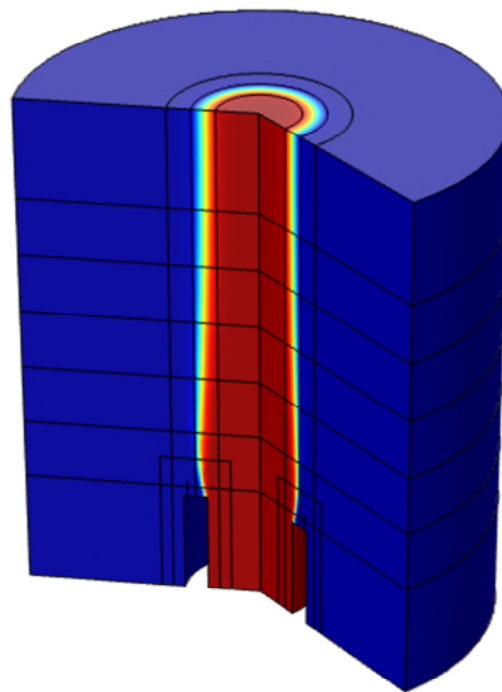


EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling



Hydrodynamics and species transport
during gel formation for converging flows

Michael Mcphail



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1. Introduction

The oil and gas industry has many uses for composite fluids, in which the physical properties change as the composition varies. One way of changing the properties of a fluid is to add fibres of cross-linked gel. The efficient manufacture of cross-linked gel fibres requires a process that can produce fibres of predictable, and controllable, properties. Some examples of fibre properties that might be useful to control are: diameter, strength, and length. As yet, no robust gel fibre manufacturing process exists.

Cross-linked gel is formed as the product of a reaction between polymer chains (such as alginate) and divalent salt ions (such as Ca^{2+}) which act to “cross-link” different polymer chains. Some experimental groups have had reasonable success by using a coaxial flow set up, like the one shown in Figure 1, to produce different gel structures. In these experiments the cross-linking solution flows through a pipe which contains a smaller pipe along the centre line. Alginate flows through the centre pipe, and when this centre pipe terminates the two solutions meet. However, the variation in the properties of gel fibres produced using different experimental setups is not well characterised. In particular, two questions that need to be addressed are:

1. What are the important parameters that determine whether or not gel fibre is produced?
2. Can quantitative predictions of the gel properties be made for certain experimental setups?

Analytic and numerical models will be used to understand what determines the final properties of the fibres.

A model capturing the dynamics of this system will serve as a tool with which we can answer these two questions. Our approach to this problem revolves around two key areas in the pipe: upstream, referring to the region of the pipe around the point the alginate is injected, and downstream, referring to the region far down the pipe away from the injection site. An experimental observation that should be captured in our model is that the alginate solution contracts as it enters the bulk flow. We believe that this feature is important as we expect the upstream behaviour to be a key factor in controllable fibre formation. To start our investigation we formulate, and analyse, a model for the fluid and chemical species flow downstream.

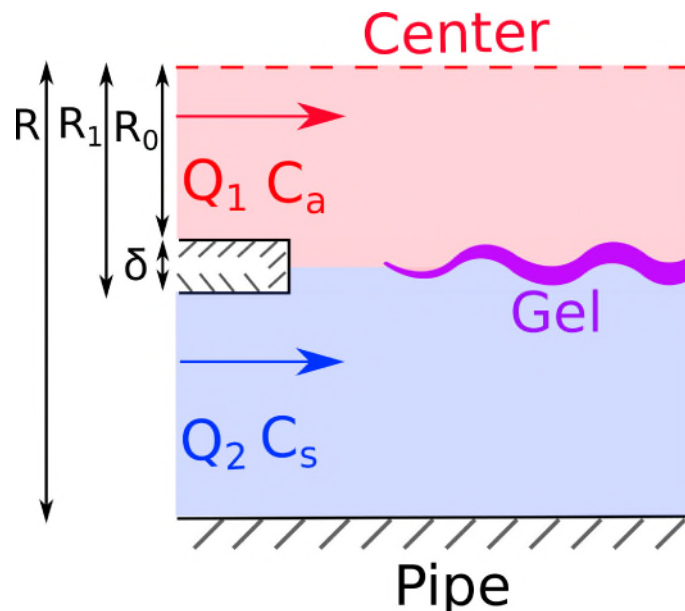
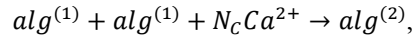


