# Effect of melting parameters during synthesis on the structure and properties of tin fluoride phosphate glasses

Nora Iturraran[a], Karine Huraux[a], Yuqing Bao[b], David Thomas Gawne[b,*], Jean Guilment[a]

[a] Arkema Cerdato, Route de Launay, Serquigny 27470, France
[b] London South Bank University, Borough Road, London SE1 0AA, United Kingdom

## ABSTRACT

FTIR and Raman spectroscopy indicate the glass structure during synthesis of tin fluoride phosphate glass was pyrophosphate, mainly built up from $Q^1$ end groups with a low concentration of $Q^2$ polymeric chains. However, sub-optimal melting produced significantly higher concentrations of orthophosphate $Q^0$ structural units. The variations in NH and P-OH vibrations in the spectra revealed that a critical time and temperature of melting were necessary for the conversion of $NH_4H_2PO_2$ to produce sufficient $P_2O_5$ for glass forming. During melting, $P_2O_5$ and $SnF_2$ form a low-temperature melt, which facilitates melting of the SnO and promotes the formation of a more stable glass structure. The fluorine breaks the P−O−P bonds and induces depolymerisation. The density of the glass reached a maximum at 450 °C for 25 min driven by the need for conversion of $NH_4H_2PO_4$ to $P_2O_5$ and miscibility of SnO in the melt. Inadequate melting times and temperatures gave low $T_g$ values because of weak F−Sn and F−P linkages. Glass stability improved with melting due to increased $P_2O_5$ and SnO miscibility enabling stronger Sn−O−P linkages. The results show that melting conditions during synthesis strongly influence critical glass properties and future industrial scale-up will require an understanding of optimum processing.

## 1. Introduction

Phosphate glasses have been developed over recent years with much lower glass transition temperatures ($T_g$) than those of conventional silicate glasses [1,2]. Specifically, phosphate glasses can have $T_g$ values as low as 100 °C as compared with 550 °C for typical silicate-based glasses. These unique thermal properties offer major potential in engineering applications including sealing [3], nuclear waste storage [4] and biomedical implants [5].

A further possible application is in polymer composites. Phosphate glasses have melting temperatures in a broadly similar range to organic polymers and so co-processing by extrusion in which both components are fluid is a possibility. A molten rather than a solid (as it is the case in conventional polymer processing) glass phase should in principle allow much higher glass loadings and enhanced properties. This paper is directed at developing an understanding of the mechanisms of melting and defining the processing conditions of phosphate glasses for *co*-extrusion with polymers with the ultimate aim of producing high-performance glass-polymer hybrids.

The structure of vitreous phosphates is based on a molecular tetrahedral building block [6,7]. Phosphorus is a pentavalent ion and so the formation of a phosphorus-oxygen tetrahedron with four bridging oxygens would result in an impracticable unit with a net positive charge of +1. Nevertheless, a charge-neutral tetrahedron can be formed if one of the oxygens forms a double bond with the pentavalent phosphorus ion (P=O), while the other three oxygens form bridging oxygens (P – O – P) with adjacent tetrahedra. In practice, the tetrahedra link up, using the covalent bridging oxygens, to form various phosphate anions. The tetrahedra may be classified using the $Q^i$ terminology [6,7], where i represents the number of bridging oxygens per tetrahedron. Phosphate glasses can be made with a range of structures, from a cross-linked network of $Q^3$ tetrahedra as in vitreous $P_2O_5$, to polymer-like metaphosphate chains of $Q^2$ tetrahedra, to glasses based on small pyrophosphate ($Q^1$) and orthophosphate ($Q^0$) anions, depending on the oxygen-to-phosphorus ratio as set by the glass composition.

Low-temperature glasses tend to show inferior chemical durability in humid environments and this hygroscopic characteristic limits their practical application. However, glasses have now been developed with much higher stability, particularly tin phosphate oxyfluorides [8,9]. The addition of SnO to binary stannous fluorophosphates glass resulted in a decrease in the volatility of the melt and dramatic improvements in the chemical durability of the glass [8,9]. The substitution of SnO for $SnF_2$ drastically reduced dissolution to rates comparable to soda-lime-silica glass [7,9]. The increase in chemical durability is attributed to the

weaker linkages of Sn-F-Sn, Sn-F-P and P-F-P being replaced by the stronger Sn-O-Sn, Sn-O-P and P-O-P linkages.

The composition of the glass will have a direct bearing on its blending with polymers as well as influencing the properties of the resulting composite [10]. A tin fluoride phosphate glass with a molar composition of 50 mol% tin fluoride ($SnF_2$), 20 mol% tin oxide (SnO) and 30 mol% phosphorus pentoxide ($P_2O_5$) was selected for investigation due to its unique combination of low $T_g$, rheological properties, water resistance and chemical durability [8]. The low $T_g$ has the possibility of making the phosphate glass fluid during polymer processing. In addition, the glass has been reported to have an affinity with some polymers, which may provide possibilities for hybridization [11–13].

