Using Greener Gels to Explore Rheology

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Abstract

A laboratory experiment was developed to investigate the rheological properties of a green calcium-crosslinked alginate gel as an alternative to the traditional borax-crosslinked poly(vinyl alcohol) gel. As borax is suspected of damaging fertility and the unborn child, a requirement for a safe, green alternative is necessary. The rheological properties of a sodium alginate solution were examined as a function of temperature using capillary viscometry. Gelation and degelation processes were followed using rotational viscometry. The non-Newtonian shear thinning properties were also exemplified by determining the viscosity as a function of spindle RPM using the rotational viscometer. Students making the transition from a first to second year undergraduate chemistry programme within a natural sciences degree have successfully conducted this laboratory experiment.

Graphic Abstract



Keywords

Second-Year Undergraduate, Polymer Chemistry, Hands-On Learning / Manipulatives, Colloids, Green Chemistry, Materials Science, Outreach, Physical Properties

INTRODUCTION

At the tertiary level, the study of rheology has been identified as a threshold concept.1 When mastered, this represents a transformed understanding of the discipline without which the learner cannot progress. To assist the transition of learners across this threshold, educators have facilitated practical laboratory experiments to reinforce content delivered in the lecture theatre.2 Experiments to investigate the viscosity of materials is one method to support student understanding of rheology. The gelation of poly(vinyl alcohol) (PVA) with sodium borate (borax) as a crosslinking agent has been extensively utilized for this purpose.3-8 Further to this, the PVA-borax system is routinely used at the primary and secondary level as part of outreach demonstrations and children’s toys.9

Prior to PVA gelation, the borate ion (B(OH)4-) is formed following hydrolysis of borax, Na2B4O7·10H2O (eq 1).8

 (1)

The PVA-borax system is ubiquitous within chemical education, although due to borax being classified as *toxic for reproduction* category 1B under Classification, Labelling and Packaging regulations, it was added to the Substance of Very High Concern candidate list. Furthermore, according to the Global Harmonized System of Classification and Labelling of Chemicals (GHS), it poses a *serious health hazard* (GHS08). Such a dangerous crosslinking agent that *may damage fertility* and *may damage the unborn child* (hazard code: H360) is not suitable for education at primary, secondary or tertiary levels. As an alternative, in combination with PVA, aluminum sulfate, a coagulant for water treatment, produces a slime-like viscoelastic fluid.10 Whilst this approach is convenient to form a viscoelastic fluid for demonstration purposes, it has not been shown to form a bulk hydrogel, which would be useful for learners to record viscosity measurements with. To this end, this study outlines an experiment to investigate rheology using a Green Reagents and Sustainable Processes (GRASP) approach. This method consists of identifying potentially hazardous chemicals within an undergraduate experiment (such as borax) substituting for a safe and green and alternative, and implementing a refined version of the activity into the undergraduate curriculum.

Sodium alginate (Figure 1) is a naturally occurring anionic polymer, typically obtained from brown seaweed. It has been utilized for many biomedical applications such as wound dressings, drug delivery, cell culture and tissue engineering owing to its biocompatibility, low toxicity and relatively low cost together with use as a food additive.11



Figure 1. Structure of sodium alginate showing repeating units of mannuronate (M) and guluronate (G). G-blocks, M-blocks and alternating blocks are present.

Gelation can occur by addition of divalent cations such as Ca2+, which results in the formation of strong and specific interactions in the form of chain-chain associations with blocks of guluronic acid residues of sodium alginate.12,13 Such chain associations constitute the junction zones responsible for gel formation. The “egg box model” depicts two helical guluronate chains packed with calcium ions located between them (Figure 2).14



Figure 2. Schematic to illustrate calcium coordination to a pair of guluronate chains as per the “egg box model”.

Degelation can be induced upon addition of trisodium citrate to the calcium chloride-crosslinked sodium alginate gel.15 It is likely that the citrate anions competitively combine with the calcium ions, leading to a loss of chain-chain associations, resulting in degelation. This system eliminates the use of borax, providing an alternative green gel for the rheological properties to be examined. Viscosity was measured by capillary viscometry and rotational viscometry.

The viscosity of a Newtonian fluid can be measured by recording the time of flow of a given volume through a vertical capillary under the influence of gravity. Such flow is described by Poiseuille’s law in eq 2 where ** is the viscosity of the fluid *dV*/*dt* is the rate of liquid flow through a cylindrical tube of radius *r* and length *L*, and (*p1 – p2)* is the pressure difference between the two ends of the tube. A pictorial representation of a capillary viscometer and associated operating instructions are provided for students and facilitators on page 6 of the supporting information.

 (2)

As the pressure difference is proportional to the density of the liquid, *ρ*, for a given total volume of liquid, eq 3 can be constructed whereby *t* is the time required for the meniscus to fall from the upper to the lower mark on the capillary viscometer and *C* is the viscometer constant that has to be determined by calibration with a liquid of known viscosity (such as water).

