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Viscosity profiles of phosphate glasses through combined quasi-static and bob-in-cup methods

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ABSTRACT

This study used a combined viscosity approach to determine theoretical fibre drawing points for glasses in the series: xP_2O_5, 24MgO, 16CaO, (60-x)Na_2O (x = 40,45,50,55) and yP_2O_5, 24MgO, 16CaO, (55-y)Na_2O, $5Fe_2O_3$ (y = 40,45,50,55). The points cannot be measured directly since the glasses are only kinetically stable at these points and would crystallise if allowed to equilibrate. Quasi-static and bob-in-cup viscosity data from above and below the range of interest were fitted to the Vogel–Fulcher–Tammann equation and provided good agreement. The theoretical drawing points were taken as the temperature at which the glass has a viscosity of 2 Log Pa·s, based on the known drawing point viscosity of silica glasses. The theoretical drawing points for the glasses ranged from 657 to 839 °C. The viscosity information was also used to assess the fragility of the glasses in comparison with a borosilicate standard by using Doremus and Angell parameters. All of the glasses were of low viscosity and high fragility in comparison to the borosilicate. The fragility improved above 50% content of phosphate in the glass and the addition of iron had little effect on the fragility. Additionally, the limitations of the borosilicate 717a standard glass and the measurement of T_g are discussed.

1. Introduction

Phosphate glasses and their fibres are being developed for use in medical applications [1–3]. This is because they possess relatively high strength values (typically 500 MPa to 1.2 GPa [4]) but can also degrade away in an aqueous environment. Ordinarily this is a surface erosion process [5], allowing for the maintenance of properties during degradation [6].

The glasses can be utilised both directly and as reinforcements in composite materials. To make use of the strength properties of the glasses when reinforcing composites, it is necessary to have them in the form of fibres. The production of phosphate optical fibres via pre-form drawing processes is well known [7], but to create reinforcing fibres for composites these processes are not well suited. Typical optical fibres are in the range >30 μm and often in the hundreds of microns; a desirable diameter for reinforcing fibres is <25 μm and preferably ~9–12 μm [8]. Additionally, reinforcing fibres are created as multi-filament tows that contain hundreds and often thousands of individual filaments all drawn at the same time, making pre-form drawing impractical (although not impossible). To create small diameter, multi-filament threads it is necessary to use melt drawing.

Melt drawing is also well known, though overwhelmingly focused on silica-based glasses. Silica fibres (commonly E-glass) have been produced on a commercial scale since the 1960s [9]. However, a commercial process for small diameter phosphate glass fibre production has never been achieved. This is partially due to a lack of perceived applications for phosphate glass fibres until relatively recently and partly due to the properties of the glass.

Silica bases glasses draw very effectively in the commercial melt drawing process because they possess viscosities at the appropriate level for fibre production when the glass is above its liquidus [10]. This means that the molten glass can be held at the correct fibre drawing temperature without a risk of crystallisation and so a continuous process is possible.

Phosphate glasses tend to be fragile and prone to crystallisation, with viscosities much lower than silicates. Critically, the 'drawing point' viscosity for glass fibre production (typically assumed to be ~100 Pa·s or 2 Log Pa·s [10]) usually falls below the liquidus point and due to the fragility of the glasses the drawing point temperature window is also relatively narrow. Conventionally this would preclude melt-drawing but a number of groups around the world, including

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ours, have been producing phosphate glass fibres successfully in the laboratory for many years. This is because glass that is flowing is more resistant to crystallisation, lending a kinetic stability to the process. As such a continuous production process is feasible but to design a long term, reliable process, good information about the viscosity of the glass is necessary. If correct conditions are not achieved and crystals nucleate then gradual growth of these crystals will occur, resulting in reduced quality fibre and eventual blockage of the drawing equipment.

Because the glasses are only usually kinetically stable at their drawing point temperatures it is impossible to take equilibrium viscosity measurements of the drawing point directly. In order to obtain close approximations of these values, this study combines parallel plate quasi-static viscosity measurements using Gent's equation [11] with high temperature bob-in-cup measurements that fall either side of the crystallisation region. Quasi-static measurements provide values in the range of 5.5–8 Log Pa·s, while bob-in-cup measurements provide values in the <2 Log Pa·s region. The data is then applied to the well-known and generally accepted Vogel–Fulcher–Tammann (VFT) equation (developed in the 1920s) in order to predict a complete viscosity profile and a drawing point temperature. Additionally, the viscosity data is combined with conventional thermal analysis methods to obtain Angell [12,13] and Doremus [14] fragility indices. The data also provides some insights to the effect of additives on the structure of phosphate glasses. The study includes eight glass formulations from the following two systems: xP_2O_5, 24MgO, 16CaO, (60-x)Na_2O (x = 40,45,50,55) and yP_2O_5, 24MgO, 16CaO, (55-y)Na_2O, $5Fe_2O_3$ (y = 40,45,50,55). The glasses were selected based on previously determined formulations with good cytocompatibility [15].

