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Predicting glass transition and crystallization temperatures of silicate bioglasses using mixture designs

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ABSTRACT

Mixture designs have been applied on bioglasses in the range 42–55%SiO_2, 13.5–48%CaO, 10–35%Na_2O, 0–5%P_2O_5, and 0–13.5%CaF_2 (mol%). This study focused on glass transition temperature (T_g), crystallization temperature (T_c) and working range (temperature gap between T_g and T_c). The designs, elaborated from data obtained by Differential Thermal Analysis (DTA), consist of equations connecting the properties with the glass molar composition. Using this powerful mathematical method, T_g, T_c and the working range of bioglasses can be precisely predicted and optimized. We found that a Na, P or F addition decreases T_g. Crystallization occurs at higher temperature when phosphorus is added in small quantity, due to network polymerization, although further addition induces a decrease of T_c related to a decrease of the overall strength of the glass network. Fluoride affects crystallization of both manners, depending on the calcium and sodium contents. Last, as a network modifier, Na lowers T_c. The widest working ranges are obtained for glasses with a large quantity of SiO_2, CaO, and P_2O_5 and a medium quantity of CaF_2, allowing to reach a difference between T_c and T_g of up to 260 °C.

1. Introduction

Since 1969 and the discovery of Bioglass® 45S5 by L.L. Hench [1], bioactive glasses have been developed for medical application, due to their ability to form a hydroxyapatite layer and bond to bone. Shape forming of these materials is widely studied nowadays, giving a great importance to the working range T_c–T_g. For instance, fabrication of coatings and porous tissue engineered scaffolds requires a viscous flow sintering and no crystallization [2,3]. Indeed, crystallization has been shown to decrease the bioactive properties of bioglasses [4,5]. An a priori mathematical estimation of these two temperatures would then be a real asset for processing such materials.

T_g and T_c values depend on several factors, the most important being the glass structure. Phosphosilicate glasses, a common kind of bioglasses, present an amorphous phase separation with small orthosphosphate domains dispersed in a silicate matrix [6]. ^{29}Si, ^{31}P and ^{17}O solid-state NMR spectroscopy confirmed the non existence of Si – O – P bonds in the 45S5 glass [7]. This glass separation induces the observation of two T_g and two T_c signatures [8,9]. Nevertheless, depending on the composition, the second T_g is not always distinguishable, since it could be combined with the first one in a composite glass transition, or hidden by the crystallization peak.

As a network disrupter, sodium is known to decrease both T_g and T_c values [10–12]. When added to the nominal glass composition, fluoride tends to complex preferentially Ca^{2+} and Na^+ cations [13–16], and thus lowers the glass transition temperature [8,17]. Molecular Dynamics (MD) calculations suggest that when incorporated, fluorine decreases the overall strength of the glass network, defined by the F_{net} parameter [14]. It is also worth noting that being thermally activated processes, both T_g and T_c are cooling rate, heating rate and sample form dependant [2,9].

About 20 years ago, Andersson described T_g as a linear function of the Na_2O content in a six oxide system [11]. Arstila et al. also proposed several equations predicting glass transition and devitrification temperatures, depending on the measurement method [12]. They concluded on the existence of a relation between the working range, the glass composition and the nature of the main phase formed during crystallization. Recently, O'Donnell gathered results from several articles and established a new formula correlating T_g to bioglass molar composition [17]. His model, elaborated from data fitted thanks to Solver in OpenOffice, allows quite a good T_g approximation to be obtained, despite results extracted from a different methods (DTA, DSC, dilatometry).

In this paper we propose a different approach for T_g and T_c prediction by mixture designs [18]. This mathematical method, recognized for its great potential in mixtures and formulation, allows characteristic temperatures and composition of bioglasses belonging in a predefined domain to be related. Mixture designs have already been demonstrated to be a valuable prediction and optimization method for bioactive properties in a simple system [19]. Designs elaborated in this study focus on a predefined domain belonging to the SiO_2–CaO–Na_2O–P_2O_5–CaF_2 system. Phosphorus, as bone constituent, is

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Table 1
Molar composition of the 100 studied glasses. An * before a glass name indicates a composition retained as checking glass.

