# CHEMICALEDUCATION

## The Rheological Properties of Poly(vinyl alcohol) Gels from Rotational Viscometry

Glenn A. Hurst,\* Malika Bella, and Christoph G. Salzmann

Department of Chemistry, Science Laboratories, Durham University, Durham DH1 3LE, United Kingdom

**Supporting Information** 

**ABSTRACT:** A laboratory experiment was developed to follow the gelation of a polyvinyl alcohol (PVA) solution upon addition of borax by using rotational viscometry. The rheological properties of the gel were examined, measuring the dependence of viscosity and shear stress on the shear rate. Time-dependent studies were also conducted in which the viscosity of the PVA gel was evaluated as a function of time for different shear rates. A range of qualitative tests were subsequently conducted to demonstrate the phenomena of die swelling, spinability and the Weissenberg effect. Overall, this laboratory experiment has been successfully conducted by over 200 students.



**KEYWORDS:** Upper-Division Undergraduate, Polymer Chemistry, Hands-On Learning/Manipulatives, Colloids, Materials Science, Physical Properties

### INTRODUCTION

Rheology is the study of the flow and deformation of materials during the application of force.<sup>1–3</sup> Investigating the viscosity of materials is one way to evaluate their rheological behavior and this will be the topic of this study. Viscosity measurements are of critical importance in a diverse range of industries including but not limited to chemistry, chemical engineering and pharmacy. For example, viscometry is an essential technique in the assessment of the quality of petroleum products, glues, paints, inks and food components.<sup>4</sup> On a more fundamental level, viscometry is an important analytical tool in macromolecular and soft-matter chemistry.<sup>5</sup>

The viscosity of a fluid is representative of its internal friction, which becomes apparent when a fluid layer is forced to move in relation to another layer. Figure 1 shows two parallel flat areas of



**Figure 1.** Schematic to illustrate the force required to move a layer of a liquid with respect to another one. This figure has been reproduced from *More Solutions to Sticky Problems* with the permission of Brookfield Viscometers Ltd. Copyright 2014.

fluid of the same size A separated by a distance dx and moving in the same direction at different velocities  $V_1$  and  $V_2$ . The force required to maintain this difference in speed is proportional to the velocity gradient as given in eq 1.

$$\sigma = \frac{F}{A} = \eta \frac{dv}{dx} = \eta \dot{\gamma} \tag{1}$$

The constant of proportionality,  $\eta$ , is the viscosity of the fluid. The velocity gradient describes the shearing that the liquid experiences and is thus defined as the "shear rate",  $\dot{\gamma}$ . The term F/A indicates the force per unit area required to instigate the shearing action, and is referred to as the "shear stress",  $\sigma$ . Viscosity values can therefore be calculated from the ratio of  $\sigma/\dot{\gamma}$  and are traditionally reported in "centipoise" where 1 cP = 0.001 Pa s.<sup>6</sup>

This study utilizes poly(vinyl alcohol) (PVA) as the model polymer. PVA has the advantage of being readily soluble in water, negating the requirement to use large quantities of organic solvents such as toluene required for polystyrene.<sup>7</sup> PVA is made via the hydrolysis of poly(vinyl acetate) where the degree of hydrolysation is 98–99%. Gelation of aqueous solutions of PVA can be induced by addition of a borate ion  $(B(OH)_4^-)$  which acts as a cross-linking agent. Sodium borate (or borax), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10 H<sub>2</sub>O, when hydrolyzed in water, forms a boric acid/borate buffer at a pH close to 9 (eq 2).<sup>8</sup>

$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+$$
(2)

PVA complexation with borate begins with an initial monodiol complexation (eq 3) followed by a subsequent cross-linking reaction (eq 4).<sup>9,10</sup>



© XXXX American Chemical Society and Division of Chemical Education, Inc.



However, it has also been suggested on the basis of infrared spectroscopic data that gelation is caused by hydrogen bonding interactions only.<sup>11</sup> The arrangement of hydrogen bonds in such a cross-linked but labile network is depicted in Figure 2.<sup>6</sup>



Figure 2. Schematic depiction of the hydrogen bonding associated with a PVA-borax network.

