

Using the Mold Filling Device to Study Nonlinear Rheology and Extensional Flows

Purpose: (1) Observe differences in mold filling between Newtonian (glycerine/water), pseudoplastic or shear thinning (CMC solution), an elastic but not pseudoplastic fluid (PAA Boger); a fluid with long relaxation time (corn starch solution); (2) determine the frictional losses (in “velocity heads”) associated with mold filling; (3) observe correlation (if any) between fluid elasticity or “stretchiness” and excess frictional losses.

Calculations and Questions:

- (1) Determine the ratio of velocity heads, experimental to theoretical, for the three fluids, using the theory below.
- (2) Does the highly elastic (PAA Boger) fluid show excess friction? If so, how much of this excess can be attributed to experimental imprecision and how much to the extra elasticity?
- (3) Does the pseudoplastic (CMC solution) fluid also have a significant elastic component? Explain, using your results.
- (4) Why is it OK to neglect the friction in the feed burette and in the piping prior to the small tube?

Background: Mold filling requires at least one contraction (to the mold runners) and one expansion (from the mold gate into the mold). Whenever you contract a fluid, it must accelerate. Think whitewater rafting in the New (W. Va.) or Kicking Horse Rivers (British Columbia) (both rivers where the instructor experienced whitewater firsthand by being thrown out of the raft). It takes energy to accelerate a fluid, so there will be extra lost energy (extra friction) for any contraction. There are also whirls, eddies and vortices (again, think whitewater) due to mismatches between fast-flowing (near the center of a contraction or expansion) and slow flowing (near the walls) fluid. It takes energy to create the whirls. For many polymer melts and solutions, even more energy can be lost in a

contraction, as energy is expended in stretching out the polymer as the entangled chains are forced through the small opening. Chains adjacent to contracted streamlines (chains already through the contraction) are also stretched out by the accelerating contraction fluid. In an expansion, the sudden decrease in velocity and shear rate can cause the polymer's viscosity to increase greatly, which results in more friction than might be expected. Flows where there are contractions and expansions are called "extensional flows".

The more "stretch-y" or elastic the fluid is, the more vortices etc. occur and the more energy lost.¹ A measure of the lost energy is the first normal shear stress coefficient, ψ_{12} . As it increases, more elastic energy is expended at a given shear rate.

Therefore we expect some polymer fluids to exhibit larger frictional losses in both contractions and expansions than a simple Newtonian fluid. How much larger? Making an energy balance on a mold filling, from start (1) to finish (2), neglecting the small changes in potential energy and kinetic energy (the fluid starts essentially at rest and ends at rest, no matter what it does in between), we get:

$$\Delta P = \rho \mathcal{F} \quad (1)$$

where ΔP is the pressure drop, the force/area driving the fluid, and \mathcal{F} is the friction. We often write friction in terms of "number of velocity heads",

$$\mathcal{F} = K_H (V^2/2) \quad (2)$$

K_H = number of velocity heads (dimensionless); V = average fluid velocity.

A way to think about this is: if we accelerate a fluid from rest to velocity V , that takes one velocity head per unit mass (kinetic energy per mass = $V^2/2$).

For a Newtonian fluid flowing in a pipe (e.g., the tube leading to the mold), then through two contractions, and finally an expansion, the number of velocity heads is:

$$K_H = 4 (16/Re)(L/D) + (15 \pi / Re) \quad (3)$$

The first term accounts for the tube friction itself, the second for the friction in the contractions and expansion.² “D” is the tube diameter, “L” the tube length, and the velocity is found in the normal way:

$V = Q / A = 4 Q / (\pi D^2)$, using the area (A) of a cylinder. Note that the velocity used in this calculation is that of the **smallest tube** in the system.

The quantity Re is the “Reynolds number”, a dimensionless number:

$$Re = (D V \rho) / \eta \quad (4)$$

If you work out the units on Re you see that it is **dimensionless**. The Re for most polymer solutions and melts is low, usually <1000. Such flows are called “laminar”, because the fluid streamlines in a straight tube don’t mix much – the fluid flows in layers (a “laminar”). Physically, Re tells you something about the ratio of inertial (kinetic) forces to viscous forces. For example, in your homes, Re for the water in the pipe is probably >10,000 when you turn the faucet on, because water is a low viscosity fluid.

