

030319 Final Polymer Processing

I) Blow molding is used to produce plastic bottles and a blow molding machine was seen during the Equistar tour. In blow molding a tubular parison is produced by extrusion using a cyclic semi-continuous operation similar to injection molding. The parison is clamped by the mold and air is injected into the clamped parison to expand the tube into the bottle mold. After cooling the part is ejected, similar to injection molding, and the process repeats.

- 1) a) During the blowing of the parison what type of model flow could be used to approximate the flow conditions?
b) Give the rate of strain tensor for this model flow.
c) Do you expect shear thinning to be an important factor in this step of bottle production? Why?
d) If you knew the extent of elongation in the horizontal and vertical directions and the thickness of the parison could you calculate the thickness of the bottle? How?
e) Would you expect the rate of expansion to vary with the air pressure difference used to expand the parison? Why?
- 2) a) What do you think is the rate limiting step for this semi-continuous operation? Why?
b) Would you expect the pressure difference needed to expand the parison to vary with the temperature of the parison? Give an equation.
c) How would you estimate the optimal temperature for the parison during the expansion stage?
d) How would you estimate the optimal temperature for extrusion of the parison?
- 3) When the parison is extruded significant die swell occurs.
a) What constitutive equation would you use to predict the extent of die swell for the parison?
b) How could you minimize the extent of die swell?
c) Would you expect the extent of die swell to depend on the molecular weight distribution of the polymer being extruded? Explain.
d) What constitutive equation would be used to predict the radial symmetry of the parison tube due to the extrusion process?

II)

1) The plant where you work had a red pigment spill into a holding pond with a **volume of 10,000 cubic feet** of water. The pond is to be flushed with a flow rate of **1 cubic foot per second** of water.

- a) Estimate how long will it take to remove **99.9%** of the red pigment? (Calculate also for removal of **90%** of the pigment.)
- b) What assumptions did you use to make this estimate?
- c) For this problem give comments on the appropriateness of these assumptions.
- d) If the pond actually flushes completely clean in 7 days how can you improve your calculation? (Give modified parameters assuming that "completely clean" means 99.9% of the pigment has been removed.) Use this modified equation to calculate the time to remove 90% of the pigment.
- e) What is the basis in this system for your modification of the parameters in part "d"?

2)

- a) Sketch the residence time distribution function **and** the cumulative residence time distribution function for a batch mixer with two chambers such as was discussed in class.
- b) Sketch the residence time distribution function **and** the cumulative residence time distribution function for a continuous mixer similar to that discussed in class.
- c) Sketch the strain distribution function **and** the cumulative strain distribution function for a batch mixer with two chambers such as was discussed in class.
- d) Sketch the strain distribution function **and** the cumulative strain distribution function for a continuous mixer similar to that discussed in class.
- e) How would you calculate the mean strain **and** mean residence time from these functions?

3) In the second lab we calculated the mean residence time for the extruder by taking the average of the time for the first sign of pigment and the time for the last trace of pigment.

- a) Sketch what you think $f(t)dt$ versus t would look like for the extruder. Explain this sketch in terms of the flow conditions in the extruder and mark the times for the earliest occurrence of pigment in the effluent stream and the final observable pigment.
- b) How is the mean residence time calculated from $f(t)dt$? In the plot of part "a" show where you think the mean residence time would fall. Does this coincide with the mean of the earliest and latest residence times?
- c) In the lab we calculated the earliest residence time using,

$$t_0 = \frac{3z}{2 F_{sr} \left(1 + \frac{Q_b}{Q_d} \right)}$$

Explain the terms in this equation. (If you don't remember try to formulate an equation for earliest residence time and compare with this equation.)

- d) Explain this equation for shortest residence time.
- e) How is Q_d estimated for the extruder lab?