Figure 1: Schematic showing the inside of gel fibre formation experiment using an axisymmetric pipe (axes of symmetry shown by red-dashed line). An aqueous polymer solution (red), with concentration C_a and flow rate Q_1 , flows inside an aqueous salt solution (blue) with concentration C_s and flow rate Q_2 , and a reaction to produce gel (purple) occurs where they meet. The solid region of width δ is the polymer injection pipe. R , R_0 and R_1 are the outer pipe radius, inner pipe radius, and distance to the outer edge of the inner pipe respectively.

2. A Fully Coupled Model

We describe a model for the experimental setup shown in Figure 1. At the termination of the inner pipe, the two different chemical species (alginate and cross-linker) meet, and react (see [1]) according to



where $alg^{(1)}$ is a single polymer chain and $alg^{(2)}$ is the cross-linked gel product. The quantity N_C is the stoichiometric coefficient which determines, on average, how many calcium ions are required to cross-link two alginate molecules. This might vary between alginate solutions, but we use a value of 3.4 in the of simulations (see [1]). The rate at which this reaction occurs will depend on how much of each species is present. We will describe the rate at which alginate is consumed according to the “law of mass action” and an experimentally measured reaction rate (k_r).

While our goal is to understand how the gels shape evolves (i.e. the chemistry), this requires also understanding how the fluid moves (i.e. the hydrodynamics). Both components will interact with each other, since the concentration of the different species will change the local properties of the fluid which is carrying them. The gel properties we are interested in are diameter (distance from the fibres centre to outer edge) or strength, which may depend on either the number of bonds formed and/or the wall thickness (for a hollow fibre this is the difference between the inner and outer radius).

Glossary of terms

- **Viscosity:** A measure of a fluids’ resistance to gradual deformation. E.g. honey has a higher viscosity than water.
- **Diffusion:** The movement of a substance from a region of high concentration to a region of lower concentration. A substance with a higher diffusivity (D) will diffuse faster than a substance with a lower diffusivity.
- **Advection:** The transport of quantity by a moving fluid.
- **Reaction:** A process in which chemical species interact with each other and are changed into different chemicals

Mathematical Model

The model described here was originally developed at Schlumberger Gould Research Center. A difficulty in modelling this system is the coupling between the flow of fluid, and the gel produced by the reaction. The fluid will advect the chemical species along the pipe. The chemical species will also diffuse and react with each other to produce gel. The reactant species and the gel affect the properties of the fluid, so as they are either consumed or produced, the fluids’ properties (viscosity) change. The equations that describe the motion of fluid are the Navier-Stokes equations which comprise conservation of mass and momentum for the fluid.

We take care with the formulation of the problem because the viscosity is a function of the chemical species concentration, describing how the fluid properties change as the species react. Typically, we consider the same base fluid (e.g. water), into which each reactant species is dissolved. An alginate solution is typically much more viscous (200 times) than the aqueous salt solution. Additionally, shearing the alginate will make it less viscous as the long molecules align and slide past each other. Fluids with this property are known as “shear thinning”. For numerical investigations, the gel will be assumed to impact the fluid properties by further increasing the viscosity. The species-dependent viscosity of the alginate will be modelled using the constitutive relation

$$\mu = a_d + b_a(C_a + \alpha C_g),$$

where C_a and C_g are the concentrations of alginate and gel respectively. The parameters a_d ,

The Navier-Stokes equations describe how a fluid will move within some region.

