Five monodisperse polystyrenes with molecular weights ranging from 110-523k were used to identify the onset of an instability in a 7:1 rounded contraction-expansion flow. Experiments were performed using a Multi-Pass Rheometer (MPR) which requires a small quantity of polymer (~10g) and melt flow was visualised using flow induced birefringence (FIB). Flow instabilities were observed for the three higher molecular weight materials above critical Weissenberg numbers based on both the Rouse and reptation time. The instability takes the form of a non-uniform periodic oscillating stress field perpendicular to the bulk flow, which is seen to originate at the slit outlet and propagate back upstream over time. The effect of increasing flowrate and contraction-expansion rounding on the form and frequency of the instability was evaluated over a range of conditions. The results illustrate a dependency of the instability formation on both the molecular weight, Weissenberg numbers and contraction-expansion rounding.

Introduction

Entangled polymer melts exhibit a variety of flow instabilities during processing which limit production rates within industrial applications, and the ability to understand and predict the onset of these instabilities provides a foundation from which to improve the performance of current industrial processes and optimise plant performance. There are numerous types of experimentally observed instability, and a recent review (Agassant et al., 2005) highlighted three forms observed in extrusion that occur at increasing rates of flow. The first two were “Sharkskin” instabilities, which develop due to free surface effects, and “stick-sput” or “stick-slip” instabilities, which result from material compression and stick-slip at the wall. The third instability was termed “gross melt fracture” or “volume instabilities”, and a number of possible mechanisms were highlighted as possible explanations for this material instability.

It is important to link experimental work to theoretical understanding and computational prediction as a step towards the prediction and elimination of industrial process instabilities. The use of highly controlled architecture materials is a first step towards this goal, but little experimental work is found in literature that focuses on instabilities in well defined monodisperse systems under tightly controlled flow conditions. Initial studies of these systems identified the formation and general form of an instability in monodisperse polystyrene melts along with the effect of blending smaller molecular weight components to extend the range of stable processing (Collis and Mackley, 2005). In this paper five monodisperse polystyrenes of molecular weights ranging from 110-523k were used to experimentally identify the onset of a flow instability in a contraction-expansion slit flow. Experiments were performed using a Multi-Pass Rheometer (Mackley et al., 1995) with three contraction-expansion slit geometries over a range of processing conditions to evaluate the effect of molecular weight, slit rounding and temperature on the form and formation of the instabilities. Results are presented in relation to the ROLIE-POLY model for linear polymer melts (Likhtman and Graham, 2003) to evaluate the role of both chain stretch and molecular orientation on the instabilities. These results are used to produce a processing stability map which will provide useful validation for computational modelling focused on the prediction of such phenomena.
Experimental

Materials characterisation

Linear rheology was taken both before and after processing experiments using a controlled strain rheometer (ARES) with frequency sweeps performed over a range of temperatures to acquire time temperature superposition (TTS) mastercurves. The material molecular weight distributions were characterised using conventional gel permeation chromatography (GPC) and then used to calculate the relative relaxation times based on the molecular model.

Processing experiments

A Multi-Pass Rheometer (MPR) was used for the processing experiments and has been previously described by a number of authors (see for example Collis and Mackley, 2005). The MPR is a dual piston capillary-type rheometer designed for small quantities of material (~10g of polymer) and consists of three sections. The top and bottom sections contain reservoirs for the polymer material, servohydraulically driven pistons and pressure/temperature transducers. The midsection enables simultaneous pressure and optical measurements to be made and resembles a cube with holes in all six faces. The horizontal faces accept a pair of stainless steel die inserts in one direction, and a pair of stress-free quartz windows in the other, while polymer flows through the top and bottom holes. All three sections are surrounded by heating channels and insulation. The material can be repeatedly passed through the midsection, from one reservoir to the other and back again at different flow rates, allowing multiple experiments to be performed on one sample.

The inserts used during this study were contraction-expansion (CE) slit geometries with varying levels of slit rounding. These were zero rounding, producing a sharp edged CE slit (CE1), rounding with radii equal to one quarter of the total slit length (CE2) and rounding with radii equal to one half the slit width, producing a completely smooth round slit (CE3). A schematic illustration of the MPR and the slit geometries is shown in Figure 1.