The aforementioned gelation process can be monitored using a rotational viscometer such as the Brookfield DV-II Pro Viscometer (Figure 3) which measures the torque required to rotate



**Figure 3.** Schematic drawing of a rotational viscometer with an analog display. The model used in this experiment has a digital screen. This figure has been reproduced from *More Solutions to Sticky Problems* with the permission of Brookfield Viscometers Ltd. Copyright 2014.

an immersed spindle in a fluid.<sup>12</sup> The spindle is driven by a motor through a calibrated spring. The deflection of the spring results in a torque, M, from which the shear stress,  $\sigma$ , is calculated (eq 5).<sup>13</sup>

$$\sigma = \frac{M}{2\pi R_{\rm b}^2 L}$$

 $R_{\rm h}$  = radius of the spindle

$$L = \text{effective length of the spindle}$$
(5)

The shear rate,  $\dot{\gamma}$ , at the surface of a spindle can be calculated according to eq 6 where  $R_c$  is the distance from the axis of rotation to the guard leg of the viscometer and  $\omega$  is the angular velocity of the spindle (rad s<sup>-1</sup>).<sup>13</sup>

$$\dot{\gamma} = \frac{2R_{\rm c}^2}{R_{\rm c}^2 - R_{\rm b}^2}\omega\tag{6}$$

The viscosity of the fluid can then be calculated from eq 7.

$$\eta = \frac{\sigma}{\dot{\gamma}} \tag{7}$$

With the use of a rotational viscometer, it is therefore possible to measure the viscosity of a fluid as a function of the shear rate by adjusting the angular velocity of the spindle.

At a given temperature, Newtonian fluids, such as water and thin motor oils, have a viscosity that is independent of shear rate and therefore exhibit a linearly proportional behavior between shear stress and shear rate (Figure 4).<sup>14</sup>



**Figure 4.** Graphs depicting Newtonian behavior. The viscosity is constant as the shear rate is varied and a linear relationship between shear stress and shear rate exists. This figure has been reproduced from *More Solutions to Sticky Problems* with the permission of Brookfield Viscometers Ltd. Copyright 2014.

However, a wide range of fluids actually show non-Newtonian behavior. Some of these fluids exhibit a variety of phenomena such as the Weissenberg effect. Upon rotation of a rod immersed in a non-Newtonian fluid, the fluid climbs the rod against the force of gravity due to a rotational force acting a horizontal plane, producing a normal force.<sup>15</sup> Die swelling is another phenomena driven by normal forces, where the fluid will have a larger diameter to that of the die. Such fluids also possess a microstructure requiring measurable time to relax and can hence store elastic energy and dissipate viscous energy. Therefore, these fluids exhibit high extensional viscosities, imparting spinability properties to these materials.<sup>16</sup> Shear-thinning (pseudoplastic) fluids will display a decreasing viscosity with increasing shear rate (Figure 5). Prominent examples are paint and ketchup.

Shear thickening or dilatant fluids display the opposite non-Newtonian behavior (Figure 6). This effect is exhibited by PVA– sodium borate solutions, which are the subject of this study.<sup>17,18</sup>

The flow properties of non-Newtonian fluids can be often described by using a power law (eq 8) where *k* is the consistency index and *n* is the flow index ( $k = \eta$  and n = 1 for a Newtonian fluid).

$$\sigma = k \dot{\gamma}^n \tag{8}$$

Furthermore, some fluids will exhibit a change in viscosity with time under conditions of constant shear rate. A thixotropic fluid undergoes a decrease in viscosity with time, while the viscosity of a rheopectic fluid increases with time. Both thixotropy and rheopexy may occur in combination with any of the aforementioned



Figure 5. Graphs depicting non-Newtonian behavior representative of shear-thinning fluids. This figure has been reproduced from *More Solutions to Sticky Problems* with the permission of Brookfield Viscometers Ltd. Copyright 2014.



Figure 6. Graphs depicting non-Newtonian behavior representative of shear-thickening fluids. This figure has been reproduced from *More Solutions to Sticky Problems* with the permission of Brookfield Viscometers Ltd., Copyright 2014.

flow behaviors, or only at certain shear rates. Time-dependent effects may or may not be reversible. Some fluids, if allowed to remain undisturbed for a period of time, will regain their initial viscosity while others never will.<sup>19</sup>

The following experiment uses a rotational viscometer to follow the gelation of a PVA solution. The shear-rate dependence of the viscosity is measured before and after gelation occurs, and the time-dependent behavior of the viscosity is investigated for the gel. Qualitative observation of the non-Newtonian Weissenberg, die swelling, and spinability effects are also conducted. These studies build on current literature content<sup>6,20</sup> while introducing new and relevant content with reference to the time-dependent behavior. This experiment teaches students the difference between Newtonian/non-Newtonian, shear thickening/ shear thinning, and rheopexy/thixotropy fluid properties. It is advantageous that these behaviors are discussed prior to the experiment to facilitate understanding.<sup>21</sup> 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. The experiment is particularly relevant for an upper-division undergraduate studying materials science or polymer chemistry modules.

