THE IMPORTANCE AND CHALLENGES OF UNDERSTANDING POLYMER BEHAVIOR IN EXTENSIONAL FLOW

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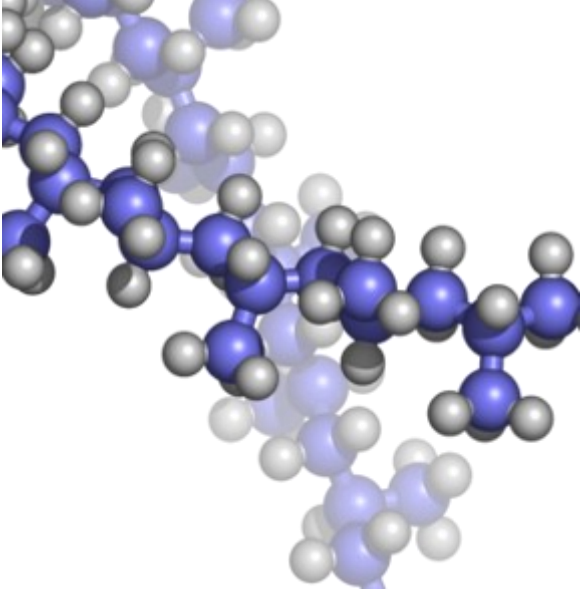
The flow of polymer materials is complex, and in general the behaviour is defined in terms of a linear and non-linear viscoelastic regime. For linear behaviour, the ratio of stress to strain is a function of time, and does not depend on the magnitude of the other parameters. Within the non-linear region the ratio between stress and strain varies as a function of deformation and this can loosely be attributed to changes in the materials molecular structure due to the applied deformation. This is shown in the Fig 1 where the additional of a small amount (3%) of Multi-walled carbon nanotubes (MWCNT's) in polycarbonate leads to a reduction in the linear viscoelastic region, represented by the constant relationship between the storage (G') and loss (G'') moduli. In this case the addition of the MWCNT's has resulted in a more sensitive material response to the applied strain used to measure the elastic and viscous behaviour of the material and the development of additional molecular structure at higher strain.



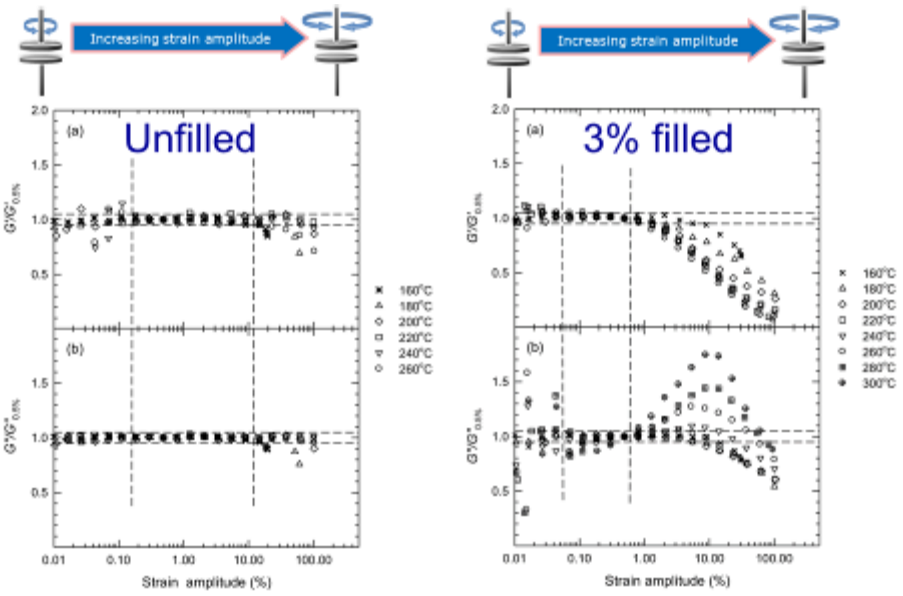


Figure 1: Frequency sweep values at 2 s-1 of storage (G') and loss (G'') for a polycarbonate material of molecular weight ~ 33,000 g mol-1 with (filled) or without (unfilled) the addition of multi-walled carbon nanotubes. Comparison values are to values at a strain of 0.5%. [Choong et al., 2013]

