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The Effect of Combined Water on the Transformation Temperature of a Phosphate Glass

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From measurements of the water content of a phosphate glass after increasing periods of refining, the number of hydroxyl groups per phosphorus atom and hence the degree of cross-linking have been calculated. The changes in transformation temperature with cross-link density are similar to the relationship observed in organic polymers and can be described by an equation derived by Di Marzio.

1. Introduction

Although the constitution of some phosphate glasses has been studied in considerable detail [1, 2], these investigations have generally been restricted to soluble glasses consisting of linear and cyclic molecules; phosphate glasses with highly cross-linked structures resembling the silicate glasses have received comparatively little attention.

Cross-linked phosphate glasses can be prepared by reacting ammonium phosphate or phosphoric acid with a stoichiometric deficiency of metal oxides or carbonates [3] and heating the mixture to eliminate water. At first linear polymers are formed; as the condensation continues cyclic, branched, and eventually cross-linked structures will be produced. The smaller the residual hydroxyl content, the greater will be the degree of cross-linking. The reaction

$$2 > \mathrm{P(O)OH} \rightarrow\ > \mathrm{P(O)\text{-}O\text{-}P(O)} < + \mathrm{H_2O}$$

is reversible, and the water formed is only eliminated slowly even at temperatures of 700 to 800°C. Since phosphorus pentoxide forms an azeotrope with water boiling at 850°C, it is probably impossible to reduce the hydroxyl content to zero unless there is an equivalence of metal ions to phosphorus atoms, as in a metaphosphate composition. For the same reason the residual water content cannot be measured accurately by simple determinations of weight loss; however, for this purpose, volatilisation of phosphoric oxide can be avoided by adding an excess of a metal oxide that forms a non-volatile phosphate.

The effect of residual water on the transformation temperature of barium phosphate glasses containing from 30 to 35 mole % barium oxide was studied by Namikawa and Munakata [4], who found that the transformation temperature was very dependent on the conditions of preparation and that the variations could be attributed to changes in combined water content in the range 1 to 3%. They also concluded that the preparation of anhydrous barium phosphate glass was impossible. The purpose of the work reported here is to relate the transformation temperature of a phosphate glass to the degree of cross-linking in its structure, as measured by the residual hydroxyl content.

2. Experimental Procedure and Results

2.1. Preparation of Glass Samples

The glass used for all the measurements was an alkali lead phosphate having the nominal composition (in moles) 70 P_2O_5, 20 PbO, 5 Li_2O, 2.5 K_2O, 2.5 BaO. It was prepared by melting an intimate mixture of ammonium dihydrogen phosphate (2415 g), litharge (670 g), lithium carbonate (55.5 g), potassium carbonate (51.9 g), and barium oxide (57.6 g) in a "Pyrex" beaker at 300 to 400°C until practically all the ammonia had volatilised, then transferring to a "Salamander" (clay-bonded graphite) crucible which was heated in a furnace at 700°C for a total of 96 h. Samples were removed at intervals by

TABLE I Measurements of transformation temperature.

Sample no.	Transformation temperature °C					Mean ± 95% confidence limits
	From DTA			By thermal expansion		
	10°/min	20°/min	80°/min	As-cast	Annealed	
2	139	140	142	138	140	140 ± 2
3	140	144	148	135	139	141 ± 5
5	146	147	151	141	147	146 ± 4
6	149	145	155	152	155	151 ± 4
7	153	155	160	156	165	158 ± 5
8	162	164	169	166	170	166 ± 3

pouring some of the molten glass onto a steel plate. To check that the composition of the glass had not altered by loss of phosphoric oxide during refining, the final sample which had been refined for 96 h was analysed for phosphorus; found, P 27.9, calculated from original composition, assuming 0.3 % H_2O (see table I), P 28.5 %. For some of the subsequent measurements specimens in the form of $\frac{1}{4}$ in. thick bars cut from the cast slabs were annealed by reheating to 50° C above the transformation temperature, and then cooling at the rate of 0.5 to 0.6° C per min to 10° C below the transformation temperature, with a 30 min. holding period at 10° C above the transformation temperature.

2.2. Measurement of Transformation Temperature

The transformation temperatures were measured with a du Pont Model 900 Differential Thermal Analyser used firstly to plot differential temperature against a silica reference sample, and secondly with the addition of a Model 940 module to plot linear expansion against temperature. Heating rates of 5, 10, 20, and 80° C per min were used. The transformation temperatures of all the samples were measured by DTA at 20° C per min, and the results are given in table II. For six of the samples, the transformation temperatures were measured by DTA at three different rates of heating, and also determined by thermal expansion measured at 5° C per min on both annealed and "as-cast" specimens. These results are given in table I; the mean of all the determinations on one sample agreed within experimental error with the result obtained by DTA at 20° C per min.