#### MATERIALS

The PVA solution was prepared by slowly adding 20.00 g of PVA (average molecular weight 31-50 kDa, 98-99% hydrolyzed, Sigma-Aldrich) to 400 mL of deionized water preheated to between 70 and 80 °C with stirring until all the polymer has dissolved. It was ensured the solution did not boil. The mixture was allowed to cool and 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.

The solution was filtered gravimetrically through glass wool. Sodium borate solution was prepared by transferring 2.00 g of sodium tetraborate decahydrate (ACS reagent  $\geq$ 99.5%, Sigma-Aldrich) into a 50 mL volumetric flask, which is dissolved in deionized water by heating, The solution was then made up to the mark on the flask.

A mechanical stirrer was used to mix PVA and sodium borate solutions. To facilitate effective mixing, a U-shaped stirrer shaft equipped with an anchor stirrer blade was used. The blades of the anchor were curved to enhance radial mixing of the solutions.

A rotational viscometer (in this case a Brookfield DV-II Pro Viscometer) was employed to analyze the rheological behavior of the PVA 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 18.84 mm and height of 80.97 mm (S1) and the second one has a diameter of 3.2 mm and height 40.54 mm (S2). Hot water should be used to clean the guard leg and spindles between appropriate sets of measurements. RPM values between 0 and 200 were available to select. Accurate viscosity values can only be obtained for torque values between 10 and 100%. A Rheocalc Brookfield application software package was used to work in conjunction with the viscometer

#### EXPERIMENTAL METHOD

## Variation in Viscosity as Borate Solution Is Added to PVA Solution

The viscosity of the PVA solution was measured using the S1 spindle. The sodium borate solution was added dropwise in 3 mL aliquots during agitation with a mechanical stirrer. Solutions were initially stirred vigorously but upon foam formation, the speed was decreased. Following each addition, the mixture was stirred for 30 s and a viscosity measurement was recorded. This was repeated until a total of 12 mL of sodium borate solution had been added. Following this, 1 mL additions were completed until a viscosity of approximately 100 cP was reached. Viscosity is reported in centipoise where 1 mPa·s is equal to 10 cP. This is in keeping with the centimeter-gram-second (CGS) system of units displayed by the Brookfield DV-II Pro Viscometer.

The gelation process was then continued by adding the sodium borate solution in 1 mL aliquots until a viscosity between 3000 and 3500 cP was achieved (where approximately 30–35 mL of sodium borate is required). The RPM values were adjusted to ensure the torque was maintained between 10 and 100%. The lowest possible RPM values were used in order to minimize (possible) non-Newtonian behavior. The speed of the U-shaped mechanical stirrer was decreased gradually to reduce the amount of air bubbles trapped in the gel.

#### Shear Rate Dependence of the Viscosity of the Gel

Using the second spindle (S2) the shear rate dependence of the viscosity of the gel between 0 and  $22 \text{ s}^{-1}$  was determined using the same parameters defined with the 100 cP mixture. 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 and 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 for accurate viscosity measurements. Following this test, the spindle was cleaned and dried.

#### Time Dependence of the Viscosity of the Gel

"Time to Stop" programs were defined with total test times of 3 min where a data point was recorded every 5 s. The programs were run at increasingly higher RPMs (e.g., 20, 40, 60, etc.) until the torque was out of range using the aforementioned gel where the shear rate dependence of viscosity was measured.

#### **Other Characterization Tests**

The gel was tested for the die-swelling effect by inserting the gel into a plastic syringe and pressing down on the syringe. A pipet was dipped into the gel and removed to investigate the spinability of the gel. All of the remaining borate solution was subsequently added to form a highly viscous gel. The network was then agitated with the mechanical stirrer to test for the Weissenberg effect.

Student lab manuscripts, student pro-forma sheets, and accompanying videos are available as part of the Supporting Information.

#### HAZARDS

Poly(vinyl alcohol) is not classified as a hazardous substance, although normal lab practice should be followed. Sodium tetraborate decahydrate may impair fertility and cause harm to the unborn child. Exposure should be avoided. 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

All the experiments have been completed by over 200 students in third-year undergraduate physical chemistry course. Students



Figure 7. Variation in viscosity of a PVA solution upon addition of borax solution.

worked in pairs and completed the entire experiment within 9 h. Representative data for all parts of the experiment are presented as follows.