III)

- 1.)
 - a) Plot viscosity versus rate of strain for a polymer melt on a log-log plot.
 - b) Explain how one point in this plot could be obtained from a simple shear flow measurement in parallel plate geometry where you measure the *force*, F_x , on the top plate with normal in the y direction and the *strain*, γ_{xy} , on the top plate for a fixed time. (show equations)
 - c) If you wanted to compare viscosities of different molecular weights, which point in this plot would you use?
 - d) Explain why you would not use a point at high strain rate.
 - e) Plot the typical behavior of melt viscosity versus molecular weight for polymers.
 - f) Give two functions that describe the two behaviors observed.
 - g) How is the entanglement molecular weight determined from this plot?

- 2.) In the coating lab we used the following equations for coating paper from solutions of PEO:

$$Ca = \frac{\mu U}{g} \quad \mathbf{T} = H \frac{g}{\mu U} \quad \mathbf{q} = \mathbf{U} \mathbf{H} \left(1 - \frac{g H^2}{3 \mu U} \right) \quad \mathbf{T} = 0.944 Ca^{1/6}$$

- a) Explain the terms in these equations.
 - b) What is the dependence of coating thickness on rate of withdrawal and viscosity?
 - c) Did your data support this functionality? Explain.
- 3) The cone and plate viscometer has distinct advantages for viscometric characterization of non-Newtonian fluids.
 - a) What is the main advantage of a cone and plate viscometer over a Couetter or capillary viscometer?
 - b) For a cone and plate viscometer the cone rotates at angular velocity, ω , and has a cone angle of $\theta_0 = 1^\circ$. Calculate the shear rate as a function of radial position r for this viscometer.
 - c) Calculate the shear stress for this viscometer if a torque T is measured on the bottom plate and the fluid covers an area of radius R.
 - d) Give an expression for the viscosity for this viscometer as measured at the bottom plate.
 - e) Explain how the first normal stress difference could be calculated for the cone and plate viscometer.

Answers Final Polymer Processing 2003:

- I) 1 a) Simple biaxial extensional flow.
 b) All components are 0 except the cross terms. $\tau_{22} = \tau_{33}$ and $\tau_{11} = 2\tau_{22}$.
 c) No. The Trouton viscosity is the constitutive parameter that governs extensional flow and it does not generally have a shear rate dependence.
 d) Yes. By mass conservation $\lambda_1 \lambda_2 \lambda_3 = 1$, where λ_i is the elongation ratio.
 e) Yes. The rate of expansion should be proportional to the pressure difference similar to the behavior seen in the film blowing lab.

- 2) a) Cooling of the bottle after blowing will limit the operation due to the low thermal conductivity of polymers.
 b) The Trouton viscosity will follow an Arrhenius or WLF function so will drop exponentially with temperature. Less pressure will be needed at higher temperatures.

$$\eta(T) = \eta_0 \exp \frac{-E}{kT}$$

- c) The optimal temperature will be determined by the drawability of the polymer which is related to the ratio of the shear and elongational viscosities. Both of these depend on Arrhenius functions. A minimum in the Trouton viscosity will exist where the polymer no longer displays sufficient melt strength to yield a stable parison with respect to gravity. At the low temperature end as one approaches the glass transition it will become impossible to blow the parison.
 d) The optimal temperature for extrusion will depend partly on the optimal temperature for the parison. The degradation of the polymer in the extruder barrel will limit the high end but before this is reached the parison will be too weak to withstand gravity. The lower limit is related to the glass transition temperature and WLF behavior of the viscosity.