Figure 1: (left) A schematic illustration of the Multi-Pass Rheometer (MPR) with a slit insert and (right) the geometries used in this work.

Stress induced birefringence was captured using monochromatic polarised light with a wavelength of 514 nm, which passed through the midsection and orthogonal analyzer before being captured using a digital video camera. Quarter wave plates were used to eliminate the isoclinic extinction bands and leave only the stress-related isochromatic fringes.

The aspect ratio of width to depth in all the CE slits is of around seven, equating approximately to two-dimensional flow (Wales 1976), while the inlet and outlet to the CE slit have an aspect ratio of order one. Fully three dimensional flow is expected in this region, although previous computational work has concluded that this three-dimensional effect does not have a great impact on the observed birefringence (Clemeur et al., 2004).
The apparent wall shear rate used to characterise the flow through the various CE slits is based on the solution for Newtonian flow through infinite parallel plates and is given by

\[ \gamma_{app} = \frac{6Q}{w^2 l} = \frac{150\pi V_p}{w^2 l} \]

where \(Q\) is the volumetric flowrate, \(w\) is the width of the slit at its narrowest point (1.4mm), \(l\) is the depth of the slit (10mm) and \(V_p\) is the speed of the pistons. The Weissenberg number (\(We\)) was used to represent the relationship between material deformation and relaxation, and is given as the deformation rate defined by the shear rate multiplied by the material relaxation time (\(\lambda\)).

\[ We = \gamma_{app} \times \lambda \]

In subsequent sections the relaxation time used to define \(We\) is either the Rouse time (\(We_{\tau_R}\)) or reptation time (\(We_{\tau_d}\)).

Results and Discussion

Material degradation

Given the expected sensitivity of material properties and molecular weight to the onset of flow instabilities, linear rheology was taken both before and after processing experiments; for all materials no change was observed between the pre and post processed material. This is similar to previous work (see for example Collis and Mackley, 2005) that found no noticeable degradation of the sample over time due to the enclosed nature of the system. The molecular weights, polydispersity indices, and Rouse (\(\tau_R\)) and reptation (\(\tau_d\)) times based on the ROLIE-POLY model are given in Table 1 for the various materials studied.

<table>
<thead>
<tr>
<th>Label</th>
<th>(M_w) (g/mol)</th>
<th>(M_n) (g/mol)</th>
<th>(M_w/M_n)</th>
<th>(T) (°C)</th>
<th>(\tau_d) (s)</th>
<th>(\tau_R) (s)</th>
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<tr>
<td>DOW PS1568</td>
<td>110,000</td>
<td>104,760</td>
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<td>140</td>
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<td>3.71</td>
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<td>DOW PS1569</td>
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<td>164</td>
<td>4.3</td>
<td>0.327</td>
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<td>165</td>
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<td>0.58</td>
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<tr>
<td>DOW PS1570</td>
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<td>1.06</td>
<td>170</td>
<td>8</td>
<td>0.343</td>
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<tr>
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<td>180</td>
<td>15.2</td>
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<tr>
<td>Dur500k</td>
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<td>1.14</td>
<td>170</td>
<td>52</td>
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<tr>
<td>Dur500k</td>
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<td>1.14</td>
<td>180</td>
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<td>0.385</td>
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Instability form

Figure 2 illustrates the form of the instability observed during flow through the CE geometries studied, in this case for flow through CE2, and is similar to that observed previously for monodisperse materials (Collis and Mackley, 2005). The instability first occurs downstream of the slit outlet, and takes the form of an antisymmetric time periodic disturbance seen in region 1 of the figure. The instability is most clearly seen in this region, where the disturbance is of order half the slit width, where it moves periodically towards the areas of high stress near the slit outlet corners. Over time it propagates back upstream, and leads to time periodic disturbances being observed upstream of the slit inlet, shown in region 2, similar to those seen in previous studies of polydisperse materials (Combeaud et al., 2004). The FIB in the slit itself is unresolved, however, preliminary Laser Doppler Velocimetry measurements indicate the flow oscillation does first occur downstream of the slit. Careful analysis of the instability development shows that the oscillations observed within the two separate regions are of the same frequency and direction, and this further suggests that the instability formation at the slit outlet subsequently dictates the upstream instability form and frequency. This frequency of oscillation, defined as the inverse of the time taken for the “zero stress eye” to move from the right slit corner to the left and back again, is not constant, and varies over time. Hence the instability observed is chaotic and cannot be defined purely in terms of a single polymer time scale, and is most probably the result of various processes occurring simultaneously.
Figure 2: FIB images (left and middle) of DOW1571 at 180°C flowing through CE2, illustrating the nature of the observed instability for (bottom) the whole field and (top) a zoomed in area downstream of the slit. A schematic (right) outlines the two regions in which the instabilities are observed. Piston speed 0.15 mms$^{-1}$, apparent wall shear rate = 3.6 s$^{-1}$, $We_{\tau R} = 1.61$, $We_{\tau d} = 73$.

