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Crystallization of phosphate glasses

Part 2 *Effects of refining time on viscosity and crystallization rate*

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The effects of refining time on the transformation temperature, viscosity, and rate of crystallization of a simple lead phosphate glass of nominal composition 60 P_2O_5, 30 PbO, 10 K_2O have been determined. As the hydroxyl content is reduced and the cross-link density increased by continued refining, the transformation temperature and melt viscosity rise. At corresponding temperatures above T_g the viscosity increases and the rate of crystallization decreases with cross-link density, but crystallization rates at isoviscous temperatures are shown to be independent of cross-link density.

1. Introduction

In Part 1 it was shown how the rates of crystallization of some lead phosphate glasses vary with composition [1]. Crystallization rates are also viscosity-dependent, and since the melt viscosities of phosphate glasses vary with refining time well as with composition, in that investigation the effects due to changes in viscosity were minimized by comparing the rates of crystallization for different compositions at corresponding temperatures above the transformation temperature. The purpose of the work reported here was to investigate the effects of variations in refining time on the viscosity and rate of crystallization of one particular lead phosphate glass.

2. Experimental procedure

All the measurements were made with a glass of nominal composition P_2O_5, 60; PbO, 30; K_2O, 10 mol %. This glass was chosen because it crystallized rapidly after short refining times; it was prepared by mixing the calculated proportions of ammonium dihydrogen phosphate, litharge, and potassium carbonate and melting at 450°C for 4 h, then refining at 700°C; samples were removed after refining for 1, 2, 16, 59 and 76 h. Portions of these samples were analysed for hydrogen and nitrogen and the hydroxyl content was calculated from the hydrogen content after correcting for residual ammonia. Hydroxyl contents were also determined by measuring the weight loss on heating the glass at 700°C to constant weight under a blanket of excess litharge which effectively prevented loss of phosphoric oxide and assisted the elimination of water by formation of metaphosphate; the loss in weight was corrected for ammonia by calculation from the nitrogen analysis. Samples were also analysed for phosphorus to confirm that no significant loss of phosphoric oxide had occurred during refining. Samples for crystallization studies were prepared by placing a small quantity of freshly ground glass between two microscope cover slips and melting with a small bunsen burner. The sample was pressed flat immediately the (lead phosphate) glass was molten, and rapidly quenched to room temperature by placing on an aluminium block. Crystallization rates, transformation temperatures, and melt viscosities were measured as previously described in Part 1.

3. Results

3.1. Transformation temperature and cross-link density

The cross-link density of a polyphosphate network can be calculated from the hydroxyl content [2]. For the glass used in this investigation the cross-link density is related to the hydroxyl content (expressed as wt % combined H_2O) by the equation

TABLE I Transformation temperatures and cross-link densities

Refining time (h)	Transformation temperature (°C)	Combined water content, wt %		Cross-link density
		From H analysis	From weight loss on heating	
1	190	1.44	1.46	0.11
2	194	0.84	1.38	0.12
16	204	0.78	1.16	0.15
59	217	0.50	0.85	0.20
76	245	0.24	0.46	0.26

Note: The large rise in transformation temperature between the 59 and 76 h samples arose from splitting the melt between two smaller crucibles; the increased surface area accelerated the evaporation of water from the glass.

$$x = 0.333\text{-}14.9\ W/(1 - W)$$

where x is the cross-link density (i.e. the fraction of triply-connected phosphorus atoms) and W is the weight fraction of combined water remaining in the glass. For a linear polyphosphate of this composition the combined water content would be 2.18%, and the maximum cross-link density for the anhydrous glass is 0.333.

The combined water contents after different periods of refining are given in Table I; the values calculated from hydrogen analysis are lower than those obtained from the weight loss on heating even though the latter have been corrected for ammonia, but both methods were found to agree for water contents greater than 2%. At the low values reported here errors in the determination of hydrogen are likely to be appreciable, and the results obtained by heating with litharge are considered to be more reliable because much larger samples were used. For this reason cross-link densities have been calculated from the latter results and the values obtained are given in Table I.

Analyses for phosphorus showed that any loss of phosphoric oxide from this glass at 700°C is negligible even after prolonged refining; analysis of the 76 h sample gave P, 24.0% (theory, 23.1%).

The transformation temperature of the glass is plotted against cross-link density in Fig. 1.

