A method for rheological measurements of air sensitive samples

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ABSTRACT

Rheology of air- or moisture sensitive liquids, gels, and glasses requires complicated rheometer-in-glovebox laboratory setups. Here, we demonstrate the use of a heavy-than-air cover gas, sulfur hexafluoride, and the design of a cover gas container that can attach to the lower geometry plate of any rheometer to carry out rheology experiments on air-sensitive liquids and soft solids. Rheological measurements of titanium(IV) propoxide, a moisture-from-air reactive liquid, are shown to demonstrate the effectiveness of the cover-gas method on acquiring correct temperature dependent viscosity data of the sample in the absence of polymeric reaction products.

I. INTRODUCTION

Rheology concerns the study of flow and deformation behavior of materials in a fluid or solid state[1]. A typical quantitative measurement consists of applying a strain to a material and observing the resulting strain. The viscosity (or more generally the elastic modulus for a solid or very viscous fluid) can be found by taking the ratio of stress to strain[2]. Viscosity describes the internal friction between molecules of a given material as they are forced past one another and is therefore a function of a multitude of parameters, *e.g.*, strain magnitude, temperature, time, *etc*. However, different information on the internal structure can be implied from the viscosity as a function of these parameters making rheology a versatile tool with a wide range of fields including the development of construction[3] and energy materials[4], quality control of food[5], development of pharmaceutical products[6] and the development of advanced materials such as polymers[7], metal-organic frameworks[8,9] (MOFs) and nanomaterials[10].

In general, rotational, and capillary type rheometers are the two most widely used methods of rheometry for studying fluids and soft solids, each with their own merits. Capillary type rheometers employ the flow of a liquid inside a tube resulting from a difference in pressure between the inlet and outlet of a tube, driven by gravity or other mechanical means. Rotational rheometers in their most basic form consist of two surfaces (plates or other geometry types), one motionless and the other driven by a high precision motor with a liquid or soft solid sample sandwiched between the two, as shown in FIG. 1. The viscosity of the liquid is then calculated from the force (stress) that the liquid imposes to an applied strain (displacement). The rotational type of rheometer is advantageous in that it offers a wider variety of experiment types that can be carried out due to the different modes the motor can operate in and so more information on the rheological properties of a sample can be observed. The rotational technique also has the benefit of needing a much smaller sample volume in comparison to capillary methods, which can be critical when studying new materials that are expensive, scarce, or not easily produced.

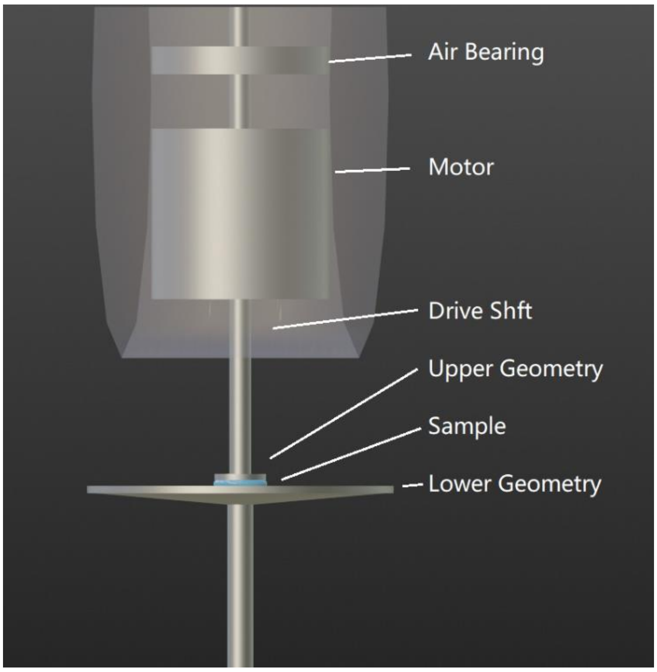

FIG. 1. Diagram of a typical rotational rheometer setup. As the upper geometry has to be lowered onto the lower geometry with a precisely controlled gap containing the sample, accessibility implies exposure to the surrounding air.