Effect of molecular weight

Figure 3 outlines the results of various experiments performed using CE2 as stability maps of molecular weight (represented as the ratio of the reptation and Rouse times, $\tau_R/\tau_d$) against both Rouse time Weissenberg number ($We_{\tau R}$) and reptation time Weissenberg number ($We_{\tau d}$). Operating conditions were such that $We_{\tau R}$ and $We_{\tau d}$ were varied over the ranges 0.25 – 36 and 10 – 190 respectively. An increase in molecular weight ($M_w$) led to an increase in $\tau_R/\tau_d$, which varied over the range 4.5 – 49.6. Temperature was used as a variable parameter to process the different molecular weight materials at similar $\tau_R$ and $\tau_d$ to determine any clear trend for instability onset in relation to these two relaxation times. For the processing flowrate and materials parameter space used in this study, flow instabilities were only observed for the 3 highest molecular weight materials. These were found at moderate flowrates equivalent to $We_{\tau R}$ above 1.1 (488k), 1.3 (523k) and 3.5 (306k), and $We_{\tau d}$ above 45.7 (488k), 68.9 (523k) and 81.5 (306k). The highest $M_w$ material, DUR500K, required larger flowrates and associated deformation before flow instabilities were observed than the slightly lower $M_w$ DOW1571. This may be due to the method of material manufacture or the result of the increased polydispersity of DUR500K, as previous work has highlighted the increased processability associated with increased low $M_w$ fractions in a blend (Collis and Mackley, 2005). While the instabilities occur for $We_{\tau R} > 1$, which suggests that the instability formation is a result of chain stretch, the process is obviously more complex than this. For the lower $M_w$ materials instabilities are not observed up to $We_{\tau R} = 35$ and thus there is also a molecular weight dependence on the instability formation. Until the polydispersity can be evaluated further, no clear trend is observed for instability formation as a function of flowrate and $\tau_R$ or $\tau_d$ other than an increase in $M_w$ coupled with an increase in $We_{\tau R}$ and $We_{\tau d}$ leads to the formation of these flow instabilities. Thus the underlying mechanism for the formation of the instability as a function of flowrate and chain stretch/molecular orientation is still unclear. However, Figure 3 does illustrate a parameter space in which work should focus for the identification of computational instabilities in these materials flowing through the geometries used.
The $\tau_R$ normalised instability frequency plotted against increasing $We_{\tau_R}$ for the three materials exhibiting instabilities is shown in Figure 4, and clearly illustrates a trend of increasing frequency with increasing $We_{\tau_R}$. This result is the opposite of those previously found for instabilities in polydisperse materials flowing through different contraction geometries, where the frequency is constant for increasing flowrate (Combeaud et al., 2004, Yesilanta et al., 1999, Nigen et al., 2003). These instabilities are seen to form in the upstream region of the flow, unlike in this case, where the instability forms just outside the slit exit. Here there is not much potential for an increase in the amplitude of oscillation given the constraint imposed by the slit walls, and this may result in the increased frequency observed. A similar development for the time from flow start-up to the onset of the instability, normalised with $\tau_R$, plotted against increasing $We_{\tau_R}$, is shown in Figure 4. It illustrates that an increase in flowrate leads to a reduction in the time required from the start up of flow for the observation of instability. This is expected given the instability is the result of material strain during the transient flow of material, and higher strains are generated more quickly at higher flowrates.
Effect of curvature

The effect of slit rounding on the formation of this type of instability was investigated for the 488k $M_w$ DOW1571 at 180 °C over a range of flowrates. Figure 5 shows the FIB pattern for the downstream instability observed for all three geometries at the two maximum positions of deviation from symmetric flow for $We_R = 1.61$. The instability is seen to take the same form for all three geometries, beginning initially downstream at the outlet of the slit and propagating upstream over time, and in all three cases the oscillation downstream of the slit has similar amplitude.