The storage and loss moduli of a polymer sample are normally determined using experiments conducted within the linear region, and the non-linear behaviour is evaluated rheologically in "simple" flows using either non-linear shear or non-linear extensional experiments. An example of this is provided in Fig 2 for three different polyethylene materials. In shear flow the materials are seen to exhibit an initial increase in viscosity with time before the value subsequent drops at higher times. However in extensional flow for the more branched low density polyethylene (LDPE) the viscosity is seen to significantly strain harden, with an increasing resistance to flow at higher times as the molecules become increasingly stretched. This strain hardening is an important physical behaviour of the material, and a result of the increasing level of molecular branching which causes higher levels of entanglement between adjacent molecules and hence additional resistance to motion. Also illustrated in Fig 2 is that the experiments don't always capture the material behaviour across the full range of time scales.

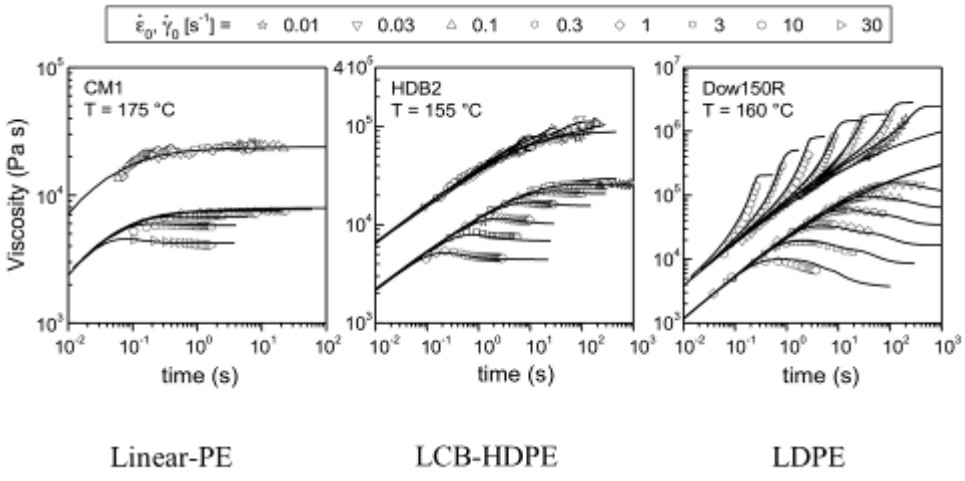


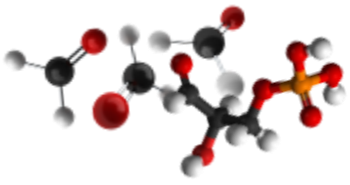
Figure 2: Transient shear (bottom) and uniaxial extension (top) for a linear polyethylene, long chain branched high density polyethylene and a low density polyethylene. The lines represent theory whilst the symbols represent experimental data. Experimental results for the full range of times were not achievable due to the polymer samples breaking. [Hassell et al., 2008]

For complex flows that mimic industrial applications, the use of a straight channel or contraction expansion slit geometry provides regions of high simple shear near the wall and extension along the inlet centreline. Results are useful in benchmarking molecular models prior to their use within industry (Agissant 2002) and a range of experimental observational techniques are used including flow induced birefringence, the brightfield technique (Collis and Mackley, 2005) and Laser Doppler Velocimetry (Combeaud et al., 2007). In these cases the Weissenberg number can be used to characterise the level of deformation experienced by the polymer, and is given by,

$$Wi = \dot{\gamma}_{app}\,\bar{\lambda} \qquad (1)$$

where is the viscosity weight average relaxation time of the material, given as a function of the moduli (gi) and relaxation times (λi) by,

$$\bar{\lambda} = \frac{\sum_{i=1}^{N} g_i \lambda_i^2}{\sum_{i=1}^{N} g_i \lambda_i} \qquad (2)$$



Most work in literature focuses on steady state flow patterns where the flow rates and Weissenberg number are limited to values that provide resolvable birefringence patterns. However this can limit the relevance to cases where the deformation rates can be very high, such as in the case of injection moulding. In this case it is possible to use the resulting stress relaxation after flow to provide an insight into the qualitative stress field present during flow.