2. Methods

2.1. Glass production

Glasses were produced by melt fusing phosphate salts and phosphorus pentoxide in 5%Au/Pt crucibles. NaH_2PO_4, $CaHPO_4$, $MgHPO_4 \cdot 3H_2O$ and $FePO_4 \cdot 2H_2O$ were obtained from Sigma Aldrich UK, P_2O_5 was obtained from Fisher Chemicals. All Reagents were used as received. Each batch was heated for 30 min at 350 °C in a Lenton Furnaces AWF 12/26 to drive off adducted water before being transferred to a Lenton Furnaces UAF 16/10 at 1100 °C for 90 min. The glasses were either cast directly onto a steel plate or poured into 4 mm diameter graphite moulds. Glass compositions and precursor recipes can be found in Table 1.

2.2. Glass sample preparation

The glass cast directly was broken up into cullet and used for density and liquidus measurements, and bob-in-cup viscosity. The glass cast into the graphite moulds was annealed at the glass $T_g + 10$ °C as recommended by Ropp [16], before careful sectioning into parallel faced, ~3 mm long rods for quasi-static viscosity by using a South Bay Technologies Inc. Model 650 low speed diamond saw. Pieces of the glasses were also ground to powder for differential scanning calorimetry (DSC), using a Retch Planetary Ball Mill PM 100 with zirconia grinding surfaces. The average particle size was <45 μm (measured using calibrated testing sieves).

Table 1
Glass recipes.

Glass code (mol% oxide)	Precursor mixture (mass% ±0.01 g)				
	NaH_2PO_4	$FePO_4 \cdot 2H_2O$	$CaHPO_4$	$MgHPO_4 \cdot 3H_2O$	P_2O_5
P40Mg24Ca16Na20	43.00	0.00	19.51	37.49	0.00
P45Mg24Ca16Na15	31.63	0.00	19.13	36.77	12.48
P50Mg24Ca16Na10	20.69	0.00	18.77	36.07	24.48
P55Mg24Ca16Na5	10.15	0.00	18.42	35.40	36.03
P40Mg24Ca16Na15Fe5	30.43	15.80	18.40	35.37	0.00
P45Mg24Ca16Na10Fe5	19.92	15.51	18.07	34.73	11.78
P50Mg24Ca16Na5Fe5	9.78	15.23	17.74	34.10	23.14
P55Mg24Ca16Fe5	0.00	14.96	17.43	33.50	34.11

2.3. X-ray fluorescence spectroscopy (XRF)

XRF compositional analysis was carried out on a Bruker S4 Pioneer XRF set. Samples were prepared by re-melting the glass diluted with lithium tetraborate at 1220 °C and casting into platinum dishes. The resulting 40 mm diameter discs are then submitted for analysis, taking care to avoid any contamination from handling. Analysis is performed with the instrument operating in the "standard-less mode" which was developed internally for these types of non soda–lime–silica (SLS) glasses. Results which provide a total sample value outside of the 99.5–100.5% range (a total value of 100% is expected) are rejected and sampling and fusion is repeated.

2.4. Differential scanning calorimetry (DSC)

Thermal analysis of the glasses was performed using a Texas Instruments SDTQ600. Measurements of glass transition temperature were taken in triplicate at 10 °C/min using platinum pans containing ~30 mg of powdered glass.

2.5. Liquidus

Liquidus measurements were undertaken according to ASTM C829-81, using a purpose built furnace. Coarse glass cullet (3–5 mm) is placed into a 155 mm × 10 mm × 10 mm 90%Pt/10%Rh tray and melted at 1450 °C for 15 min in order to allow the glass to flow and fill the tray. The tray is then held in the liquidus furnace for 24 h to stabilise before being removed and cooled in air. The extent of crystallisation is determined by using an optical microscope and observing the centre of the resulting glass bar (some nucleation could occur at the walls). The thermal gradient in the furnace is determined by 15 thermocouples with a spacing of 10 mm and confirmed by using a movable thermocouple. The temperature gradient across the length of the sample is typically ~80 °C. An approximate temperature can be obtained from the DSC data in order to reduce experimental time.

2.6. Density

Glass density was measured using bubble free cullet in a Micromeritics AccuPyc 1330 gas pycnometer, using helium gas. The pycnometer was calibrated and checked by using steel calibration standards, with 10 measurements made. For the glass, 5 measurements were made for each of three different glass batches of each composition.

2.7. Quasi-static viscosity

The quasi-static viscosity data was obtained via a process described elsewhere [17–19]. Briefly, a small rod of the glass (4 mm diameter × 3 mm length) is subjected to a constant axial force while heated and the rate of change of height of the rod provides a viscosity vs temperature profile. The measurements were taken in triplicate for each composition.

2.8. Bob-in-cup viscosity

Bob-in-cup viscosity measurements were taken essentially in accordance with ISO 7884–2:1987 by using a Theta industries Rheotronic II 1600 °C Rotating Viscometer. The system uses a 10 mm diameter, 14 mm high platinum double cone bob in a 40 mm high, 30 mm internal diameter platinum crucible with a 1 mm wall thickness. The glass density was used to determine the amount of cullet required to achieve a glass height of ~24 mm in the crucible (with the bob inserted). The