- 3) a) $\lambda_1 = \lambda_2^{-2}$
 b) Lower the shear rate and lower the molecular weight of the polymers.
 c) Yes, the coefficient of the first normal stress depends strongly on molecular weight, by a power-law relationship.
 d) $\lambda_2 = \lambda_1^{-2}$

II) 1)a) You can approximate the holding pond as a CSTR and use

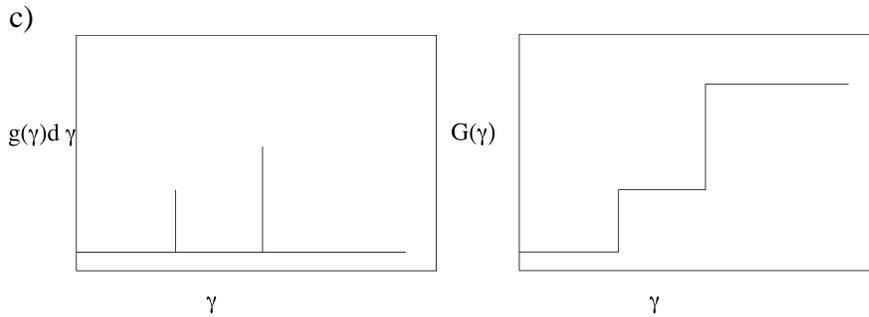
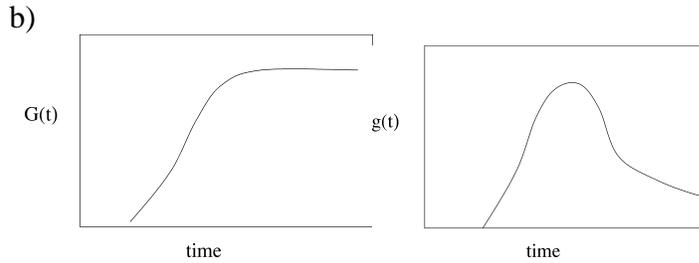
$$F(t) = \frac{C(t)}{C_0} = 1 - e^{-t/Q}$$

For $Q = 10,000 \text{ ft}^3$ and $V = 3,600 \text{ ft}^3/\text{hr}$ we set $F(t)$ to 0.999 and find that $t = 19$ hours. For $F(t) = 0.90$ we find $t = 6.4$ hours.

- b) This equation assumes perfect mixing, that is the concentration of effluent is the same as the concentration at all points in the pond. This does not account for dead space in the pond or for the actual time for the pigment to travel from the inlet to the exit of the pond.
 c) These assumptions are not very good for the pond since there is no mechanical mixing.
 d) If we set $t = 168$ hours for $F(t) = 0.999$ we can calculate the mean residence time, V/Q and use this as a time constant for this pond with this influx. The mean residence time for the original assumptions is $10,000/3,600$ hours or 2.8 hours. The mean residence time using the observed residence time is 24.3 hours. Using this residence time the time to remove 90% of the pigment is 56 hours.

e) The basis of this modification is incomplete mixing and dead space in the pond. Both of these lead to a longer mean residence time.

2) a) Single peak and single step since the residence time is the same for the two chambers.



e) Mean strain is calculated from the strain distribution function through an integral,

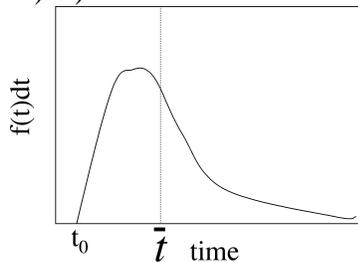
$$\bar{\gamma} = \int_0^{\max} g(\gamma) d\gamma$$

or

$$\bar{\gamma} = \int_0^{\max} f(\gamma) d\gamma$$

similar functions define the mean residence time.

3.) a)



The initial observation is the shortest possible time to travel through the extruder, the time to travel along the rotations of the screw. Most of the material is not traveling this fast and the majority of the material runs through the extruder at \bar{t} in the plot. Some material remains in the extruder for a very long time since there is no-slip at the barrel wall.

b)
$$\bar{t} = \int_0^{t_{\max}} t f(t) dt$$

This does not correspond to the mean of the earliest and latest times. The average of these two times involves a square profile approximation.