Fig 3 illustrates the transient stress relaxation behaviour at the cessation of flow for a polydisperse polystyrene having undergone flow into a contraction geometry, and illustrates both the additional information which can be gained by stress relaxation comparisons and the impact on material behaviour of the extensional component of flow. For Wi ≈ 230 the principal stress difference (PSD) is resolved during flow and similar to other published work (Lee et al., 2001, Hertel et al., 2008) the region of highest stress is at the slit entrance corners. At higher values of Wi the PSD becomes unresolved during flow, however the general pattern of flow is captured during stress relation. It can be seen that at higher deformation rates the region of highest stress is no longer at the slit corner but rather in the region of high extension along the inlet centreline. These "inlet stress islands" resemble the "cusping" seen in Cross-Slot extensional flow (Verbeeten, 2001) which again occur as a result of extensional flow. This increased stress can be seen to correspond to a change in the velocity profile of the polymer entering the slit, shown in Fig 4, which is of relevance in understanding and predicting the flow behaviour of polymers entering confined geometries.

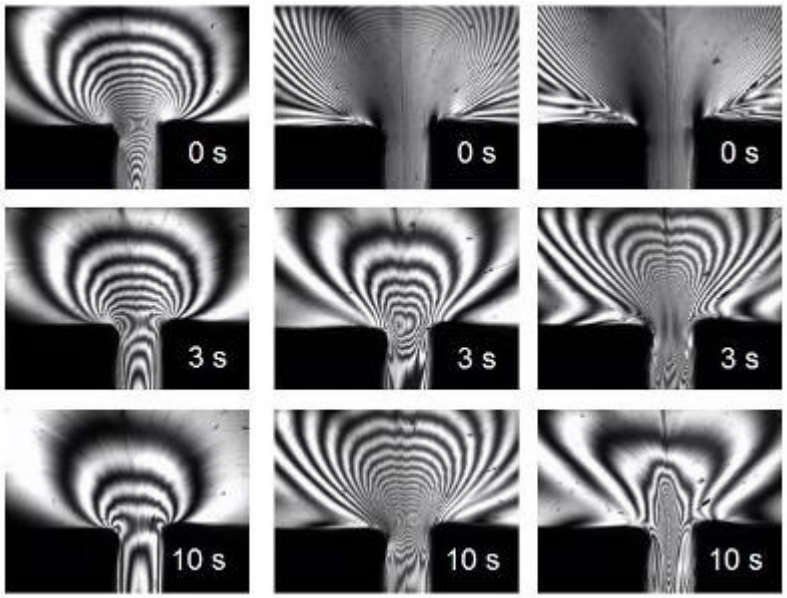


Figure 3: A sequence of images outlining relaxation of the flow induced birefringence in polystyrene at 170ºC at times after the cessation of flow for (a) $\dot{\gamma}_{app}$ » 2.36 s^{-1}, (b) $\dot{\gamma}_{app}$ » 23.6 s^{-1} and (c) $\dot{\gamma}_{app}$ » 47.1 s^{-1}. The flow direction was initially from top to bottom.

At lower Wi the velocity profile pattern along the inlet is similar to that reported in other work (Hertel et al., 2008) and the increase in upstream extension has little impact on the downstream flow profile. However at higher Wi the velocity profile changes, and a local minimum is observed in the centre of the slit inlet, with higher velocities either side of the centre-point. This seems to indicate that the "inlet stress island" presents a region of higher resistance to flow due to higher extensional viscosity and alters the velocity profile entering the slit. This change in velocity profile and stress pattern will ultimately affect the material properties downstream of the inlet, as the polymers molecular alignment is a consequence of past and present deformation. This is important in industries where polymers are subjected to high deformation rates and quick temperature cycle times that result in molten polymer morphology and stress becoming frozen into the final product. As a result, modern experiments and predictive tools including constitutive models should accurately capture this behaviour during extensional flows.

Fig 3 and 4 highlight the impact that extensional flow can have on polymer melt flow in complex geometries, whilst Fig 2 has indicated a limitation in conventional rheological characterisation of polymers during simple extensional flow. A number of recent studies have looked to bridge this gap and increase our understanding and characterisation of extensional flows. Auhl et al (2011) used a cross-slot geometry to probe material response in high strain extensional flows to characterise materials for which conventional uniaxial testing were not sufficient.

