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Effect of TiO_2 addition on structure, solubility and crystallisation of phosphate invert glasses for biomedical applications

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ABSTRACT

Phosphate invert glasses in the system P_2O_5–CaO–MgO–Na_2O are completely soluble and exhibit a neutral pH in aqueous media, and they are therefore of interest for use as degradable implant materials. Their structure consists of small phosphate units such as pyrophosphate ($P_2O_7^{4-}$), and hence they are prone to crystallisation. Addition of TiO_2 is known to improve processing of the melt and also to control glass solubility. The glass structure of phosphate glasses with 37 and 35 mol% P_2O_5 and addition of 1 to 10 mol% TiO_2 was analysed using ^{31}P MAS NMR, and the influence of structural changes on solubility, thermal properties, processing window and crystallisation behaviour was investigated. Glasses showed an increase in activation energy for crystallisation with increasing TiO_2 content, resulting in an increased processing window, thereby allowing for fibre drawing and sintering of porous scaffolds. Deconvolution of ^{31}P MAS NMR and calculation of network connectivity and average chain lengths suggest that Ti is acting as a network modifier with Ti^{4+} units acting as ionic crosslinks between phosphate units thereby impeding crystallisation as well as chain hydration and subsequent chain dissolution.

1. Introduction

Phosphate glasses in the system P_2O_5–CaO–MgO–Na_2O dissolve completely in aqueous solutions, and they have a composition similar to that of the mineral phase of bone, which makes them interesting materials for degradable implants. Structure and properties of phosphate glasses strongly depend on the phosphate content, and phosphate glasses can be divided into groups corresponding to their phosphate content and structure: ultraphosphate glasses contain more than 50 mol% P_2O_5, they exhibit a phosphate network glass structure consisting of Q^3 structural units and give an acidic pH in water. Polyphosphate glasses contain 50 mol% P_2O_5 or less. At 50 mol% P_2O_5 (metaphosphate composition) they consist of phosphate Q^2 chains of in theory infinite length with the chain length decreasing with decreasing phosphate content. At 33 mol% P_2O_5 (pyrophosphate stoichiometry) the glass structure consists of $P_2O_7^{4-}$ units, i.e. Q^1 dimers, while for 25 mol% P_2O_5 or less only orthophosphate (Q^0) groups are present [1].

Phosphate glasses containing less than 40 mol% P_2O_5 are often referred to as invert glasses, as their properties depend on the network modifier ions rather than on the network former [1]. These glasses degrade more slowly than compositions in the meta- or ultraphosphate region [2–4]. Their structure is highly disrupted and consists of small phosphate units such as pyrophosphate or orthophosphate groups, and therefore these glasses are prone to crystallisation. This makes processing difficult, and stabilisation is desirable. Processing of phosphate invert glasses can be successfully improved by addition of TiO_2 [5–7]. In addition, the only phosphate glass shown to form an apatite layer in simulated body fluid *in vitro* was a TiO_2-containing invert glass [5], and this apatite layer is generally thought to facilitate attachment of osteoblasts *in vivo*, thereby allowing for the formation of an intimate bond to bone [8].

Aim of this work was to investigate how the addition of TiO_2 influences glass structure and crystallisation behaviour in the system P_2O_5–CaO–MgO–Na_2O with phosphate contents of 37 and 35 mol%.

2. Materials and methods

2.1. Glass synthesis

Phosphate invert glasses in the system P_2O_5–CaO–MgO–Na_2O–TiO_2 were produced using a melt quench route as described earlier [4]; nominal glass composition is given in Table 1. For glasses A to D TiO_2 was added in increasing amounts (1 to 10 mol%) while P_2O_5 content was kept at 37 mol% and the ratio CaO:MgO:Na_2O was kept constant. An additional glass (E) was produced with a lower phosphate content (35 mol%). Glass monoliths were produced by quenching the melt between copper blocks to prevent surface

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Table 1
Nominal (top) and analysed (bottom) glass composition in mol% (95% confidence interval).

Glass	P_2O_5	CaO	MgO	Na_2O	TiO_2
A	37.0	29.0	10.0	24.0	–
	36.93 (0.74)	29.39 (0.21)	10.05 (0.13)	23.63 (0.30)	–
B	37.0	28.6	9.8	23.6	1.0
	36.88 (0.75)	29.37 (0.22)	9.91 (0.13)	22.73 (0.31)	1.11 (0.13)
C	37.0	26.7	9.2	22.1	5.0
	n.m.	n.m.	n.m.	n.m.	n.m.
D	37.0	24.4	8.4	20.2	10.0
	n.m.	n.m.	n.m.	n.m.	n.m.
E	35.0	27.5	9.5	22.5	5.5
	34.04 (0.76)	28.84 (0.22)	10.48 (0.14)	20.86 (0.31)	5.78 (0.13)

n.m. = not measured.

crystallisation and subsequent annealing at glass transition temperature (T_g) before cooling to room temperature.

2.2. Glass characterisation

Glass frit was ground to powder in a vibratory mill (Gyro Mill, Glen Creston, UK). Powder X-ray diffraction (XRD; PANalytical, X'Pert PRO MPD, 40 kV, 40 mA, Cu*K*α, data collected at room temperature) was performed to confirm the amorphous structure of the quenched glass. For chemical analysis of the glass composition, the glasses were dissolved in 37% hydrochloric acid (HCl) and analysed using inductively coupled plasma with optical emission spectroscopy (ICP-OES). Glass solubility in deionised water was investigated and analysed using ICP-OES as described earlier [4]. Temperature behaviour was investigated by differential scanning calorimetry (DSC) using both glass frit and milled glass powder (50 mg). The glass transition temperature (T_g) was determined as the onset temperature of the transition temperature range. The processing window was calculated as the difference between crystallisation onset ($T_{c,ons}$) and T_g. From DSC traces obtained using different heating rates (5, 10, 15, 20 and 25 K/min) activation energies (E_a) for T_g and crystallisation were calculated [9].

