Courtaulds – Blebbing

1. Introduction

In the spinning of synthetic fibres, a polymeric dope is extruded from a small die to form a thin jet, which is then stretched into a thread, solidified, washed and dyed. Unlike Newtonian viscous fluids, the diameter of the polymeric jet is often several times wider than the exit of the die, due to an elastic recovery of the fluid which was stretched as it passed through the die. For normal polymers, this die-swell increases with flow rate, tending to a plateau. Courtaulds have noticed an abnormal behaviour for polyelectrolytes which show a plateau die-swell at high flow-rates, but below some critical flow-rate a jet fails to form and instead clings to the plate in which the die is situated – a sort of infinite die-swell. The study group was set to explain this phenomenon, and after a week had only limited success.

2. Stress estimates

To find which forces might be important in the phenomenon, we calculate the effect on the stress distributed over the die exit of gravity, surface tension, elastic stresses and pressure pushing the fluid out.

For the effect of gravity, we support the weight of a column of fluid of height h and radius R_j over the die exit of radius R_d, $\sigma_g = \rho\pi R_j^2 hg/\pi R_d^2$. Substituting in the experimental values $\rho = 10^3\,\mathrm{kg\,m^{-3}}$, $R_j = \frac{3}{10}\,\mathrm{mm}$, $h = 20\,\mathrm{cm}$, $g = 10\,\mathrm{m\,s^{-2}}$ and $R_d = \frac{1}{10}\,\mathrm{mm}$, we find $\sigma_g = 2 \times 10^4\,\mathrm{Pa}$.

For the effect of surface tension χ, we consider the surface tension force pulling down around the perimeter of the jet $2\pi R_j \chi$ distributed over the area of the die exit, $\sigma_\chi = 2\pi R_j \chi/\pi R_d^2$. Substituting in the experimental values, $\chi = 7 \times 10^{-2}\,\mathrm{N\,m^{-1}}$, we find $\sigma_\chi = 10^4\,\mathrm{Pa}$.

For the effect of inertia, we calculate the Reynolds stress $\sigma_v = \rho v^2$. The velocity can be found from the flow-rate Q as $v = Q/\pi R_d^2$. Substituting the experimental values of $Q = 10\,\mathrm{mg\,s^{-1}}$, we have $v = 0.3\,\mathrm{m\,s^{-1}}$ and $\sigma_v = 10^2\,\mathrm{Pa}$. Note that the shear rate in the die is $\gamma = v/R_d = 3 \times 10^3\,\mathrm{s^{-1}}$.

Now the pressure difference applied across the die to drive the flow is about 5 bar. From some further experiments on similar dies with capillaries of different lengths, it seems that perhaps 2 bar is due to viscous dissipation in the $100\,\mu$m long capillary, and a further 1 bar due to viscous dissipation in the $300\,\mu$m long 20° cone before the capillary. That leaves 2 bar to establish the elastic stresses in the convergence and to push these elastic stresses through the die exit. We arbitrarily estimates these last two stresses at 1 bar each, i.e. 10^5 Pa elastic stresses in the exit of the die and 10^5 Pa pressure to push the fluid out of the die.

Note that we assume that the elastic stresses have not relaxed significantly during the $400\,\mu\text{m}/0.3\,\text{m}\,\text{s}^{-1} = 10^{-3}\,\text{s}$ transit time through the die.

Rheological hypothesis

From the above estimates, it is clear that gravity, surface tension and inertia are negligible compared with the elastic stresses and the pressure in the experiments. We therefore suggest that the phenomenon of blebbing is entirely rheological.

Rheological phenomena are governed by one externally variable non-dimensional parameter, the Deborah number $= \gamma\tau$ where γ is the strain-rate or shear-rate and τ is the relaxation time of the microstructure of the elastic liquid.

Thus the hypothesis that rheology is the sole cause of the blebbing could be tested by performing further experiments with a fixed material and a fixed shape of the die and varying the overall size of the (geometrically similar) dies. One would expect that the onset of blebbing would occur at the same value of Q/R_d^3 as the flow-rate is decreased. It would be interesting whether this critical shear-rate varied with some material property, say varying the solvent concentration or the pH of the solvent.

Further rheological measurements

Courtaulds believed that the rheological behaviour of the normal polymers and the blebbing polyelectrolytes overlapped, although the data was far from complete due to instrumental difficulties at the high shear-rates of interest.

We recommend a further examination of the rheological response of the materials.

1. Measuring the flow-rate as a function of pressure drop for a series of short capillaries of different lengths (with uniform radii, and with the fluid emerging into a bath of the same fluid) would yield a measure of the elastic end effects and also the steady shear viscosity. These results could be checked by a series with different radii.

2. The extensional response of the fluid at large stretches can be found from the variation of the thread diameter along a highly tensioned spinline, an apparatus which should be readily available at Courtaulds.

3. An alternative and more convenient apparatus might be the Moscow RheoTester, which measures how surface tension squeezes a fine filament, working with 1 cc small samples, and working in a hostile environment using a conductivity sensor.

4. Traditional cone-and-plate rheometry is unlikely to work at the high steady shear-rates required, and in oscillatory mode is limited to small total strains.

Clearly one is looking for a special combination of the rheological responses which marks out the blebbing polymers as being different.

The electrically charged subgroups of the polyelectrolytes will make the persistence length of the polymer backbone longer and so the random coil will be more open for the same number of repeating monomeric units. The charges may also lead to some weak temporary bonding between chains, which may give an enhanced elasticity at low flow-rates, below some critical flow strength which can break these temporary bonds.

Note that the polyelectrolyte solutions carry no net electrical charge. Co- and counter-ions in the solvent will lead to a Debye screening of the polyelectrolyte on a scale of nanometers.

Origin of die-swell

To understand blebbing, one must understand why the fluid emerges from the die in the form of a jet, why the jet swells significantly for normal polymers, and why the polyelectrolytes are different. In this section we present our speculations on these questions.

When a Newtonian viscous fluid emerges initially from a die, it will begin to spread radially, wetting the plate. The pressure at the die exit needed to drive this flow increases in time as more fluid must be pushed against the resistance of the rigid plate. After a short time it becomes more efficient if the fluid forms a jet, because in the uniform jet there is no pressure loss, and so there is just a pressure gradient within a diameter of the die where there is a modest die-swell.

Elastic liquids swell much more due to the recovery of stored elastic energy. Some of the elastic stress is lost in viscous dissipation as the jet swells. We speculate that the difference between the normal polymers and the polyelectrolytes is in the distribution and origin of these elastic stresses. We suggest that for a normal polymer, the elastic stresses are primarily normal stresses from the shearing flow in the capillary and cone. These normal elastic stresses would vanish on the centreline where the shear vanishes and are largest on the outside. For polyelectrolytes, we suggest that the elastic stresses are primarily due to the stretching extensional flow in the convergence before and during the cone, and so are largest on the on the centreline. It might also be that there is larger shear-thinning near the walls for the polyelectrolytes. We see the elastic stresses concentrated in the centre with the slippery coating as leading to a very much larger and more abrupt die-swell, or blebbing. This should be contrasted with the case with the elastic stresses concentrated on the periphery of the jet, where they may act as an effective surface tension, thus inhibiting abrupt surface curvature.

It would be useful to see whether the measured rheological properties support these speculations. One could also examine the ideas by making finite element computations of the flow using different constitutive equations reflecting the suggested different material properties.