With the development of more exotic advanced materials environmental considerations such as humidity, air reactivity, lighting conditions are becoming more important when studying new materials in the laboratory setting. For example, MoltenFLEX, an energy company have recently installed a high temperature rheometer in an inert glove box at great complexity and cost to study the viscosity and density of molten salts at high temperature that will be used as fuel and coolant in a novel energy reactor[11]. Manufacturers of rheometer systems have made strides to supply accessories that alleviate environmental problems such as relative humidity chambers, which can finely control the humidity of the air around the sample during measurement but are limited

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by the temperature ranges, they can operate in and generally cannot remove all moisture from the sample chamber air. Moreover, these accessories are expensive and are not universally suitable for all apparatus setups. Air sensitivity is less catered for currently, with the typical solution being to situate your rheometer inside a sealed glove box pumped with the inert gas of your choice. This, however, is costly and not always a viable option either due to confined laboratory space or the heating/cooling elements of the rheometer requiring regular air to control temperature.

Here we show that these problems can be overcome in a simple and cost-effective manner, by the development of a method of isolating the measuring geometries of a rotational rheometer and sample using a heavier than air gas, sulfur hexafluoride (SF_6). We demonstrate its use to study a family of moisture-from-air sensitive molecular liquids, titanium alkoxides, in a standard rotational rheometer with heating and cryogenic cooling capabilities.

II. METHODS, CONTAINER DESIGN, AND INITIAL TESTING

To hold the cover gas in place around the sample and measurement geometries, a cup was designed made of plastic which seals to the surface of the bottom geometry through a ring shaped graphite gasket (outer ring diameter 57 mm, inner ring diameter 42 mm) cut from a 1 mm Klinger graphite sheet purchased from RS-Components , typically found in vehicle engine seals and other high temperature/pressure environments. Graphite was chosen due to its ability to withstand a large range of temperatures and the ease in which it can be cut and shaped from readily available sheets of material. The cover gas container described here (see FIG. 2) was specifically designed to fit the lower measuring plate (L-PP50) of an Anton Paar MCR 702e Multidrive type rheometer (with an oven heating and cryogenic cooling accessory attached) with an open top to allow the upper measuring geometry to contact the sample unrestricted. While the cup was designed to fit this particular setup, it would be trivial to alter the cup dimensions to fit other apparatus. FIG. 2 shows a graphical representation of the of the cup as well as its attachment to the rheometer, while a 3D CAD design file is available as supplementary information.

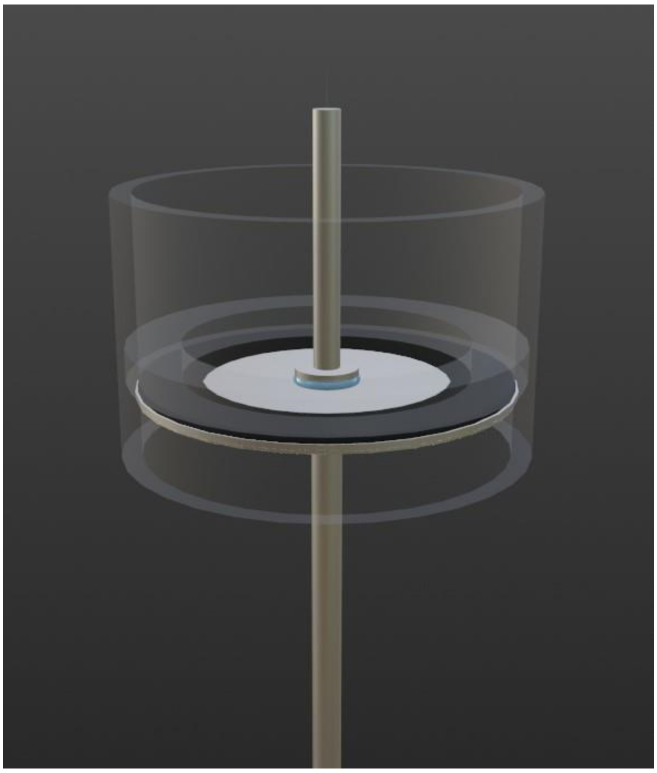

FIG. 2. Cover gas cup for carrying out rheometry isolated from the environmental air. Computer rendering of the cover gas cup (transparent) with connecting gasket (black ring) sealed to the lower plate geometry.