In our simulations, the gel is considered to be a very viscous fluid, typically 200 times more viscous than water.

b_d and α are measures of the relative effects of each species. a_d is the viscosity of the base solution (i.e. no alginate or gel present), b_d describes how the viscosity of the base carrier increases with the concentration of alginate, α describes the additional impact on viscosity if the alginate is cross linked (i.e. it is gel). We list relevant parameter values used in our investigation in table 1. The chemical species will be advected by the fluid, while also diffusing and reacting. These three behaviours are captured in Advection-Diffusion-Reaction equation for each species. Each species will have a different diffusivity (D), which depends on the molecular weight and size of each species. The diffusion coefficients for each species can be found in table 1, but the key point is that the calcium ions diffuse about 10 x faster than the alginate molecules, and the gel will not diffuse in our model (as it is bound together).

| | D_a m ² /s | D_s m ² /s | D_g m ² /s | a_d Kg/s m | b_d Kg m ² /s mol | α | k_r 1/s mol ² |
|--------------|----------------------------|----------------------------|----------------------------|-----------------|-----------------------------------|----------|-------------------------------|
| Value | 10 ⁻⁹ | 10 ⁻¹⁰ | 0 | 0.001 | 0.277 | 100 | 5300 |

Table 1: Default parameter values used (unless otherwise stated). D_a , D_s and D_g , are the diffusivities of the alginate, salt and gel respectively. k_r is the reaction rate coefficient.

Solving a set of equations like this requires us to describe what happens to the fluid and the chemicals at the boundaries of our system. In our case, we enforce that neither the species or the fluid escapes through any of the pipe walls and, additionally, any fluid at the pipe walls is stationary (this is conventionally referred to as the “no-slip” condition in fluid mechanics). At the start of the pipe (upstream) we prescribe the fluid flow rates through each pipe (ml/min) and the concentration of each species in this inflow (mol/m³). Downstream we will prescribe that pressure acts down the pipe only (i.e. not into the pipe wall).

Comments

- These equations describe a complex system with interacting components. We solve these equations using commercial software (COMSOL) specifically built for dealing with systems of coupled equations.
- Due to the many coupled parts, a full analytical solution is unlikely. Instead, we made suitable simplifications in specified regions that resulted in reduced, tractable problems.

Dimensionless Parameters

The two important dimensionless parameters in this model are; the Péclet number, which is the ratio of advective to diffusive mass transport, and the Reynolds number which is the ratio of inertial to viscous forces in a fluid. The Reynolds number can be on the order of 10 - 1000 depending on the experimental apparatus. Reynolds numbers of this order indicate that we do not have to worry about turbulence in our pipes. The Péclet number is very large (greater than 10⁵) which means that the distance over which the species diffuses will be small relative to the other length scales in the problem. The large Péclet number makes it difficult to resolve the chemical dynamics numerically, requiring extra care to be taken to produce accurate simulations (and indicates that there is a region near the nozzle where the concentrations vary rapidly). Efficient and accurate resolution of the numerical solution of gel formation models with such large Péclet numbers is an ongoing challenge which we approach using adaptive mesh refinement.

The final two dimensionless parameters are the ratio of the length of the channel to the width, which we take to be large, and the dimensionless reaction rate, which we assume to be order one.

The Péclet number is the ratio of the rate of advection to the rate of diffusion. In fibre formation experiments, this number is very large (>10⁵).

3. Results

Simulations Near Injection Site

We implement this model in COMSOL to simulate gel growth for a range of input parameters. The parameters that are controllable in an experiment are: the flux through each pipe (Q_1 for the inner pipe and Q_2 for the outer pipe), the viscosity of each solution by either changing the base fluid or increasing the alginate concentration (μ_1 for the inner pipe and μ_2 for the outer pipe), or the sizes/thicknesses of the pipes used. By varying these control parameters, a sweep can be carried out to try and characterise interesting flow behaviours and the impact on the gel downstream.

Focusing our analysis on the region where the two flows meet (see the red box on Figure 2), we observe some unexpected behaviour. Experiments on fibre formation have shown the alginate solution immediately contracting (its diameter decreases) as it exits the inner pipe. All our simulations, and specifically those where the parameters are chosen to represent experiments, show some degree of alginate expansion before tending towards its downstream behaviour. No level of mesh refinement or manipulation of the viscosity parameters reproduces contraction immediately after the nozzle of the inner pipe. This suggests that our model either neglects, or misrepresents some key physics. We investigate the possibility that we are not accurately capturing the gels properties in our viscosity relationship. It is known that solids and viscous fluids exhibit very different responses to applied forces, which will change the behaviour of the system in both the upstream and downstream.