According to Di Marzio [3] these observations should be related by an equation of the form

$$\frac{T_x - T_0}{T_x} = \frac{Kx}{1 - Kx}$$

where T_x, T_0 are the transformation temperatures of the cross-linked glass and the corresponding linear polymer respectively, x is the cross-link density, and K is a constant. Fitting such an equation by least squares to the experimental points in Fig. 1 gives $T_0 = 163 \pm 1$°C and $K = 0.51 \pm 0.01$, and the curve shown in Fig. 1 is calculated from this equation.

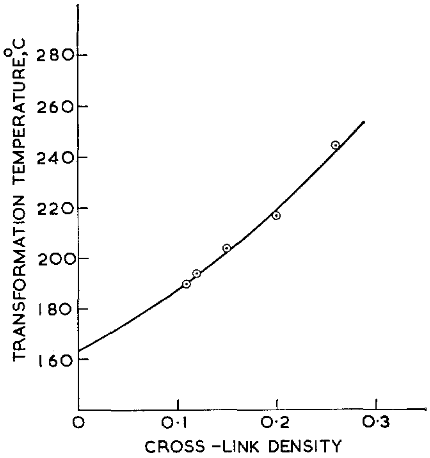

Figure 1 Change in transformation temperature with cross-link density; the points are experimental results, the curve is calculated from the equation given in the text.

3.2. Melt viscosity

The viscosity of the glass after different periods of refining is plotted against ΔT, the difference between the melt temperature and the transformation temperature in Fig. 2. In Part 1 it was shown that for glasses of different composition but similar refining time the transformation temperature is approximately an isoviscous temperature, so that melt viscosities plotted against ΔT approximate to a single curve common to all glasses of the same type. However, it is evident from Fig. 2 that this relationship no longer holds for glasses of the same composition but different refining times.

In Fig. 3 the melt viscosities at 100 and 110°C

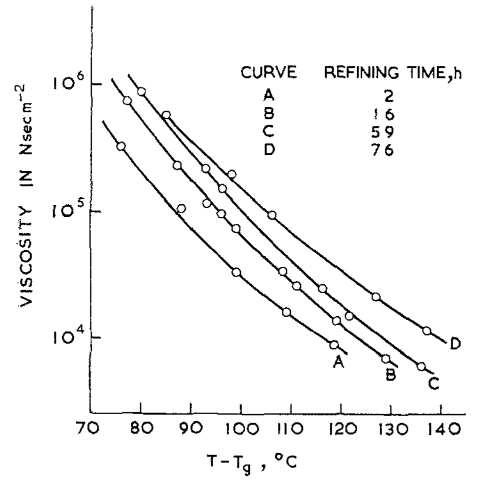

Figure 2 Viscosity at corresponding temperatures above the transformation temperature.

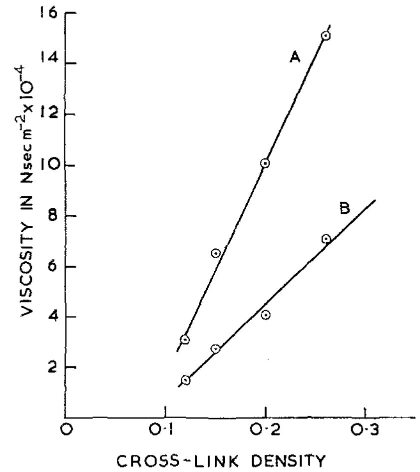

Figure 3 Change in viscosity with cross-link density; curve A at 100°C above T_g; curve B at 110°C above T_g.

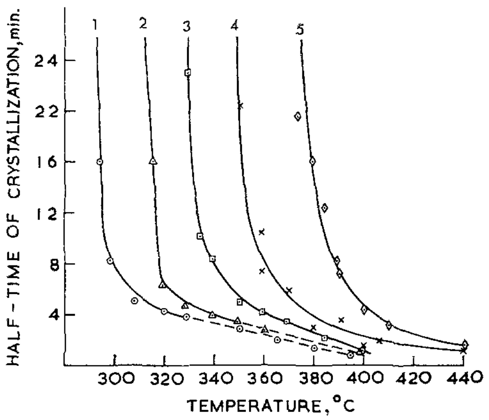

Figure 4 Effect of temperature on rate of crystallization. Sample 1, 1 h; 2, 2 h; 3, 16 h; 4, 59 h; 5, 76 h refining.