2.3. Measurement of Water Content

The samples were analysed for hydrogen and nitrogen with a Hewlett-Packard Model 185 C, H and N AutoAnalyser using a sample weight of 6.5 mg. The samples were powdered in a dry atmosphere, mixed with tungstic oxide and manganese dioxide, and heated to 1250° C in the analyser. The procedure was checked by determining hydrogen in a sample of AR quality potassium dihydrogen phosphate, which gave 1.46% (theory 1.47%).

Selected samples were also analysed by measuring the weight loss on heating with an excess of litharge. Samples of about 1 g were

TABLE II Water content and transformation temperature.

Sample no.	Refining time, h	Analysis		Calculated % H_2O	Wt loss at 700° C %	Wt loss corrected for NH_3 %	Transformation temperature °C
		%H	%N				
1	—	0.65	0.70	4.5	—	—	119
2	0.5	0.57	0.80	3.6	4.65	3.7	140
3	1.0	0.54	0.73	3.4	4.22	3.3	141
4	2.0	0.44	0.48	3.1	—	—	151
5	2.0	0.52	0.70	3.3	4.02	3.2	146
6	4.0	0.45	0.59	2.9	3.40	2.7	151
7	8.0	0.35	0.45	2.3	2.91	2.4	158
8	16.0	0.32	0.42	2.1	2.79	2.2	166
9	24.0	0.22	0.27	1.4	—	—	183
10	96.0	0.03	—	0.3	—	—	256

weighed, crushed to a powder, and covered with 5 g of litharge in a platinum crucible. The crucible was heated at 700°C for 1 h, and the loss in weight measured. Control weighings showed that the weight loss after 15 min was within 0.1% of the final value; heating litharge alone under the same conditions produced a weight loss of 0.036% after 30 min with no further change in 3 h. The observed weight loss of the glass was corrected for this.

All but one of the samples contained small but significant amounts of nitrogen due to incomplete decomposition of the ammonium phosphate. The water contents were calculated both from the hydrogen analysis and from the weight loss on heating, after correcting each figure for ammonia according to the nitrogen content. The results are given in table II, and there was good agreement between the two methods.

3. Discussion

3.1. Calculation of Cross-Link Density

The polycondensation of phosphoric acid has been studied in detail [2, 5, 6] and it has been established that as the water content decreases to a molar ratio H_2O/P_2O_5 only slightly greater than unity, the polymer consists entirely of straight chains; branching and cross-linking occur only when the H_2O/P_2O_5 ratio is reduced to one or less. It is reasonable to assume a similar behaviour in the formation of a phosphate glass; as dehydration proceeds only linear P-O-P chains will be formed until there is only one hydroxyl group left on every phosphorus atom that is not linked to a metal ion. There may be branching and cross-linking through ionic bonds if di- and tri-valent metals are present, but no P-O-P cross-linkages form until nearly all the primary hydroxyl groups have reacted. Since the ratio of phosphorus atoms to metal ions in the glass studied is 7/3, at this stage four-sevenths of the phosphorus atoms will carry a pendant hydroxyl group, corresponding to a combined water content of 4.53% by weight. The water content of the first sample (table II) is very close to this, showing that in the first stage of the reaction which was carried out at 300 to 400°C, hardly any cross-linking occurs. This is confirmed by the observation that this glass dissolves in cold water to give a clear, highly viscous solution.

In the second stage of the reaction which is brought about by heating at 700°C, the water content is reduced further and P-O-P cross-links must be formed. The products obtained are no longer soluble in cold water, and only partially dissolved by boiling water. The cross-link density in a polymer has been defined [7] as the fraction of monomer units which are cross-linked; in the case of a phosphate glass this is the fraction of phosphorus atoms that are linked, through oxygen, to three other phosphorus atoms. If p is the fraction of hydroxyl groups originally present in the linear polymer that have reacted, the cross-link density is $4p/7$, and the fraction of phosphorus atoms which still carry a hydroxyl group is $4(1-p)/7$; it follows that the combined water content is

$$72000(1-p)/[15167 + 720(1-p)]\% \text{ by weight}$$

and that the cross-link density is related to water content by the equation

$$\begin{array}{l}\text{fraction of cross-linked} \\ \text{phosphorus atoms}\end{array} = \frac{41.2 - 9.06W}{72 - 0.72W}$$

where W is the combined water content, wt %.