In the initial part of the investigation, students are asked to study how the viscosity varies as a function of borax addition. This is depicted in Figure 7. As shown, the viscosity increases sharply at the gelation point, displayed by the dashed line. Following gelation, the fluid becomes non-Newtonian. This is confirmed in latter experiments (Figure 8).

Students then examined how the viscosity and shear stress of the gel changed upon variation in shear rate (Figure 8). Shear stress is reported using the CGS system of units in the form of dynes/square centimeter whereby 1 N m<sup>-2</sup> is equivalent to 10 dyn cm<sup>-2</sup> where dyn symbolizes dynes. From this, they were able to deduce as to whether the observed behavior was Newtonian or non-Newtonian in nature and subsequently that the PVA-borax gel displays shear-thickening as opposed to shearthinning properties. By utilizing a rotational viscometer in this fashion, information with regard to shear stress behavior can be attained. Throughout the experiment, students needed to consider the limitations of the viscometer in terms of the available torque range and may needed to decrease RPM values or change the type of spindle.

Power-law parameters were subsequently determined (Figure 9) according to eq 8. Such parameters were subsequently used to determine the quality of the fit upon investigating the variation in shear stress of the PVA solution as a function on shear rate (Figure 8b).



**Figure 9.** A double-logarithmic graph of shear stress and shear rate to determine the power law parameters for the aforementioned borax-cross-linked PVA gel characterized in Figure 8.



**Figure 8.** Variation in (a) viscosity and (b) shear stress of PVA gel upon changes in shear rate following the addition of 30–35 mL of a sodium borate solution. Curve fitting in part b is performed using parameters determined in Figure 9.





Finally, students investigated how the viscosity measured at different speeds varied as a function of time (Figure 10). This time-dependent study is particularly novel as a student experiment and is a good learning experience, requiring a thoughtful and careful experimental technique. Furthermore, these measurements can help explain deviations from the power-law behavior at high shear rates as seen in Figure 8b above  $\sim 19 \text{ s}^{-1}$ . Figure 10 shows that the viscosity up to  $12.68 \text{ s}^{-1}$  is essentially time-independent. However, at 16.91 s<sup>-1</sup>, a gradual increase in viscosity is observed after about 60 s. This effect is even more pronounced at 21.14 s<sup>-1</sup>. To conclude, the deviations from the power-law behavior seen in Figure 8b above  $\sim 18 \text{ s}^{-1}$  can be attributed to time-dependent effects. The time-dependent study highlights the difference between thixotropic and rheopectic fluids, and directs students to come to the conclusion that further to displaying non-Newtonian shear-thickening behavior following the rate-dependent experiments, the PVA-sodium borate gel also exhibits rheopexy (exemplified at higher speeds). Due to the innate rheopectic property of the network, at higher shear rates, the viscosity will increase, and as the power law is dependent on viscosity, a positive deviation is observed.

As the last part of the experiment, students conduct several qualitative tests to investigate the phenomena of die swelling, spinability and the Weissenberg effect. Students particularly enjoyed this exercise while learning the practical differences between Newtonian and non-Newtonian fluids. Upon forcing the gel through a tube, its diameter will expand (die swelling). This could be due to recoiling of the polymeric chains against the shearing action and poses problems in the manufacture of synthetic fibers to achieve desired tubule diameters.<sup>6</sup> The PVA gel also possesses the spinability property and can therefore be drawn out into long and fine threads, vital to the fiber industry to produce yarns. Students found the Weissenberg effect particularly interesting and surprising. Upon stirring Newtonian fluids, a vortex is created; however, the opposite behavior is found for the gel prepared here. Upon shearing, a radially inward force is initiated, pushing the fluid to and subsequently up the stirrer.

#### CONCLUSIONS

This experiment utilized a rotational viscometer to examine the gelation and rheological properties of a borax-cross-linked PVA gel. With the use of a rotational viscometer, information such as shear rate dependency and time-dependent effect on viscosity can be obtained. This investigation teaches students the need to conduct practical experiments within the limitations of the apparatus that they are using. A careful and thorough experimental

technique is required throughout this experiment making this an ideal task for an upper-division undergraduate.

#### ASSOCIATED CONTENT

#### **Supporting Information**

Student lab manuscripts, student pro forma sheets and accompanying videos. This material is available via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: glenn.hurst@york.ac.uk.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors wish to thank the students who participated in this experiment and the Chemistry Department at Durham University for funding. Figures 1 and 3–6 have been reproduced with the permission of Brookfield Viscometers Ltd., for which we are grateful.

