cm$^3$ to 64cm$^3$. Although in our studies these blade elements were machined to be triangular and used to investigate the time to phase inversion, their design features can be exploited for studying other element shapes and process phenomena of interest. In addition, due to the modular nature of the blades different blade configurations can be tested for determining the most efficient design for the process on hand. The design can also be used as a screw-element evaluator. For example, by constructing a blade configuration that resembles the kneading block section of a twin-screw extruder, the effects of different geometric parameters on mixing can be systematically investigated. This allows us to isolate individual screw sections and study their mixing characteristics in greater detail. This will lead to better screw designs
and the optimal use of different mixing and conveying elements to achieve the target blend morphology.

For a materials engineer looking to develop compounding operations for a new blend or to optimize those of an existing blend this thesis provides: a framework for analyzing the compounding behavior (Chapter 3), a possible equipment and process design for scaleup studies (Chapter 4), and a methodology for capturing the microscopic details of morphology development during the compounding operation (Chapter 5).

### 6.2 Recommendations for Future Work

From our observations, it is clear that during typical compounding operations, the initial softening of blend components is governed by their solid-state moduli and that formation of a low-viscosity melt of one component delays the softening or melting of the second component. Below a shear modulus ratio of 0.1 and a melt-viscosity ratio of about 0.2 an initial continuous phase of the minor component was observed. It would be of great interest to investigate blends which have comparable melt viscosities but very different shear moduli in the solid state. This would help in identifying the forces and nature of dispersion in the very initial stages of compounding before sufficient melt has been formed. Such an investigation would also provide clues to the relevant dispersion mechanisms of blends with an inorganic filler or a component that does not melt during compounding. The framework of Chapter 3, can be used as a guide in the selection of different blends for further study.

Further advances in the theoretical description of material behavior close to the melting/softening temperature are required to better understand how the microstructure of the components affects their bulk deformation. This would explain the observed differences between compounding of blends with semi-crystalline and amorphous blends. Model experiments that measure material properties in this temperature range under deformations characteristic of the processing equipment need to performed. An example of such an effort would be the calculation of material response to large-step-strain deformation for a finite time interval, at different testing temperatures. This would
represent the deformation of a material element as it passes through the high-stress regions of the mixer.

The mechanism of phase inversion during compounding studied here was restricted to two-component blends. Possible occurrence of phase inversion in three-component blends needs to be investigated. Even with two-component blends applications of phase inversion should be explored further. For example, by a suitable control of addition protocol and blend component rheologies, dispersed domains of the minor component with inclusions of the major component can be created. Having developed a good understanding of the factors influencing phase inversion we are now in a position to exploit this phenomenon to create exciting new morphologies.

This thesis has introduced a new modular blade design for scaleup studies in batch mixers. Controlled increase in the batch size while maintaining geometric similarity can be achieved with these blades. Our goal was to study the time to phase inversion in the compounding of low-viscosity ratio blends. Use of these blades for other compounding runs is strongly encouraged to build a better understanding of the effect of blade design on mixing behavior. As mentioned above, these blades can be used to evaluate mixing efficiency of different screw elements.

The microscopic model as presented in Chapter 5 uses a strain-based criterion to determine the time to phase inversion. This was shown to provide good agreement of $t_{P.I}$ dependence on different blend and process parameters. A strain-based criterion is a better representation of phase inversion during compounding than the viscosity volume-fraction relation used in Chapter 2. The modeling approach needs to be developed further to better predict the actual time to phase inversion. Possible steps would be to incorporate a more detailed description of the flow-field or a critical strain that is a function of processing conditions.
7. REFERENCES