For investigation of crystal phases, milled glass powder was heat-treated in analogous fashion to the DSC experiments: The samples were heated to $T_{c,ons}$ at a heating rate of 10 K/min and then were allowed to cool to room temperature without holding at $T_{c,ons}$. Crystal phases were analysed using XRD and NMR (cf. below).

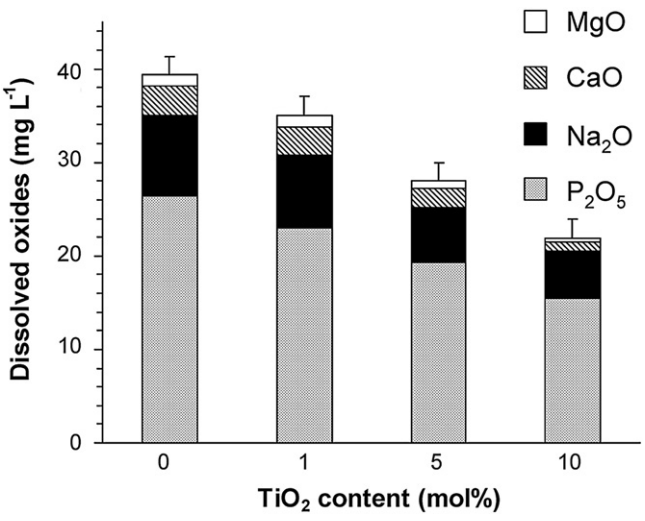

Fig. 1. Glass solubility in deionised water at 98 °C analysed using ICP-OES. (Error bars show the 95% confidence interval.)

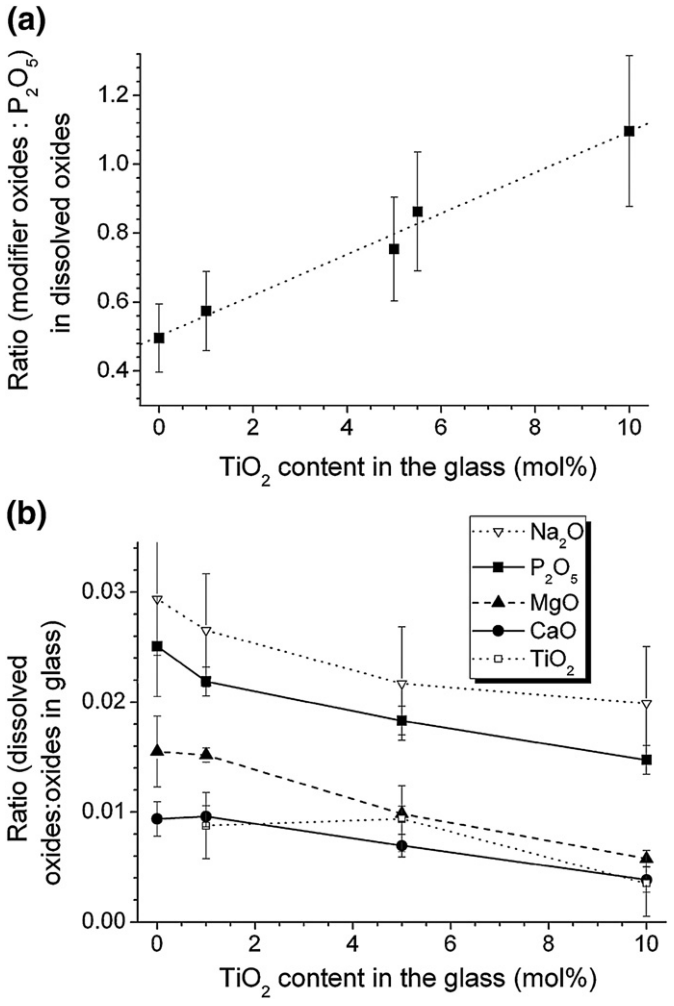

Fig. 2. (a) Ratio of network modifier oxides (CaO, MgO, Na_2O, and TiO_2) to P_2O_5 in dissolved ions. Dotted line represents linear regression of data for glasses A to E (Regression coefficient: $R = 0.993$), (b) ratio of dissolved ions calculated as oxides relative to original concentration of oxides in the glass *vs.* TiO_2 content in the glass. (Error bars show the 95% confidence interval. Lines are drawn as a guide to the eye.)

2.3. Structural investigation

Glass structure was investigated using Raman spectroscopy and ^{31}P MAS NMR. Raman spectra were obtained using glass monoliths at Raman shifts between 500 and 1500 cm^{-1} (Renishaw RM 2000 connected to Leica Microscope with 50× objective). ^{31}P MAS NMR spectra were acquired at 81.0 MHz in the 4 mm rotor spinning at 4.5 kHz (Bruker 200 MHz (4.7 T) spectrometer). 64 transients of a

Table 2
Glass transition (T_g), crystallisation onset ($T_{c,ons}$) and crystallisation peak ($T_{c,pk}$) temperatures and processing window ($T_{c,ons} - T_g$) from DSC traces (heating rate 10 K/min) run on frit and milled glass powder (shown in brackets).

Glass	T_g °C	$T_{c,ons}$ °C	$T_{c,pk}$ °C	Processing window K
A	426	558	601	132
	(421)	(525)	(537)	(104)
B	432	567	616	135
	(417)	(523)	(534)	(106)
C	454	616	661	162
	(444)	(568)	(579)	(124)
D	481	664	711	183
	(473)	(618)	(643)	(145)
E	472	617	641	145
	(470)	(599)	(612)	(129)