 (3)

A rotational viscometer measures the torque required to rotate a spindle in a fluid, which is driven by a motor through a calibrated spring. The deflection of the spring results in a torque, from which a value for the viscosity can be determined. An introduction and accompanying equations and schematic are provided for students and instructors on page 3 of the supporting information. Rotational viscometry of borax-crosslinked PVA solutions has been previously utilized as an undergraduate laboratory experiment to explore rheology.3

The following experiment uses a capillary viscometer to investigate the variation in viscosity of sodium alginate solutions as a function of temperature. A rotational viscometer is subsequently utilized to follow the gelation of the sodium alginate solution as a function of calcium chloride addition. The shear-thinning properties of the gel were investigated by determining the viscosity as a function of spindle speed. Finally, degelation was monitored as a function of trisodium citrate addition to the calcium-crosslinked alginate gel. These studies provide an alternative green system to the traditional borax-crosslinked PVA experiment for students to safely examine the rheological properties of polymer gels. This experiment teaches students the difference between Newtonian/non-Newtonian, shear thickening/shear thinning fluid properties together with how to perform error analyses. It is advantageous that these behaviors are discussed prior to the experiment to facilitate understanding. This can be done via a demonstration to contextualize shear thickening fluids (with cornstarch) and shear thinning fluids (with ketchup). Particular emphasis is placed on showing students the necessity to work within the experimental constraints of the instrument selected for an experiment. This is exemplified here by careful consideration of the geometry of the spindle used and angular velocity selected for different scenarios when taking measurements with the rotational viscometer. The experiment is particularly relevant for a second-year undergraduate studying materials science or polymer chemistry modules.

MaTERIALS

A 1% w/v sodium alginate solution was prepared by slowly adding 5.00 g of sodium alginate (medium molecular weight, CAS 9005-38-3, Sigma Aldrich) to 450 mL of deionized water with stirring until all the polymer has dissolved. The sodium alginate can be difficult to dissolve; therefore to aid dissolution, the mixture can be heated to 50-60 °C ensuring the solution does not boil. If heated, the mixture should be allowed to cool. The sodium alginate solution was transferred quantitatively into a 500 mL volumetric flask. The solution was then made up to the mark with deionized water and mixed by slowly inverting a few times. A 25 mM solution of calcium chloride was prepared by dissolving 0.92 g of calcium chloride (CAS 10035-04-8, Sigma Aldrich) in deionized water in a 250 mL volumetric flask. The solution was then made up to the mark on the flask. A 25 mM solution of trisodium citrate was prepared by dissolving 1.85 g of trisodium citrate (CAS 6132-04-3, Sigma Aldrich) in deionized water in a 250 mL volumetric flask. The solution was then made up to the mark on the flask.

An Ostwald U-tube capillary viscometer (Size B, Poulton Self) was used to examine the viscosity of sodium alginate solutions. This was immersed in a transparent water bath (in the form of a 5 L beaker) at the required temperature.

A rotational viscometer (in this case a Brookfield DV-E RV Viscometer) was employed to analyze the rheological behavior of the gel. A spirit level can be used to ensure the instrument is level. The experiments could also be conducted using other viscometers available on the market (e.g. Cole-Parmer, Thermo Scientific or Rheosys). Two different spindles were used: The first one has a diameter of 27.3 mm and height of 49.21 mm (RV4) and the second one has a diameter of 14.62 mm and height 49.21 mm (RV6). Hot water should be used to clean the guard leg and spindles between appropriate sets of measurements. RPM values between 0 and 100 were available to select and accurate torque values could be obtained between 10 and 100%.

EXPERIMENTAL METHOD

Variation in viscosity as a function of sodium alginate solution temperature

The capillary viscometer was thoroughly cleaned and dried using copious amounts of hot water, followed by deionized water, ethanol and finally acetone. The capillary viscometer was then immersed in a transparent water bath maintained at 25 °C. Deionized water was used to calibrate the capillary viscometer where the time for the meniscus of the solution to fall between the highest and lowest marks was recorded. This was repeated twice and an average time recorded was determined to calculate the viscometer constant, *C*.

The 1% w/v sodium alginate solution was diluted to 0.1% w/v so that the time measurements were of the order of 2-3 min. The alginate solution was then transferred to the capillary viscometer and three time measurements were recorded where the density of each of the solutions was determined using a 2.5 mL pycnometer. This was repeated by immersing the capillary viscometer into water baths at 35 °C and 45 °C. Time permitting, students can record time measurements while the alginate solution is maintained at other temperatures. The data collected can be subsequently utilized to explore Arrhenius-type behavior.

Variation in viscosity as a function of calcium chloride addition

From the 1% w/v stock solution of sodium alginate, 400 mL was quantitatively transferred to a 600 mL beaker. The viscosity of the sodium alginate solution was measured using the RV4 spindle. The calcium chloride solution was added dropwise in 10 mL aliquots during rigorous agitation with a glass rod. The aliquot size can be varied according to the time available to conduct the experiment. Following each addition, the mixture was stirred for 30 seconds in order to contribute towards the formation of a uniform gel and a viscosity measurement was recorded. The spindle was cleaned between each measurement. This was repeated until a total of 100 mL of calcium chloride solution had been added. Viscosity is reported in centipoise where one milli-Pascal-second is equal to 1 cP. This is in keeping with the centimeter-gram-second (CGS) system of units displayed by the Brookfield DV-E Viscometer.