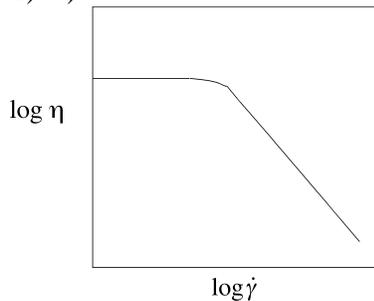
c) z is the distance down the barrel along the screw path. V_{bc} is the velocity along the screw path. Q_p is the volumetric flow rate due to pressure and usually flows back towards the feed. Q_d is the flow rate associated with drag and is positive in the direction of the die.

d) if you multiply the top and bottom by Q_d and realize that $Q_p + Q_d = Q$, then the fastest residence time is the ratio of the drag flow rate to the total flow rate times $3/2$ of the time it takes the screw path to reach the end of the extruder, z/V_{bz} . The factor of $3/2$ results from integration.

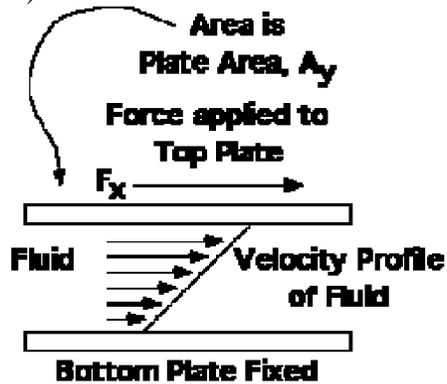
e) Q_d is estimated by running the extruder with no die.

III)

1) a)



b)



$$\tau_{xy} = F_x / A_y$$

$$\gamma_{xy} = dx/dy \quad \tau_{xy} = \eta \dot{\gamma}_{xy}$$

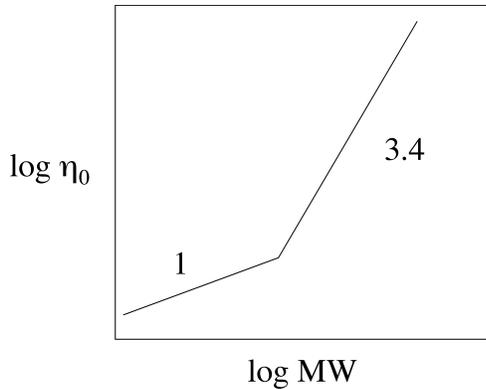
$$\dot{\gamma}_{xy} = dx_x/dy$$

$$v_x = dx/dt, \text{ so } dv_x/dy = (dx/dy)/dt = \dot{\gamma}_{xy}/dt$$

c) You would use the extrapolated zero shear rate viscosity.

d) The zero shear rate viscosity reflects the unperturbed viscosity.

e)



f) $\eta_0 = kMW^1$ **Rouse Behavior**

$\eta_0 = kMW^{3.4}$ **Entangled Behavior**

g) The crossover point between the two power law functions is the entanglement molecular weight.

2) a) Ca is the capillary number (dimensionless), T is the dimensionless thickness of the coating, H is the coating thickness, ρ is the density of the coating, g is the gravitational constant, μ is the viscosity of the coating solution, U is the pull out rate.

b) $H = K(\mu U)^{2/3}$

c) Not in most cases. When coating thickness was divided by this functional dependence the value was not constant.

3) a) The main advantage is that the shear rate is constant for all fluid points in the viscometer. This means that the shear rate dependencies of the viscosity can be directly measured in this viscometer.

b) The shear rate is not a function of r so calculation of the shear rate at any point in the viscometer will suffice. For instance, at a distance r from the center the velocity is ωr at the cone and 0 at the plate. The gap size at this point is $r \sin \theta_0 \approx r_0 \theta_0$ so the rate of strain is $\dot{\gamma} = \omega / \theta_0$.

c) If the shear rate is the same across the gap then the shear stress must be the same also. The

differential F/A is
$$= \frac{3T}{2R^3}.$$

d) The viscosity is the ratio of b) and c),
$$= \frac{3T_0}{2R^2}.$$

e) The first normal stress difference can be calculated from the force pressing down on the bottom plate.
$$\sigma_1 = 2F/R^2.$$