For a fixed glass composition, however, the processing conditions are also expected to influence the formation of its final structure and the properties. No systematic investigations were found in the literature on the quantitative effect of melting conditions on the final properties of tin fluoride phosphate glass. This paper will characterize the effect of melting on glass structure [13–16] and properties [17–19] by techniques including FTIR, Raman, DSC, TGA and density and complex viscosity in comparison with related systems in the literature. The research will have value in understanding the sensitivity of glass performance to melting conditions and relevance for upscaling of the glass synthesis in the development of possible future industrial applications.

## 2. Experimental details

### 2.1. Glass formation

A tin fluoride phosphate glass with a molar composition of 50% Sn $F_2$ + 20% Sn O + 30% $P_2O_5$ was prepared from reagent-grade powders of tin fluoride ($SnF_2$), tin oxide (SnO) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$ powders supplied by Sigma Aldrich Ltd. The ammonium dihydrogen phosphate is a source for producing $P_2O_5$. The ingredients were premixed and ground at room temperature. Melting of mixed ingredients was performed in a porcelain crucible placed in a convection oven for various times at various pre-setting temperatures in order to study the influence of melting conditions on glass properties and their thermal stability. The detailed melting conditions used in the investigation are given in Table 1. Finally, the molten glass was poured into a stainless steel plate mould and cooled down to room temperature for structure and property evaluation.

### 2.2. Properties

The density of glass is known to vary greatly with its composition. This paper, however, investigates the effect of melting conditions on the end properties of the glass. The density of the glasses under study was measured using a Sartorius IAC 210P digital balance according to the standards ISO 1183-1:2004 and ASTM D792:2008. The samples were weighed in air and in an immersion liquid and calculated automatically by the integrated software. The results are presented and discussed in Sections 3 and 4 respectively.

The thermal behaviour of the glasses made under various melting conditions were analysed. The glass transition temperature (Tg) was determined by differential scanning calorimetry (Netzsch F1ASC). The

**Table 1**
Glass melting conditions.

| Samples | Temperature (°C) | Time (minutes) |
|---|---|---|
| 1 | 350 | 25 |
| 2 | 400 | 25 |
| 3(a,b,c,d,e,f,g) | 450 | 15,20,25,30,35,40,45 |
| 4 | 500 | 25 |
| 5 | 550 | 25 |

sample was heated from 20 °C to 300 °C in dry nitrogen atmosphere at a linear heating rate of 2 °C/min. The tests were run twice for each sample in order to remove the effect of thermal history. The mass loss of glasses was determined using thermogravimetric analyzer (TG209 F1 Netzsch). The test was carried out within the temperature range of 25 °C to 550 °C at a heating rate of 10 °C/min under atmosphere. The tests were run twice for each samples and the average mass loss was reported.

The rheological properties of the glass were measured by a rotational rheometer (Physica MCR 301) at temperatures of 230, 250 and 270 °C respectively. These temperatures were selected to simulate the extrusion processing temperatures that would be applied for melt-blending the glasses with polymers [10]. The tests were run using parallel plate geometry at a frequency of 1 Hz.

### 2.3. Glass structure

The structural variations of the glasses induced by melting conditions and moisture were investigated using both FTIR and Raman spectroscopy The infrared spectra of the glass powder samples were measured using a Vertex 70 (FTIR) spectrometer in the range 400–4000 $cm^{-1}$ in absorbance mode to estimate the glass structural changes. A Bruckner Raman Spectrometer was also used to observe the variation in vibrational, rotational and other low frequency modes in the glass samples. The chemical durability was determined by assessing the moisture attack on the samples using the Raman spectrometer.

## 3. Results

### 3.1. Glass formation

The final performance of the glass was found to be influenced by the conditions pertaining in glass formation and melting. Specifically, the glass properties were sensitive to the temperature of melting over the range of 200 to 550 °C and time over 15 to 45 min. This study investigates the response of properties and structure to glass melting parameters.

### 3.2. Properties

The density of the glass was measured (Fig. 1) and found to rise with melting time to reach a maximum and a plateau at 25 min for a fixed melting temperature of 450 °C. Raising the melting temperature also increased the density and reached a maximum at 450 °C (Fig. 2) for a fixed time of 25 min.

The experimental results in Fig. 3 show that the glass transition temperature $T_g$ of the glass is strongly influenced by the duration of melting at a temperature of 450 °C. The Tg changes from a value of



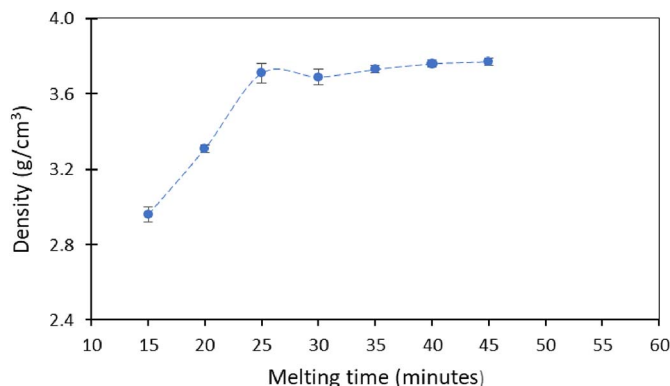**Fig. 1.** Measured densities of tin fluoride phosphate glass melted at 450 °C for different times. Dotted line drawn as a guide to the eye.