So using the data from the mold filling experiment you can structure your calculations as:

- (a) Find the average flow rates ($Q = \text{volume}/\text{time}$) over the different time periods in the data.
- (b) For each Q, calculate the average velocity in the tube.
- (c) Using V and ΔP , calculate the actual numbers of velocity heads, K_H , which are direct measures of the total friction in the system.
- (d) Calculate the Re numbers using the physical properties provided below. These numbers are <1000, probably <100. Check units to be sure it’s dimensionless.
- (e) Use Re to calculate the theoretical number of velocity heads using eq. (3).

The ratios of experimental to theoretical velocity heads gives you some idea how much “excess” friction is present. For a Newtonian fluid, this ratio should be near

1. Deviations can be attributed to: (a) neglect of potential and kinetic energy contributions to the energy balance; (b) neglect of friction in the large piping leading to the small tube.

For the highly elastic or stretchable fluid, theory would suggest a higher ratio; for the purely pseudoplastic fluid you might actually find a lower ratio, depending upon how elastic this fluid actually is (e.g., if the experimental time scale is long, you may be well above the relaxation time and so it's not too elastic). If not elastic at all, the ratio of experimental to theoretical velocity heads should be lower than the Newtonian fluid.

Apparatus: The plastic molds hold 300 mL. The tubing inside diameter is 0.335 cm and its length is 46 cm. The apparatus is built to simulate the primary features of an injection molder. There is a large contraction upon entering the tube (mold “sprue” and “runners”), then another contraction when you enter the small fitting on top of the tube (mold “gate”), then an expansion when you enter the mold itself.

The feed burette’s (King 40 Rotameter) volumes are:

Mark	Cumulative Volume, mL
Top red line	0
40	48
30	100
20	151
10	201

The other burette’s (Omega) volumes are:

Mark	Cumulative Volume, mL
11	0
9, 7, 5, 3	35 mL each
1	40 mL

Material Properties:

6 wt% carboxymethylcellulose solution (in water) - $\rho = 1.04 \text{ g/mL}$; $\eta = 100 \text{ cp}$ at zero shear, 20°C

95 wt% glycerine/5% water - $\rho = 1.25 \text{ g/mL}$; $\eta = 520 \text{ cp}$ at zero shear, 20°C

PAA Boger fluid – consists of (wt%) 90.97% glycerine, 7.5% water, 1.5% NaCl and 300 ppm PAA, $\rho = 1.25 \text{ g/mL}$, viscosity = 300 cp at zero shear, 20°C .

6.2 wt% cornstarch / water - $\eta = 1300 \text{ cp}$ at zero shear, 20°C ; $\rho = 1.01 \text{ g/mL}$.

References

1. *Visualizations of Boger Fluid Flows in a 4:1 Square-Square Contraction*, M.A. Alves, F.T. Pinho, P.J. Oliveira, *AIChE J*, 51, 2908-2922 (2005).
2. *Principles of Polymer Processing*, Z. Tadmor and C.G. Gogos, Wiley Interscience, Hoboken, 2006, pp. 693-695.

Detailed Properties of Materials

Carboxymethylcellulose, sodium salt, low viscosity – MP Biomedicals 101278

6 wt% solution ~ measured ~100 cp in capillary viscometer at 20°C.

Properties – ~90 kDa, DP ~ 400, degree of substitution ~ 0.65-0.90 carboxy groups per 10 anhydroglucose units, ~8 wt% Na.

Preparation - The CMC is added to the water in portions so that it is well dispersed. Add CMC to the vortex of vigorously agitated water. The rate of addition must be slow enough to permit the particles to separate and their surfaces to become individually wetted, but it should be fast enough to minimize viscosity buildup of the aqueous phase while the gum is being added. High heat is not needed and may actually slow down the solubilization process. Solutions are stable between pH 2 and 10, pKa ~ 4.30. If problems, heat for several hours at 37°C. Place in a shaker for one to two days at 2-8°C to completely dissolve the product. Bring the solution back to 25°C.