SF_6 is a heavier than air, colorless, non-flammable, non-toxic hypervalent gas with octahedral geometry. At a density of 6.170 g/L the gas is around 5 times heavier than air at 1.225 g/L, allowing it to settle in sealed bottom vessels (as such, it is critical to work in either an open ventilated area or monitor the oxygen levels at low height to avoid accidental asphyxia while working with SF_6)[12]. Additionally, SF_6 is virtually inert, driven largely by the fluoride atoms sterically hindering the sulfur atom at the core of the molecule making it an ideal cover gas for use in separating reactive materials from air during rheometry measurements. It must however be noted that SF_6 is an extremely powerful greenhouse gas, trapping heat in the atmosphere with a radiative efficiency ~23,500 higher per molecule than carbon dioxide. Therefore, actions to recover the gas after use must be taken, despite the relatively small volume used for each experiment. An alternative to SF_6 that isn't damaging to the environment is Xenon, however with a density of 5.894 g/L, it is harder to work with as it's more likely to disperse from the cup.

Before testing the cover gas cup *in situ* initial watertight and gas tight tests were carried out. The initial watertight test was carried out so that in the rare event that the rheometer was overloaded with a liquid sample, or the top geometry failed and pushed a liquid sample into contact with the gasket seal it would still be functioning. The watertight test consisted of setting up the lower plate geometry with cover gas cup attached outside the rheometer and filling with water. A standard high vacuum silicon-based grease was applied to the contact area between the cup gasket and lower geometry plate to ensure complete union between the two parts. The water was then left in the cup for 48 hrs and the volume before and after was found to be unchanged. The gastight seal was more difficult to observe due to the colorless nature of SF_6. To track the volume of the gas a small boat made from aluminum foil was floated on the SF_6 gas, and the height of the foil was noted. The cup was filled with the gas via a 7 mm diameter tube connected to a regulated SF_6 cannister, making sure the tube was at the bottom of the cup and filled at as low a pressure flow as possible. Over a 48-hour period no change to the gas volume was observed. Prior to measuring with the cup under cover gas conditions, lowering of the upper geometry into the cup while situated in the rheometer was tested to make sure the geometry's movement did not displace the gas. This was carried out again using an aluminum foil boat to test the initial gas volume within the cup. The foil boat was then removed while the upper geometry (PP10 – diameter 10 mm) was lowered into a measuring position at a speed of 13 mm/s and placed back to measure the subsequent cover gas volume. It was seen that the boat position had moved down slightly but negligibly with respect to the sample coverage. All further experiments were conducted using an Anton-Paar MCR702e with an oven rated from -160 to 550°C attached and fed with liquid nitrogen boil-off gas. L-PP50 and PP10 geometries were used throughout with a measuring gap of 1.00 mm using the viscoelastic movement configuration. The temperature ramp used throughout was 2°C/min. Rotational measurements were taken with a shear rate of 0.3/s.

FIG 3: Cover gas cup *in situ* with upper geometry lowered into place on Anton-Paar MCR 702e.

All titanium(IV) propoxide samples were purchased from Sigma-Aldrich and stored under dry air conditions in a glove box until used.

III. EXPERIMENTAL RESULTS

Titanium(IV) propoxide, is a molecular liquid recently studied by us[13] that does not undergo crystallization in its pure form and which readily reacts with moisture in air, so was chosen to test the cup and cover gas method under real-world conditions. The structure of titanium(IV) propoxide consists of 3 central titanium atom cores linked together by X-O-X type alkoxide bridges and terminal alkoxide ligands which can easily exchange with other alkoxide ligands. In the presence of water, titanium(IV) propoxide readily hydrolyses, producing polymeric oxo-bridged species and ultimately titanium dioxide (TiO_2) as a thin white film easily seen by eye on the surface of the liquid. This reaction can take place within minutes in a suitably humid environment and shorter alkoxide chain titanium alkoxides have been observed to react on the seconds timescale, making long duration rheometry measurements of the pure liquids impossible in open air (see FIG. 4).

FIG 4: Reaction of titanium(IV) propoxide liquid with moisture from the air. On the left titanium(IV) propoxide under dry air conditions, on the right a droplet of titanium(IV)propoxide exposed to natural air after 5 minutes. Note the humid air exposed sample has turned to a chalky white, indicating the formation of TiO_2 and loss of original liquid structure.