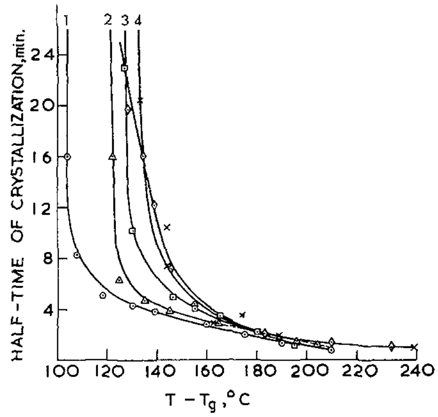

Figure 5 Rates of crystallization at corresponding temperatures above the transformation temperature. Samples as in Fig. 4.

above the transformation temperature are plotted against cross-link density and a linear relationship is obtained at both temperatures; needless to say the slopes of these lines must decrease at lower values of cross-link density.

3.3. Crystallization rates

The half-time for crystallization is plotted against temperature for each refining time in Fig. 4, and the half-times for crystallization at corresponding temperatures above the transformation temperature are shown in Fig. 5. This shows that the temperature at which crystallization starts to occur rises with increased refining faster than the transformation temperature. In Fig. 6, the half-times for crystallization are plotted against an artificial temperature scale obtained by taking as a reference point for each sample the temperature at which it has a viscosity of 10^5 N sec m^{-2}; this is a scale of isoviscous temperatures for each glass sample and on this basis it is found that within experimental error the rate of devitrification is independent of refining time and hence of cross-link density.

3.4. Crystalline phases produced

Samples of glass refined for 1 and for 76 h were heated in an oven at 300°C until crystallization occurred, and X-ray diffraction patterns were obtained from the powdered material. These

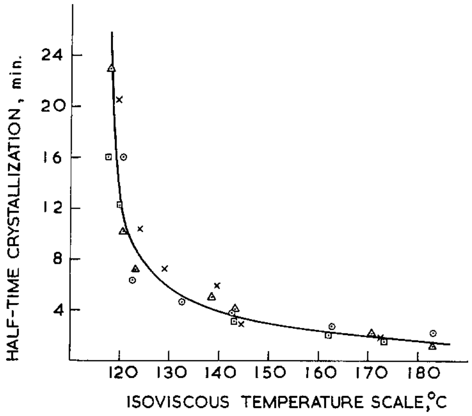

Figure 6 Crystallization rates at isoviscous temperatures. Data points for samples as in Fig. 4.

showed that the crystalline phase in both samples was lead metaphosphate, apparently in the dimeric ring form $[Pb(PO_3)_2]_2$.

4. Discussion

It has been shown previously [2] that the relationship between the transformation temperature and cross-link density of an ultraphosphate glass is similar to that found in organic polymers. However, it is not possible to measure the viscosity of cross-linked organic polymers in the molten state. The present results confirm the earlier observations and show in addition that even after allowing for changes in transformation temperature by using it as a reference point, the viscosity in the molten state increases linearly with cross-link density. Thus increased cross-linking not only raises the temperature at which viscous flow can begin but also increases the viscosity at corresponding temperatures well above the transformation temperature. The effects of cross-linking are therefore evident in the molten state and it must be concluded that structural differences persist in the melt. It might therefore be expected that the rate of crystallization would be strongly dependent on the degree of cross-linking, because crystallization must involve a considerable reorganization of the structures in the melt. However, the comparatively low viscosities observed in the melt and the size of the crystals formed indicate a high degree of structural mobility in the molten state, suggesting that a state of dynamic equilibrium exists in which bonds are continually breaking and reforming. Under such conditions there is a high probability of finding units of suitable size and composition to fit the crystal lattice and the rate of crystal growth will be governed only by viscosity. The results presented in Fig. 6, showing that crystallization rates measured at constant viscosity are independent of cross-link density, are in accordance with this description.

Glasses of this simple composition crystallize rapidly at temperatures more than 180°C above the transformation temperature and large numbers of growth centres are formed under these conditions, while glasses of different composition show quite different behaviour [1]. This indicates that crystallization is initiated by homogeneous nucleation, the ease with which stable nuclei are established depending on the solubility of lead phosphate in the melt.

References

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