Glass	SiO_2	CaO	Na_2O	P_2O_5	CaF_2	Glass	SiO_2	CaO	Na_2O	P_2O_5	CaF_2
G1	51.50	13.50	35.00	–	–	G51	55.00	13.50	24.75	–	6.75
G2	55.00	13.50	31.50	–	–	G52	55.00	28.25	10.00	–	6.75
G3	55.00	35.00	10.00	–	–	*G53	55.00	20.88	17.38	–	6.75
G4	42.00	23.00	35.00	–	–	G54	42.00	38.75	10.00	2.50	6.75
G5	42.00	48.00	10.00	–	–	*G55	48.50	32.25	10.00	2.50	6.75
G6	42.00	35.50	22.50	–	–	*G56	55.00	19.63	16.13	2.50	6.75
G7	55.00	24.25	20.75	–	–	G57	55.00	13.50	22.25	2.50	6.75
G8	53.25	13.50	33.25	–	–	G58	55.00	25.75	10.00	2.50	6.75
G9	48.50	41.50	10.00	–	–	G59	42.00	36.25	10.00	5.00	6.75
*G10	46.75	18.25	35.00	–	–	G60	48.50	29.75	10.00	5.00	6.75
G11	49.10	26.60	24.30	–	–	*G61	55.00	18.38	14.88	5.00	6.75
G12	49.00	13.50	35.00	2.50	–	G62	55.00	23.25	10.00	5.00	6.75
G13	55.00	13.50	29.00	2.50	–	G63	55.00	13.50	19.75	5.00	6.75
G14	55.00	32.50	10.00	2.50	–	*G64	42.00	25.00	23.70	2.50	6.80
G15	42.00	20.50	35.00	2.50	–	*G65	48.60	13.50	28.60	2.50	6.80
G16	42.00	45.50	10.00	2.50	–	G66	42.00	13.50	35.00	2.50	7.00
G17	42.00	33.00	22.50	2.50	–	G67	42.00	26.50	24.20	–	7.30
*G18	55.00	23.00	19.50	2.50	–	*G68	49.10	13.50	30.10	–	7.30
*G19	52.00	13.50	32.00	2.50	–	G69	42.00	13.50	30.50	5.00	9.00
G20	48.50	39.00	10.00	2.50	–	G70	42.00	13.50	35.00	–	9.50
*G21	45.50	17.00	35.00	2.50	–	*G71	42.00	13.50	31.75	2.50	10.25
*G22	48.60	25.10	23.80	2.50	–	G72	42.00	13.50	33.00	–	11.50
G23	46.50	13.50	35.00	5.00	–	G73	42.00	24.00	20.50	–	13.50
G24	55.00	13.50	26.50	5.00	–	G74	42.00	34.50	10.00	–	13.50
G25	55.00	30.00	10.00	5.00	–	G75	42.00	13.50	31.00	–	13.50
G26	42.00	18.00	35.00	5.00	–	G76	48.50	28.00	10.00	–	13.50
G27	42.00	43.00	10.00	5.00	–	*G77	48.50	20.75	17.25	–	13.50
G28	42.00	30.50	22.50	5.00	–	G78	48.50	13.50	24.50	–	13.50
G29	55.00	21.75	18.25	5.00	–	G79	55.00	21.50	10.00	–	13.50
G30	50.75	13.50	30.75	5.00	–	G80	55.00	13.50	18.00	–	13.50
G31	48.50	36.50	10.00	5.00	–	G81	55.00	17.50	14.00	–	13.50
G32	44.25	15.75	35.00	5.00	–	*G82	42.00	22.75	19.25	2.50	13.50
*G33	48.10	23.60	23.30	5.00	–	G83	42.00	13.50	28.50	2.50	13.50
*G34	43.50	15.00	35.00	5.00	1.50	G84	42.00	32.00	10.00	2.50	13.50
G35	42.00	15.75	35.00	5.00	2.25	G85	48.50	25.50	10.00	2.50	13.50
*G36	44.25	13.50	35.00	5.00	2.25	G86	48.50	13.50	22.00	2.50	13.50
*G37	44.33	15.83	35.00	2.50	2.33	*G87	48.50	19.50	16.00	2.50	13.50
*G38	45.17	16.67	35.00	–	3.17	G88	55.00	19.00	10.00	2.50	13.50
*G39	42.00	17.00	35.00	2.50	3.50	*G89	55.00	13.50	15.50	2.50	13.50
*G40	45.50	13.50	35.00	2.50	3.50	*G90	55.00	16.25	12.75	2.50	13.50
G41	42.00	13.50	35.00	5.00	4.50	G91	42.00	29.50	10.00	5.00	13.50
G42	42.00	18.25	35.00	–	4.75	G92	42.00	13.50	26.00	5.00	13.50
G43	46.75	13.50	35.00	–	4.75	G93	42.00	21.50	18.00	5.00	13.50
*G44	47.65	20.45	21.05	5.00	5.85	G94	48.50	23.00	10.00	5.00	13.50
G45	47.90	21.70	21.80	2.50	6.10	*G95	48.50	18.25	14.75	5.00	13.50
*G46	42.00	23.50	23.20	5.00	6.30	G96	48.50	13.50	19.50	5.00	13.50
*G47	48.10	13.50	27.10	5.00	6.30	G97	55.00	16.50	10.00	5.00	13.50
G48	48.15	22.95	22.55	–	6.35	G98	55.00	15.00	11.50	5.00	13.50
G49	42.00	41.25	10.00	–	6.75	G99	55.00	13.50	13.00	5.00	13.50
G50	48.50	34.75	10.00	–	6.75	*45S5	46.10	26.90	24.40	2.60	–