#### REFERENCES

(1) Ferguson, J.; Kemblowski, Z. *Applied Fluid Rheology*; Kluwer Academic Publishing Group: Dordrecht, Netherlands, 1991.

(2) Barnes, H. A. A Handbook of Elementary Rheology; University of Wales, Institute of Non-Newtonian Fluid Mechanics: Aberystwyth, U.K., 2000.

(3) Mezger, T. G. *The Rheology Handbook*, 3rd rev. ed.; Vincentz Network GmbH & Co.: Hannover, Germany, 2013.

(4) Dolz, M.; Delegido, J.; Casanovas, A.; Hernandez, M. J. A Low-Cost Experiment on Newtonian and Non-Newtonian Fluids. *J. Chem. Educ.* **2005**, *88* (3), 445–447.

(5) Perrin, J. E.; Martin, G. C. The Viscosity of Polymer Fluids. *J. Chem. Educ.* **1983**, *60* (6), 516–518.

(6) de Zea Bermudez, V.; Passos de Almeida, P.; Feria Seita, J. How To Learn and Have Fun with Poly(Vinyl Alcohol) and White Glue. *J. Chem. Educ.* **1998**, 75 (11), 1410–1418.

(7) Smith, D. R.; Raymonda, J. W. Polymer Molecular Weight Distribution: An Undergraduate Physical Chemistry Experiment. *J. Chem. Educ.* **1972**, *49* (8), 577–578.

(8) Casassa, E. Z.; Sarquis, A. M.; Van Dyke, C. H. The Gelation of Polyvinyl Alcohol with Borax: A Novel Class Participation Experiment Involving the Preparation and Properties of a "Slime". *J. Chem. Educ.* **1986**, 63 (1), 57–60.

(9) Keita, G.; Ricard, A.; Audebert, R.; Pezron, E.; Leibler, L. The Poly(vinyl alcohol)-Borate System: Influence of Polyelectrolyte Effects of Phase Diagrams. *Polymer* **1995**, *36*, 49–54.

(10) Lin, H. L.; Liu, Y. F.; Yu, T. L.; Liu, W. H.; Rwei, S. P. Light Scattering and Viscoelasticity Study of Poly(vinyl alcohol)-Borax Aqueous Solutions and Gels. *Polymer* **2005**, *46*, 5541–5549.

(11) Bolewski, K.; Rychły, B. Über die Struktur der Bindung von Polyvinylalkohol und Borsäure. *Kolloid Z. Z. Polym.* 1968, 228, 48-54.
(12) *More Solutions to Sticky Problems*; Brookfield Engineering Labs, Inc.: Middleboro, MA, 2014; pp 8-18.

(13) Steffe, J. W. Rheological Methods in Food Process Engineering, 2nd ed.; Freeman Press: East Lansing, MI, 1996; pp 158–164.

(14) Hamley, I. W. Introduction to Soft Matter: Synthetic and Biological Self-Assembling Materials, Revised ed.; John Wiley and Sons Ltd: West Sussex, England, 2007; pp 25–28.

(15) Bourne, M. C. Food Texture and Viscosity: Concept and Measurement; Academic Press: San Diego, CA, 2002; pp 95–96.

(16) Macosko, C. W. Rheology Principles, Measurements and Applications; Wiley VCH Publishers: New York, 1994; pp 226–230.

(17) Savins, J. G. Shear Thickening Phenomena in Poly(vinyl)alcohol-Borate Complexes. *Rheol. Acta* **1968**, 7 (1), 87–93.

(18) Inoue, T.; Osaki, K. Rheological Properties of Poly(vinyl alcohol)/Sodium Borate Aqueous Solutions. *Rheol. Acta* **1993**, 32 (6), 550–555.

(19) Goodwin, J. W.; Hughes, R. W. *Rheology for Chemists: An Introduction*; Royal Society of Chemistry Publishing Group: Cambridge, United Kingdom, 2000; pp 213–219.

(20) Seckin, T.; Kormali, S. M. An Easy-to-Build Rotational Viscometer with Digital Readout. *J. Chem. Educ.* **1996**, *73* (2), 193–194.

(21) Willenbacher, N.; Georgieva, K. Rheology of Disperse Systems. In Product Design and Engineering: Formulation of Gels and Pastes; Bröckel, U., Meier, W., Wagner, I. G., Eds.; Wiley VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2013; pp 7–49.