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# Effect of loading history on visco-elastic potato starch gel

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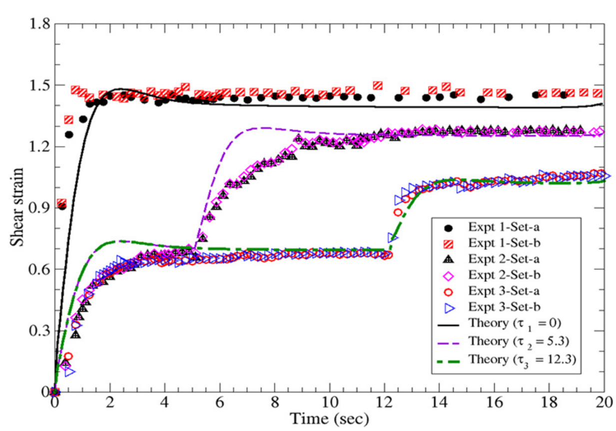
## HIGHLIGHTS

- A starch paste is subjected to squeeze flow.
- The sample retains memory of loading history.
- Complex modulus of the fluid on dynamic loading is also studied.
- The system is modelled as a visco-elastic three parameter solid.
- Generalised calculus is incorporated to reproduce observed oscillation in strain.

## GRAPHICAL ABSTRACT

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## ABSTRACT

In this work gelatinised potato starch is shown to retain the memory of past loading history. It exhibits a visco-elastic response which does not depend solely on instantaneous conditions. A simple squeeze flow experiment is performed, where loading is done in two steps with a time lag $\tau\sim$ seconds between the steps. The effect on the strain, of varying $\tau$ is reproduced by a three element visco-elastic solid model. Complexity is introduced through a generalised calculus approach by incorporating a non-integer order time derivative in the viscosity equation. A strain hardening proportional to the time lag between the two loading steps is also incorporated. This model reproduces the three salient features observed in the experiment, namely – the memory effect, slight initial oscillations in the strain as well as the long-time solid-like response. Dynamic visco-elasticity of the sample is also reported.


## 1. Introduction

Complex fluids such as starch gels generally behave differently from both Newtonian fluids and Hookean elastic solids as discussed by Evans and Haisman [1], Che et al. [2] and Schofield and Blair [3]. Their rheology involves visco-elastic or visco-plastic behaviour. Generalised calculus is a useful technique for describing and analyzing such materials, as shown by Das [4], Heymans and Bauwens [5], Heymans [7] and Dutta Choudhury et al. [6]. New applications and approaches along these lines continue to be developed. Zopf et al. [8] use a visco-elastic Zener model with a non-linear elastic element and a fractional Maxwell element to study moulding and

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curing of rubber. Yang et al. [9] develop a model utilising fractional derivatives, which can describe strain hardening in visco-elastic fluids.

One typical signature of the complexity of visco-elastic materials is that in a stress-strain experiment their response at a certain time instant does not depend only on the stimulus acting at that instant, they 'remember' the history of previous treatment and respond accordingly. We describe a simple experiment which clearly demonstrates the effect of different histories of loading on a drop of potato starch, squeezed between two parallel glass plates.

A very simple experiment, which leads to interesting results for various simple and complex fluids is the so-called 'squeeze-flow' as described by Laun et al. [10] and Lee et al. [11]. The results have practical applications in areas such as tribology, lubrication theory and in particular in food industry [13–15] where *mouth-feel* of food products [16] is an important parameter.

Squeeze-flow experiments on different fluids, where a drop of the sample is subjected to a load in a Hele-Shaw cell, have shown interesting results by Nag et al. [17]. The experiment consists of placing a load of the order of kilograms on a drop of fluid sandwiched between two transparent plates. Spreading of the fluid is measured by video-recording. Fluids with non-Newtonian character show novel features like oscillations in the area of contact [6]. Oscillatory behaviour in compressive flow of a viscoelastic fluid (silicone polymer) was also studied analytically as well as experimentally by Lee et al. [12]. In the present experiment we report the effect of step-loading on a gelatinised starch solution. We show that when two loads are placed one after the other with a certain time lag, the asymptotic area of spreading is different from what is observed when the same two loads are applied simultaneously. We show that a three-element visco-elastic model, incorporating a non-Newtonian dashpot and a strain hardening of the elastic component, is successful in reproducing the experimental observations. The strain hardening is proportional to the time lag between the two successive loading steps. Dynamic visco-elasticity measurements have been done using a standard set up for supporting characterisation of the sample. All experiments show that the sample exhibits long-time solid-like behaviour.