Figure 6 shows the instability oscillation frequency against increasing $We_R$ for the three geometries, and highlights the increased flowrates required for the formation of the instability as the level of slit rounding is increased. These results are similar to previous work on low angle contractions (Combeaud et al., 2004) and illustrate that a reduction in the velocity gradients at the contraction inlet, for equivalent flowrates, leads to an increase in the flowrate required to obtain flow instabilities. The method of flow characterisation is also affected by the slit rounding, where as the rounding increases towards order the slit length, the material is subjected to the higher rates used to characterise the material deformation for less time. What is less obvious is why an increase in oscillation frequency is observed with increasing rounding. The rounded geometries lead to more gradual velocity gradients towards the slit inlet and hence lower deformation rates, which leads to lower stresses as the polymer relaxation has a greater time to effect the stress field. As a result of this, the deformation/relaxation process taking place would be expected to be on a longer time scale than for the high deformations associated with the lower levels of rounding. The dynamic mechanism however, responsible for the instabilities observed in this work occurs more quickly as the level of slit rounding increases and hence maximum deformation decreases, and this may provide an insight to help understand the instability mechanism as the different levels of rounding lead to different levels of shear and extension within the flow.
Figure 5: Visual comparison of the observed instability for DOW1571 at 180°C at the slit outlet for (top) CE1, (middle) CE2 and (bottom) CE3 over an instability half cycle. Piston speed 0.2 mms$^{-1}$, apparent wall shear rate 4.8 s$^{-1}$, $\text{We}_{\tau R} = 1.61$, $d\text{We}_{\tau d} = 73$.

Figure 6: Rouse time normalised instability frequency against increasing Rouse time Weissenberg number for DOW1571 at 180°C.
Conclusion

This experimental study reports the form taken by instabilities that occur for monodisperse polystyrenes flowing through a curved contraction-expansion (CE) slit geometry. It provides observations of the instability formation and is a useful validation for computational modelling focused on the prediction of such phenomena. The instabilities are similar to those seen in previous work (Collis and Mackley, 2005) and take the form of an oscillating flow perpendicular to the bulk flow, which is seen to originate at the slit outlet and propagate back upstream. For the five materials studied, with $M_w$ ranging from 110-523k, flow instabilities were observed for flow of the three higher molecular weight materials for values of $We_{SR}$ above 1.1 (488k), 1.8 (523k) and 3.5 (306k). As the $We_{SR}$ was increased above these critical values there was an increase in the frequency of the oscillation and a reduction in the instability onset time from the start up of flow. When these two parameters were non-dimensionalised with respect to $\tau_d$ and compared to $We_{SR}$, a linear relationship was found to exist for the frequency of oscillation, with increasing frequency found with increasing flowrate. This is different to previously published work for polydisperse materials, and is possibly the result of the more enclosed location of the initial instability formation. The relationship is less clear for the onset time, but the general trend shows a reduction in onset time with increasing flowrate, which can be accounted for by the increased strain at equivalent times for increasing flow and deformation. Comparison of the stable and unstable flow for various $We_{SR}$ and $We_{cal}$ with molecular weight, represented by $\tau_d/\tau_R$, illustrates that instabilities are observed with increasing $\tau_d/\tau_R$ for flowrates above the critical values given previously. However no clear relationship between these two parameters and the occurrence of flow instabilities is obvious, and the instability mechanism is more complex than simply chain stretching or chain orientation. The effect of CE slit rounding on the formation of the instability was analysed for one of the materials (488k). The increased rounding led to an increase in the required flowrate for the onset of the instability, which is expected given the lower deformations occurring within these flows. Whilst the form and amplitude of the instability remained the same for increasing rounding, however, an increase in instability frequency at equivalent flowrates was also observed. No explanation can yet be given for this trend and future efforts will focus on understanding this observation and linking current work to previous polydisperse studies.

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References