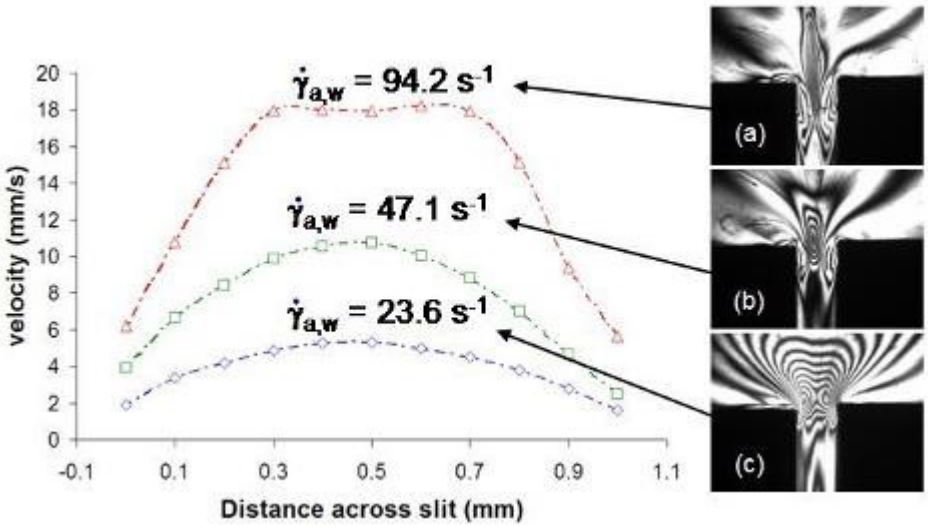


Figure 4: (left) Velocity profiles in polystyrene at 160ºC along the entrance line of the slit for three different flowrates; (diamond) $\dot{\gamma}_{app}$ » 23.6 s^{-1}, Wi ≈ 230; (square) $\dot{\gamma}_{app}$ » 47.1 s^{-1}, Wi ≈ 460 , (triangle) $\dot{\gamma}_{app}$ » 94.2 s^{-1}, Wi ≈ 920. (right) representative PSD images for flow from top to bottom, at a point during stress relaxation for each (a) $\dot{\gamma}_{app}$ » 23.6 s^{-1}; (b) $\dot{\gamma}_{app}$ » 47.1 s^{-1}, (c) $\dot{\gamma}_{app}$ » 94.2 s^{-1}.

Whilst successful, this approach is not as straight forward as current uniaxial extensional testing, and currently requires more specialist rheological apparatus. Hoyle et al (2013) have also used a cross-slot geometry, alongside a filament stretching apparatus, to explain the formation of "W-cusps" in complex extensional flows shown in Fig 5 (Soulages et al., 2008, Hassell et al., 2009). Whilst expanding our understanding of the behaviour of polymers during extensional flow, this again requires more complex and varied apparatus than is usually required in a conventional testing laboratory. Extensional flow poses particular challenges in both measurement and understanding for polymer behaviour, and is of obvious relevance to industrial flows and product quality. The brief results presented here indicate that there is still work required to fully understand polymer behaviour in these highly extending and orientating flows, as well as develop experimental protocols to quickly and easily characterise polymer behaviour prior to industrial/further academic use.

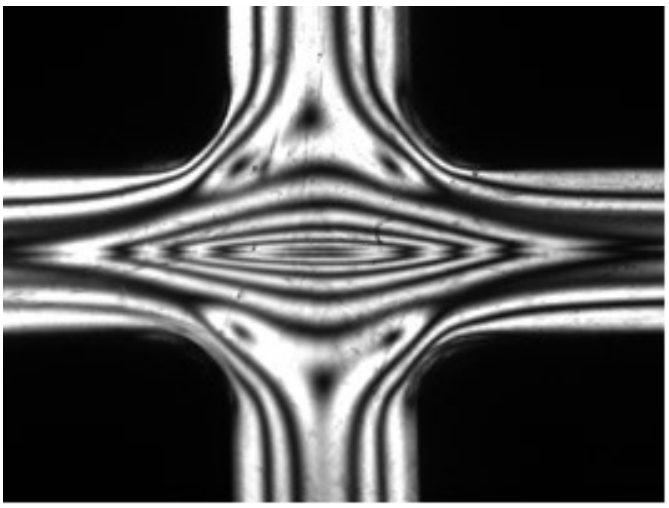


Figure 5: Visualisation of the formation of "W cusps" in the principal stress difference formed along the inlet outlet centre line of a cross slot geometry, in the region of maximum extension. The polymer is a long chain branched high density polyethylene at 155ºC.

Acknowledgements

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