Like many polymers, the viscosity of CMC can go through large changes as it is swollen and dissolved in water and other H-bonding solvents.¹ As the particles are swollen the viscosity will increase rapidly as their excluded volume increases. Ultimately the particles are broken up into fully hydrated individual chains, and the zero-shear viscosity decreases back to a much lower value, nearer to that of the solvent itself. The “disaggregation” process usually proceeds better at low than high T. The degree of substitution of carboxy groups also greatly affects the viscosity. Those polymers with a low number of groups can form very viscous gel structures upon contact with poorer (solvent power) solutions.

CMC dissolved in glycerine-water mixtures show a maximum in viscosity at ~20 wt% water.³ The following table gives viscosities of the glycerine-water-2 wt% CMC solutions, using a CMC similar to MP Biomedicals 101278 at 20°C.

Water amount, wt%	Viscosity, cp
0	900
20	20000
40	7000
60	3000
80	1000

Glycerin-Water Mixtures

The best source for the properties of both glycerin and its aqueous mixtures is the Dow glycerine website.⁴ Glycerine mixes readily with water in high concentrations. Shaking is sufficient. Typical properties at 20°C are:

Wt% glycerine	Specific gravity	Viscosity, cp
85	1.22	109
90	1.24	219
95	1.25	523
97	1.26	765

Cornstarch

Typical solutions in water are viscous, at ambient T ~340 cp at 0.9 wt% and 1300 cp at 6.2 wt%. Cornstarch can be dissolved in a similar manner as CMC, or you can alternate stir – heat (a few min, low setting) – stir. If using a microwave keep the heating to ~30 s.

A suspension which has phase separated can be redissolved. You do this by draining off the water, then taking some of it (~a volume equal to the cornstarch at the bottom) into a separate container. Save the rest of the water you drained and boil it. Mix up the cornstarch with the smaller amount of water by hand, using a rod. When

you have it mixed as best you can, add the boiling water and keep stirring. This should dissolve the rest of the cornstarch.

The cornstarch movie can be found at:

http://chaos.ph.utexas.edu/research/vibrated_cornstarch.htm .

If you ever want to do the “cornstarch experiment” showing instant dilatency, the proper proportions are roughly equal volumes of cornstarch and water. Add the water slowly to the cornstarch, then mix thoroughly before you try it.

PAA “Boger” Fluid

The PAA stands for poly(acrylamide). The properties of a typical PAA fluid consisting of (wt%) 90.97% glycerine, 7.5% water, 1.5% NaCl and 300 ppm PAA are supposed to be density = 1247 kg/m^3 , viscosity = 735 cp (20°C).¹ However, we measured 300 cp at 20°C for our fluid in a capillary viscometer (probably we had a lower MW poly(acrylamide), ours is Dow Separan NP20).

Other Boger fluids can be prepared by dissolving a small amount of polymer in its oligomer, e.g., high molecular weight PS in oligomeric PS. When preparing, the polymer should be added last.

PDMS

The material here is a vinyl dimethoxy-terminated PDMS from Gelest, DMS-V31, with nominal kinematic viscosity = 1000 cSt, specific gravity = 0.97, molecular weight = 25-30 kDa, CAS 68083-19-2.

References

3. *Visualizations of Boger Fluid Flows in a 4:1 Square-Square Contraction*, M.A. Alves, F.T. Pinho, P.J. Oliveira, *AIChE J*, 51, 2908-2922 (2005).

4. *Principles of Polymer Processing*, Z. Tadmor and C.G. Gogos, Wiley Interscience, Hoboken, 2006, pp. 693-695.
5. *Technical Information, Aqualon Cellulose Gum*, Bulletin VC-497C, Hercules, Inc., 2002, http://www.herc.com/aqualon/product_data/tech/vc497c.pdf
6. *Dow OPTIM© Glycerine Resources*,
<http://www.dow.com/glycerine/resources/physicalprop.htm>
7. *MSDS for DMS-V31 Vinyl dimethyl-terminated PDMS*, Gelest Inc.,
<http://www.gelest.com/msds.asp?DMS-V31> .