an important element in bioglasses and fluoride is known "to prevent and arrest caries" [20,21].

2. Experimental methods

2.1. Mixture designs: D-optimal designs

Preliminary feasibility tests have allowed the studied domain to be limited to the range: 42–55%SiO_2, 13.5–48%CaO, 10–35%Na_2O, 0–5%P_2O_5, 0–13.5%CaF_2 (mol%). Four constraints from a previous study have been retained: synthesis temperature, vitreous compounds, fast bioactive reaction, and non solubility [19]. Thus, SiO_2, CaO and Na_2O limit content values come from this previous paper. Phosphorus and fluoride were added in order to follow the same constraints except for synthesis temperature which has been increased to 1450 °C. In recent studies, authors prepared glasses below 40 mol% silica [16,22,23], but due to apparatus limitations and our preparation method, we limited our compositions to silica contents above this value.

Using five constituents, each content defined by an upper and lower limit, implies the resulting domain representation to be an irregular hyperpolyhedron (i.e. a 4D figure). The study of this extremely complicated volume implies two choices:

- The use of a mixture design dedicated software (JMP 5.1 [24]) in order to extract interesting compositions. The software selection agrees with Scheffé's proposal [25,26], as the 99 extracted points are 20 tops, 40 edges, 29 2D faces, 9 3D faces and the gravity center of the domain (Table 1).
- The selection of a fifth degree postulated model (a priori model), in order to minimize the difference between calculated and experimental temperatures (Eq. 1).

$$\begin{aligned} T(^{\circ}C) = {} & B_1{*}X_1 + B_2{*}X_2 + B_3{*}X_3 + B_4{*}X_4 + B_5{*}X_5 + B_{12}{*}X_1{*}X_2 + B_{13}{*}X_1{*}X_3 \\ & + B_{14}{*}X_1{*}X_4 + B_{15}{*}X_1{*}X_5 + B_{23}{*}X_2{*}X_3 + B_{24}{*}X_2{*}X_4 + B_{25}{*}X_2{*}X_5 \\ & + B_{34}{*}X_3{*}X_4 + B_{35}{*}X_3{*}X_5 + B_{45}{*}X_4{*}X_5 + B_{123}{*}X_1{*}X_2{*}X_3 \\ & + B_{124}{*}X_1{*}X_2{*}X_4 + B_{125}{*}X_1{*}X_2{*}X_5 + B_{134}{*}X_1{*}X_3{*}X_4 + B_{135}{*}X_1{*}X_3{*}X_5 \\ & + B_{145}{*}X_1{*}X_4{*}X_5 + B_{234}{*}X_2{*}X_3{*}X_4 + B_{235}{*}X_2{*}X_3{*}X_5 + B_{245}{*}X_2{*}X_4{*}X_5 \\ & + B_{345}{*}X_3{*}X_4{*}X_5 + B_{1234}{*}X_1{*}X_2{*}X_3{*}X_4 + B_{1235}{*}X_1{*}X_2{*}X_3{*}X_5 \\ & + B_{1245}{*}X_1{*}X_2{*}X_4{*}X_5 + B_{1345}{*}X_1{*}X_3{*}X_4{*}X_5 + B_{2345}{*}X_2{*}X_3{*}X_4{*}X_5 \\ & + B_{12345}{*}X_1{*}X_2{*}X_3{*}X_4{*}X_5 + e \end{aligned} \quad (1)$$