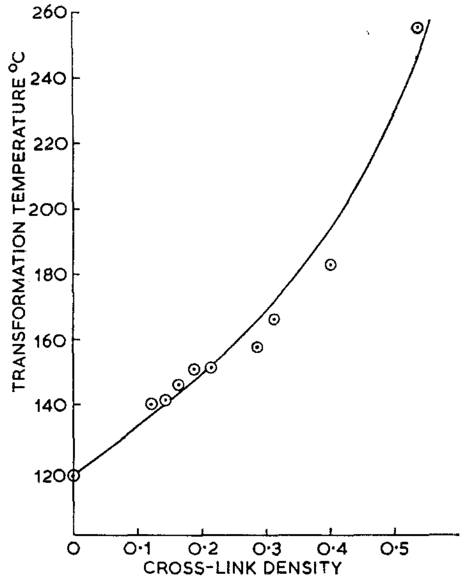

Figure 1 Change in transformation temperature with cross-link density.

3.2. Effect of Cross-Linking on Transformation Temperature

The changes in transformation temperature with cross-link density calculated in this way are shown in fig. 1. The transformation temperature at first increases almost linearly with cross-link density, but when more than one-third of the phosphorus atoms are cross-linked the transformation temperature rises much more steeply.

The effect of cross-linking on the glass transition temperature in organic polymers has been discussed by Fox and Loshaek [8] and by Di Marzio [9]. The simpler theory rests on the assumption that the glass transition temperature is an iso-free volume temperature. Where polymer chains are joined by a cross-link the free volume is reduced and the glass transition temperature is increased. On this basis Fox and Loshaek derived a linear relationship between cross-link density and transition temperature,

$$T = T_\infty - K_1/M + nK_2$$

where T_∞ is the glass transition temperature for an infinite straight chain polymer, M is the molecular weight that the polymer would have if all the cross-links were severed, and n is the number of cross-links per gram; K_1 and K_2 are constants for a particular polymer system. This equation has been found to fit experimental results for polystyrene and polymethylmethacrylate up to moderate degrees of cross-linking, and the present results can be approximated by a linear relationship up to about 0.3 cross-links per phosphorus atom. In this system M is very large and the term K_1/M in Fox and Loshaek's equation can be neglected, giving a value for the transformation temperature of the near-infinite straight chain molecule,

$$T_\infty = 118\,°\mathrm{C}$$

At higher degrees of cross-linking, the glass transition temperature rises more rapidly than the cross-link density. On the Gibbs-Di Marzio theory, the criterion of glass formation is that the temperature-dependent configurational entropy becomes zero; cross-linking raises the transition temperature because it decreases the configurational entropy from what it would be in the absence of cross-links. Di Marzio [9] calculated the following relationship between glass transition temperature and cross-link density.

$$\frac{T(X) - T(O)}{T(X)} = \frac{Kx}{1 - Kx}$$

where $T(X)$, $T(O)$ are the transition temperatures of the cross-linked polymer and the corresponding straight chain molecule respectively, x is the cross-link density, and K is a constant which to a first approximation should be independent of the material.

The value of $T(O)$ for the glass used in the present investigation must be close to 119 °C, the transformation temperature of the sample having the lowest cross-link density. Trial calculations show that the value for $T(O)$ which gives the smallest variation in the values of K in Di Marzio's equation between the ten results in table I is 118 °C, which agrees with the previous estimate of T_∞. The value of K for each of the results was calculated with $T(O) = 391\,°\mathrm{K}$ and the results are given in table III.

The line drawn in fig. 1 gives the expected correlation between transformation temperature and cross-link density calculated from Di Marzio's equation with $T(O) = 391\,°\mathrm{K}$ and $K = 0.358$. This shows a reasonable fit with all the experimental results, and correctly shows the steep rise in transformation temperature as the maximum cross-link density is approached. It is concluded that the relationship between cross-link density and transformation temperature in a phosphate glass is similar to the relationship observed in organic polymers.

TABLE III Values of K in Di Marzio's equation assuming $T_0 = 118\,°\mathrm{C}$

Sample no.	Transformation temp. °C	Water content wt %	Cross-link density	Value of K in equation	Deviation from mean
1	119	4.5	0.006	0.407	0.049
2	140	3.6	0.123	0.409	0.051
3	141	3.4	0.149	0.352	− 0.006
4	151	3.1	0.188	0.384	0.026
5	146	3.3	0.162	0.386	0.028
6	151	2.9	0.213	0.338	− 0.020
7	158	2.3	0.289	0.293	− 0.065
8	166	2.1	0.315	0.313	− 0.045
9	183	1.4	0.402	0.311	− 0.047
10	256	0.3	0.536	0.386	0.028

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