Numerical simulations predict that the alginate solution will expand, experiments show that it contracts.

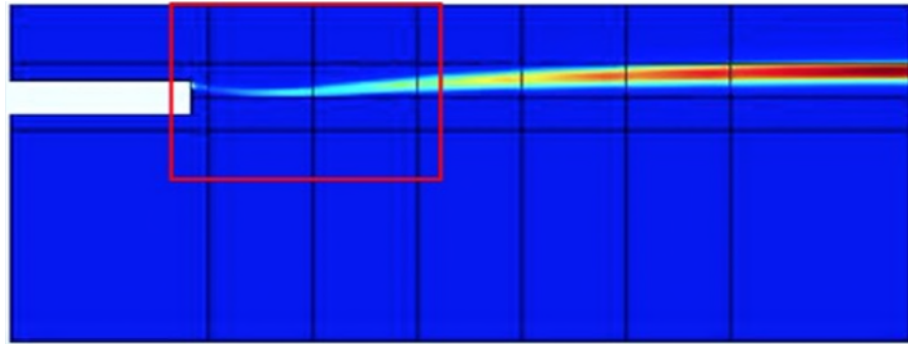


Figure 2: A simulation of the gel concentration profile in the pipe illustrating alginate expansion at the end of the inner pipe. Blue indicates no gel, red indicates higher concentration of gel. In this case, the fluid is flowing from left to right, the top of the image is the centre of the pipe, the bottom of the image is the pipe wall and the white rectangle is the end of the injection pipe.

Downstream Behaviour

In order to better understand the difference between treating the gel as a solid or a viscous fluid, we model the behaviour of the system downstream. We can then simplify a lot of the dynamics of the system under the assumption that the chemistry and hydrodynamics are “fully-developed” (there will be no more changes in either as you move further downstream). We solve the model equations analytically in two cases, assuming (i) the gel fibre is a pure viscous fluid, and (ii) the gel fibre is a solid structure (plug) moving through the pipe. In each case, we determine the velocity and final radius of the gel fibre.

Having obtained solutions for the final radii and velocities of (theoretical) gel fibres, the effect of varying the control parameters can be investigated. In Figure 3 left, we display the velocity of the fluid (/solid) throughout the pipe for a range of viscosities for the gel fibre and under the assumption it is solid. We see that increasing the viscosity of the gel results in velocity profiles that more closely resemble solid plug flow. This behaviour implies that, downstream, a very viscous gel fibre behaves just like a solid one. Even the alginate solution without gel is known to have a much larger viscosity than the base fluid, so we conclude that either of the simple models provide a good estimate of the downstream behaviour.

We also compare the fibre radius downstream predicted by COMSOL and both analytic models. In Figure 3 (right), we illustrate the predicted fibre gel radii for each model as the flux through the outer pipe (Q_2) is increased. Roughly, the models tend to agree for smaller values of Q_2 , however the COMSOL predictions diverge as Q_2 gets bigger. This is because, for larger flow values, the system requires a longer spatial length to develop, so the system has not yet fully developed by the end of the domain modelled in COMSOL.

The domain for which the equations are solved in COMSOL is representative of a typical experimental setup, and therefore flow development is another thing to consider when deciding on a suitable model.

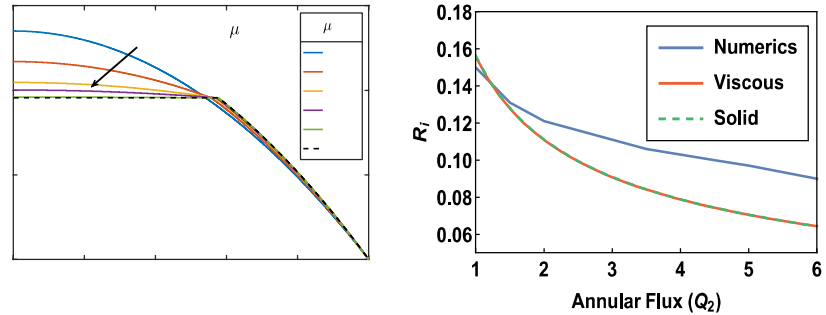


Figure 3: (Left) The downstream fluid velocity throughout the pipe, considering the gel fibre as a viscous fluid of viscosity μ_1 (colours), and as a solid (black-dashed). The centre of the pipe is at radial distance 0 and the pipe wall is at 1. (Right) The dependence of the predicted fibre radius (scaled with respect to the pipe radius) on the annular flow rate (Q_2), as predicted by COMSOL and our two analytical models.


