

Microscale Processing of Polystyrene Melts

This thesis examines the processing behaviour of molten polystyrenes with different molecular weights and architectures, using experimental results obtained from a micro-scale processing apparatus and numerical simulations applying both empirical and molecular-based constitutive models.

Processing experiments were performed using a multi-pass rheometer, a two piston capillary-type machine which principally employed a contraction then expansion slit geometry. This was able to provide flow-induced birefringence and pressure difference data at a range of flow rates from ten gram sample quantities. The parameters required to rheologically characterise the linear and non-linear viscoelastic behaviour of the polystyrenes were obtained from experiments performed using parallel plate strain-controlled rheometers.

A commercial grade polydisperse polystyrene was used as a reference material and to validate the techniques used. Five monodisperse polystyrenes with molecular masses ranging from 66,000 to 485,000 kg/kmol were studied, together with two differently weighted blends of two of these. As well as these linear molecules of varying molecular weight distribution, observations were made of two polystyrenes with branched structures, one an asymmetric H, and the other a comb structure.

Experimental data from the range of materials tested has shown that it is possible to distinguish differences between the types using flow birefringence in a processing flow. Monodisperse polystyrenes are notable for a high degree of symmetry between entry and exit patterns for lower molecular weights and flow rates. Blends of a small proportion of low molecular weight monodisperse with high molecular weight showed significantly improved processability, and similar birefringence to the broadly polydisperse type. Branched molecules were seen to exhibit transient stress fangs in start-up flow. A further significant experimental observation was the onset of instabilities and breakdown of continuum flow in high molecular weight monodisperse polystyrenes.

The experimental data was compared with the predictions made by advanced numerical simulations, and it was found that empirical models gave generally good steady state predictions in most cases, while a molecular approach was able to predict the different transient behaviour characteristic of long chain branching, and make predictions for more extreme experimental conditions.