To show the effect of measuring under normal air conditions, titanium(IV) propoxide was loaded as rapidly possible onto the rheometer lower geometry using a 1 ml pipette, bringing the upper into contact and leaving only the outer edge of the sample open to air. The oven was then closed, and the temperature controlled from that point on by the oven which blows a constant supply of dry air into the chamber. The viscosity was then measured in rotational mode while lowering the temperature until the liquid titanium(IV) propoxide vitrified at *circa* -97°C.

The same experiment was then carried out but with the sample loaded in the same manner under cover gas conditions described in the previous section when testing the cup *in situ*, with the cup lifted from the lower rheometer plate to close the oven shut. The difference in viscosity as a function of temperature can be seen in FIG. 5.

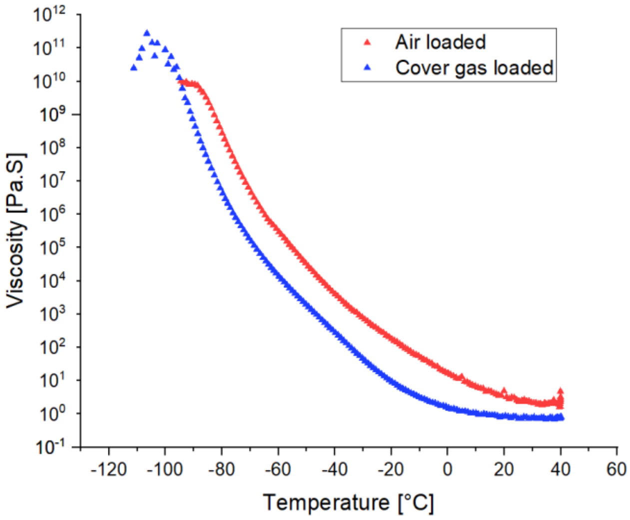

FIG 5: Titanium(IV) propoxide viscosity as a function of temperature. Red indicates sample loaded in air, while blue indicates gas loaded into cover gas.

The air loaded sample can be seen to have overall a much higher viscosity at all temperatures due to the presence of titanium oxide crystals forming as the liquid interacts with water in the atmosphere. The viscosity is also noticeably greater at high temperatures due to the formation of OXO-bridged polymers, which consequently leads to shear dependent non-Newtonian effects and the breakdown of the double glass transition effect[13].

IV. CONCLUSION

The cover gas method of carrying out rheology on air sensitive liquids proved to be a success and allowed for the determination of the correct rheological properties of a pure titanium(IV) propoxide liquid uncontaminated by hydrolysis products. This method was relatively simple to set up with minimal skill needed in construction or design in comparison to designing and building an airtight glove box for an individual rheometer. While SF_6 was deemed to be the most suitable gas for the cover gas purpose, other inert heavier than air gases such as krypton may also be sufficient to use, however, we expect it would be harder to contain with an open vessel as used here. Modification of the cup could rectify this, by giving it a mouth that tapers to a small opening it may be easier to contain gases other than SF_6, however loading of the sample would become more difficult and the upper geometry plate diameter would be limited to the cup mouth opening. Measurements at temperatures higher than the plastic's melting point are obvious concerns but could easily be rectified by manufacturing the cup from aluminum or stainless-steel materials. With access to an inexpensive 3D printer or other means of rapid production it could be relatively trivial to prototype several different dimensions of cup to fit around the individual's rheometer setup and case study, making the cover gas method a rapid method for undertaking rheological measurements of air sensitive materials and no doubt could be applied to other scientific methods.

V. SUPPLEMENTARY MATERIAL

A .stl file of the cover gas cup used in the manuscript can be found in the supplementary material online.

VI. ACKNOWLEDGEMENTS

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VII. AUTHOR DECLARATIONS

1. Conflicts of Interest

The authors have no conflicts of interest to disclose.

2. Author Contributions

Ben A. Russell: Conceptualization, prototyping, experimentation, writing – original draft. **Klaas Wynne**: Conceptualization, writing – review & editing.

VIII. DATA AVAILABILITY

The data that support the findings of this study are available in Enlighten: Research Data Repository (University of Glasgow) with the identifier: http://dx.doi.org/10.5525/gla.researchdata.@@@.

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