Expanding the Model

There are several ways to enhance the model:

- More accurately capture the rheology by using a constitutive relationship that describes a material that has both viscosity and elasticity (visco-elastic materials).
- Incorporate the downstream behaviour into the visco-elastic model.
- Use the sizes of the Péclet number and the Reynolds number to generate boundary layer models to give insight into the gel's structure.
- Make quantitative experimental measurements of the gel radius to compare with the analytical model.

4. Discussion, Conclusions and Recommendations

We have simulated fibre formation in a coaxial flow field. To do so, we assumed that the gel behaves like a very viscous fluid. Comparison between our simulations and experiments indicates a disparity in what we observe. Numerical simulations predict that the alginate solution expands as it enters the system, however experiment suggests a contraction. We hypothesise that this difference arises because of the properties we assign the gel in our simulation. Our attempt to model the system, incorporating “solid-like” properties such as elasticity began by looking downstream. Simplified analytical models for the gel profile downstream were constructed which predict the radius and velocity of the gel fibre. These models roughly agree with the predictions made using COMSOL on the “full” system described in the model section. The next step in investigating the contraction phenomena is to incorporate the downstream behaviour of the system into a model for the upstream region. A comprehensive model of the fibre manufacturing system both upstream and



downstream will allow for a greater understanding of the conditions that produce fibres of different properties, or no fibres at all.

At this stage, numerical simulations of fibre formation are a useful tool in gaining a qualitative understanding of the process. It is important to ensure that our numerics accurately capture all of the relevant physics. The two outstanding challenges with the simulations are capturing the expansion of the alginate solution just after the injection site, and the difficulty in accurately resolving high Péclet number boundary layers.

If we are not accurately simulating the region at which the flows meet, important information may be missed. The behaviour of the system around the injection site of the alginate plays an important role in the gel structure produced. Fibre production means avoiding situations where continuous fibre will not form, the gel ends up clogging the system, or the gel is not stiff enough due to incomplete reaction. Hence there is a need for a thorough understanding of how the gel will evolve in this region. If an important physical mechanism is being ignored, the next step will be incorporating this into a fully coupled numerical model.

Downstream Behaviour

Our analytical models for the downstream behaviour of the system provide a method for calculating some of the key parameters such as the fibres velocity and radius. Importantly, they provide a way to determine how these parameters respond as our control variables are changed (e.g. input fluxes and concentrations). With experimental validation, it is possible that these models provide all of the required parameters over some range of the control variables. If the gel exhibits any “solid-like” properties (e.g. elasticity) then prescribing a downstream velocity may influence the gel’s behaviour upstream (as the gel fibre will be under some tension). Modelling the behaviour of the flow around the injection side, incorporating information from downstream as a bottom up approach (e.g. prescribe the velocity of the gel to be that of the downstream gel) is one path forward.

Downstream, we predict the same fibre diameter regardless of whether we consider it as a very viscous fluid core or a solid core.

5. Potential Impact

Understanding how cross-linked gel fibres are made is an important first step towards controlling their properties. Our models provide a tool for exploring parameter space and enable optimization of production.

Harvey Williams, Principle research scientist, Schlumberger Gould Research, said “*In our first project with InFoMM, we have focused on exchanging insights on a complex physical modelling problem through detailed investigation of a numerical model and development of lower-order analytical model. We look forward to building on our mutual knowledge in this problem area with follow-up research projects.*”

References

1. A. Mikkelsen, A. Elgsaeter (1995) *Density distribution of calcium-induced alginate gels. A numerical study* Biopolymers. **1-36**, 17-41.