## 2. Materials and method

### 2.1. Sample preparation

The non-Newtonian fluid under study is an aqueous gel of potato starch (Lobachemie, Mumbai). In our experiment, 2.5 g of potato starch is dissolved in 100 ml of distilled water and it is heated up for 10 min and boiled for 2 min, stirring continuously, allowing it to gelatinise. The solution is cooled for 1 h and a pinch of dye is added to enhance the contrast. Room temperature during the experiment was 32 °C and relative humidity was 66%.

### 2.2. Squeeze-flow set up

A droplet of the non-Newtonian fluid is placed on a smooth glass plate of thickness 1.3 cm and diameter 15.5 cm. The mass of the droplet varies between 0.04 g and 0.06 g. A similar glass plate is placed on top of the drop. The mass of the upper plate is 0.56 kg. We consider this configuration (with the drop spread out uniformly by the upper plate) as the initial condition of our experiment. Subsequent variation is measured with this as the reference point. The entire experiment consists of three parts:

- **Experiment 1: Full loading**
  30 s after placing the upper plate, a load $W$ = 4 kg is placed on it and a CCD camera (WATEC-202D, Japan) below the lower plate, records the spreading of the area of contact. The video recording is analysed using the software Image-Pro-Plus, Media Cybernetics, USA.
- **Experiment 2: Step-loading-A**
  The procedure is repeated with a drop of equal volume, this time the loading is done in 2 steps. 30 s after placing the upper plate, load $W_1$ = 2 kg is placed on it. After a further interval of $\tau_2$ s another load $W_2$ = 2 kg is added to the load on the upper plate. Here the final load $W = W_1 + W_2$. The strain development in this case for $t > \tau$ is compared with the case for one-time loading.
- **Experiment 3: Step-loading-B**
  The procedure for experiment 3 is repeated exactly, only with a different time lag $\tau_3$ between placing $W_1$ and $W_2$ on the upper plate.

It is difficult to set an exact specified time interval $\tau$ in the experiment, so we read off the exact time from the video recording. $\tau_2$ = 5.3 s for Experiment 2 and $\tau_3$ = 12.3 s for Experiment 3. For Experiment 1, there is no time lag, so $\tau_1$ = 0 s.

We now compare results of the above three experiments. Taking the instant of placing the first load as $t = 0$, the fractional change in the area of contact of fluid and glass at time $t$

$$\epsilon(t) = [A(t) - A(0)]/A(0) \tag{1}$$

is measured using Image-Pro-Plus software. Here $A(t)$ is the area at time $t$ and $A(0)$ the initial area. Since the separation between the plates, i.e., the height of the squeezed fluid film is very small, we identify $\epsilon$ in Eq. (1) as the *strain* in the spreading experiment.

To establish reproducibility of results, the experiment was repeated several times only those sets where $\tau$ has exactly the desired values were considered.

### 2.3. Measurement of complex visco-elastic moduli

Response of the sample to a sinusoidally varying dynamic load has been done for additional characterisation of the visco-elastic behaviour. Measurements have been carried out at the Pharmaceutical Engineering Department, Jadavpur University using MCR102 SN81260812, Anton Paar GmbH, Austria.

## 3. Results

### 3.1. Squeeze flow results

The strain $\epsilon(t)$ is plotted as a function of time for all 3 experiments. The results are summarised in Fig. 1. Two sets of data for $\epsilon(t)$ versus $t$ for each of the experiments (1–3) are plotted. The two sets designated as data sets *a* and *b* demonstrate the reproducibility of the results. The experimental results are shown on a logarithmic scale in the inset, to demonstrate that the strain reaches a nearly constant value in the time interval of observation.

In Experiment 1, $W$ = 4.0 kg and in Experiments 2 and 3, $W_1 = W_2$ = 2.0 kg. The time lag $\tau$ between placing the two loads is $\tau_2$ = 5.3 s in Experiment 2 and $\tau_3$ = 12.3 s in Experiment 3. Fig. 1 clearly shows the deviation from both ideal Hookean elastic behaviour as well as from the behaviour of an ideal Newtonian fluid. The strain does not reach the final value instantaneously as expected for a perfectly elastic material, neither does it rise from zero and continue to creep indefinitely like a perfect fluid. Moreover there is clear evidence of history dependence in strain for $\epsilon(t)$ when $t > \tau$. The final asymptotic strain (within the observation time of this experiment) is different in all three cases – being maximum when the loading is done at once and decreasing as $\tau$ increases. Clearly, the continued loading changes the elastic and/or viscous properties of the material. We analyse the strain build-up using different visco-elastic models and see which model is best suited to reproduce