Shear rate dependence of the viscosity of the gel

Using the second spindle (RV6) the shear rate dependence of the viscosity of the gel between 0-100 RPM was determined using the crosslinked gel (100 mL of calcium chloride solution had been added to 400 mL of sodium alginate solution). It is necessary to use the other spindle as upon increasing viscosity, shear stress, and therefore torque also increase and in order to maintain torque values between 10-100%, a spindle with a reduced radius and effective length is more appropriate for measuring viscosity accurately. The number of air bubbles around the spindle was kept at a minimum by stirring carefully to allow accurate viscosity measurements. Following this test, the spindle was cleaned and dried.

Variation in viscosity as a function of trisodium citrate addition to the calcium-crosslinked alginate gel

The viscosity of the crosslinked gel was measured using the RV6 spindle. The trisodium citrate solution was added dropwise in 10 mL aliquots during rigorous agitation with a glass rod. Following each addition, the mixture was stirred for 30 seconds and a viscosity measurement was recorded. The spindle was cleaned between each measurement. This was repeated until a total of 100 mL of trisodium citrate solution had been added.

A student lab manuscript is available as part of the supporting information.

HAZARDS

Sodium alginate and trisodium citrate are not classified as hazardous substances, although normal lab practice should be followed. Calcium chloride causes serious eye irritation and if this is in the eyes, they should be rinsed cautiously with water for several minutes. Students should wear safety spectacles and a long-sleeved lab coat throughout the investigation. For safe disposal, hot water should be added to the gel to decompose the network.

RESULTS

This experiment has been completed by students as part of a transition course from first to second-year in undergraduate chemistry within natural sciences. Students worked in groups of three and completed the entire experiment within 5 hours. Representative data for all parts of the experiment are presented as follows.

Students initially investigated the effect of varying the temperature on the viscosity of a 0.1% w/v sodium alginate solution using a capillary viscometer. The results are represented in Figure 3. As shown, the viscosity decreases upon an increase in temperature owing to an enhancement in the thermal velocity of the sodium alginate molecules in solution.



Figure 3. Variation in viscosity of a 0.1% w/v sodium alginate solution as a function of temperature.

Subsequently, students investigated as to how the viscosity of a sodium alginate solution varied as a function of calcium chloride addition by rotational viscometry (Figure 4). The viscosity rises sharply at the gelation point, after which, the fluid becomes non-Newtonian.



Figure 4. Variation in viscosity of 400 mL of a 0.1% w/v sodium alginate solution upon addition of a 25 mM calcium chloride solution. This was recorded using a rotational viscometer at an angular velocity of 10.47 s-1.

Upon forming a gel, students determined how the viscosity changed upon variation in the spindle RPM (Figure 5). From this, they were able deduce as to whether the observed behavior was Newtonian or non-Newtonian in nature and subsequently that the calcium-crosslinked alginate gel displays shear-thinning properties. Students likened this to the ketchup demonstration at the start of the session. Throughout the experiment, students needed to consider the limitations of the viscometer in terms of the available torque range (10 – 100%) and may need to change the type of spindle in order to record data.



Figure 5. Variation in viscosity of a calcium-crosslinked alginate gel upon change in shear rate. The gel studied was that obtained upon completion of the experiment detailed in Figure 4 with a final volume of 500 mL and final concentrations of 0.8% w/v sodium alginate and 5 mM calcium chloride respectively.

Finally, students investigated how the viscosity of the gel varied as a function of trisodium citrate addition (Figure 6). As the amount of trisodium citrate added is increased, the viscosity of the gel decreases as citrate moieties competitively bind with calcium ions, leading to disruption of alginate chain-chain associations, resulting in degelation. This is also a convenient route to safely disposing the gel.



Figure 6. Variation in viscosity of calcium-crosslinked alginate gel upon addition of a 25 mM trisodium citrate solution. This was recorded using a rotational viscometer at an angular velocity of 10.47 s-1. The gel studied was that obtained upon completion of the experiment detailed in Figure 5 with a final volume of 500 mL and final concentrations of 0.8% w/v sodium alginate and 5 mM calcium chloride respectively.

CONCLUSIONS

This experiment enables students to explore the rheological properties of green gels using capillary and rotational viscometry. A GRASP approach was employed to identify and substitute the harmful crosslinking agent in the traditional borax-crosslinked PVA gel. A green calcium-crosslinked alginate gel was implemented as an alternative system. The rheological properties of the green gel were determined to include the temperature effects of viscosity, gelation, non-Newtonian behavior and degelation. It is noteworthy that the viscosity regimes of traditional borax-crosslinked PVA gels (shear thickening) and the green alginate gels (shear thinning) detailed here are comparable. This would facilitate facile adoption of this GRASPed methodology without a requirement for additional apparatus.

Associated content

Supporting Information

A student lab manuscript and an instructor guide are provided as supporting information. This material is available via the Internet at *http://pubs.acs.org.*

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Notes

The authors declare no competing final interest.

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