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Glass transition temperature of glasses in the SiO_2–Na_2O–CaO–P_2O_5–Al_2O_3–B_2O_3 system

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A total of 24 glasses in or near the bioactive region in the system SiO_2–Na_2O–CaO–P_2O_5–Al_2O_3–B_2O_3 were studied. By differential thermal analysis their glass transition temperatures, T_g, were determined. On basis of an experimental plan for 16 glasses, two phenomenological equations describing the relationship between T_g and glass composition were developed. The equations describe T_g within the compositional ranges: SiO_2, 38.0–65.5; Na_2O, 15.0–30.0; CaO, 10.0–25.0; P_2O_5, 0–8.0; B_2O_3, 0–3.0; Al_2O_3, 0–3.0 wt%. The glass transition temperature shows a linear dependence of the Na_2O content. The higher the Na_2O content, the lower the T_g. Compositional alterations not including Na_2O influences T_g little in comparison with changes in the Na_2O content.

1. Introduction

Bioactive glasses form *in vivo* a chemical bond with bone [1]. Thus these materials are interesting candidates for bone replacement and repair. The clinical applications are, however, still very few. One of the main reasons is the difficulty to simultaneously control physical, chemical and biological properties of the glasses. In developing bioactive glasses it is desirable to be able to predict the properties of a given glass composition. Even more desirable is the opposite problem, i.e. to specify the properties and estimate a composition possessing these properties. The latter problem can be solved by an optimization procedure [2]. For both tasks the property–composition relationship must be known. In the present work the glass transition temperature, T_g, of glasses in or near the bioactive compositional region in the system SiO_2–Na_2O–CaO–P_2O_5–Al_2O_3–B_2O_3 was studied. T_g is the temperature below which the glass can be considered rigid and above which it can be considered viscous. This temperature is of importance in annealing and in sintering of glass as well as in firing of glass powder coatings. It is only above this temperature that a glass powder densifies. If a dual glass coating is to be applied to a metal substrate the T_g of the first layer must not be lower than that of the second one, since otherwise the first layer will flow during the firing of the second layer.

In a previous work phenomenological models for bone contact, thermal expansion, glass transition temperature and hydrolytical resistance (P_{98}), were developed [3]. The model for the biological behaviour was later improved [4]. The T_g-model was based on dilatometric measurements. However, for one of nine investigated glasses no T_g could be detected. Thus the model was based on only eight measurements which reduces its reliability. As a matter of fact it was recently observed that the model failed to predict the T_g of a new glass [5]. In the present work an improved model for the glass transition temperature is presented.

2. Materials and methods

To provide a basis for statistical evaluation of the results, 16 glass compositions (A1–A16) were chosen by a method described by Plackett and Burman (see [6]). The compositions were chosen within the following ranges: SiO_2, 38.0–65.5; Na_2O, 15.0–30.0; CaO, 10.0–25.0; P_2O_5, 0–8.0; B_2O_3, 0–3.0; Al_2O_3, 0–3.0 wt % (Table I). The correlation matrix for this experimental plan as well as the *in vivo* behaviour of the glasses were recently reported [4]. Compositions A9, A10, A12, A14 and A15 are bioactive. The raw materials used were SiO_2, Na_2CO_3, $CaCO_3$, $CaHPO_4 \cdot 2H_2O$, Al_2O_3 and H_3BO_3. The glasses were melted in a platinum crucible for 2–3 h at 1340–1410 °C and cast in a preheated graphite mould. All glasses were clear although at least the bioactive glasses are liquid–liquid phase separated. However, opacification only occurs at above about 650 °C. After annealing, the glasses were ground to fine powders and analysed by differential thermal analysis (DTA). The heating rate was 20 °C min^{-1} and the sample mass was 50 mg. Al_2O_3 was used as reference.

In the DTA run, T_g is seen as a downward shift in the base line followed by the establishment of a new base line. This is due to a change in heat capacity. T_g was estimated as demonstrated in Fig. 1.

3. Results and discussion

Table II summarizes the glass transition temperatures for compositions A1–A16. By regression analysis a model which gives T_g as a function of the composition

TABLE I Glass compositions by synthesis (wt %). These compositions were used to develop the models

Sample	Glass	Na_2O	CaO	P_2O_5	B_2O_3	Al_2O_3	SiO_2
A 1	S63.5P6	15.00	14.00	6.00	0.50	1.00	63.50
A 2	S57.5P5	16.00	18.00	5.00	3.00	0.50	57.50
A 3	S65.5P1	17.00	13.00	1.00	1.00	2.50	65.50
A 4	S52P3	18.00	24.00	3.00	0.00	3.00	52.00
A 5	S56P6	19.00	16.00	6.00	1.50	1.50	56.00
A 6	S51P7	20.00	17.00	7.00	3.00	2.00	51.00
A 7	S51P2	21.00	21.00	2.00	2.00	3.00	51.00
A 8	S64P0	22.00	10.00	0.00	2.50	1.50	64.00
A 9	S53P4	23.00	20.00	4.00	0.00	0.00	53.00
A10	S45P7	24.00	22.00	7.00	2.00	0.00	45.00
A11	S52P8	25.00	12.00	8.00	0.50	2.50	52.00
A12	S46P0	26.00	25.00	0.00	2.00	1.00	46.00
A13	S38P8	27.00	23.00	8.00	1.00	3.00	38.00
A14	S48P2	28.00	19.00	2.00	1.50	1.50	48.00
A15	S55.5P4	29.00	11.00	4.00	0.00	0.50	55.50
A16	S45.5P5	30.00	15.00	5.00	2.50	2.00	45.50

TABLE II Glass transition temperatures for glasses in the A-series determined by DTA and estimated by Equations 1 and 2

Sample	Exp.	Eq. 1	Eq. 2
A 1	573	584	580
A 2	575	564	574
A 3	570	568	568
A 4	582	575	561
A 5	552	554	555
A 6	540	539	549
A 7	535	542	543
A 8	530	529	536
A 9	540	540	530
A10	525	523	524
A11	517	521	518
A12	504	512	511
A13	514	512	505
A14	500	499	499
A15	495	497	493
A16	482	478	486

in wt % was developed.

$$T_g(^\circ\mathrm{C}) = 44.3136 + 6.27159 \times [SiO_2] + 6.90715 \times [CaO] + 6.32101 \times [P_2O_5] + 6.75157 \times [Al_2O_3] \quad (1)$$

$$R^2 = 96.5\%, \omega = 6.7\,^\circ\mathrm{C}$$

R^2 is the regression coefficient and ω is the residual standard deviation. The T_g can, however, be almost equally well described as a simple linear function of the sodium content.

$$T_g(^\circ\mathrm{C}) = 674.483 - 6.26843 \times [Na_2O] \quad (2)$$

$$R^2 = 93.4\%, \omega = 8.2\,^\circ\mathrm{C}$$

Glass transition temperatures predicted with these models are compared with experimental data in Table II. As a first approximation not only Equation 2 describes a linear dependence of the Na_2O content but also Equation 1, since all coefficients are very close (6.3–6.9) and sum up to 100 – $[Na_2O]$. The effect of B_2O_3 lacks, however, significance. The equations demonstrate the importance of the Na_2O content and the limited possibility to affect T_g by compositional changes not involving Na_2O. According to Equation 2 the transition temperature decreases by about 6.3 °C for every wt % unit of any component that is replaced by Na_2O in the glass.

Fig. 2 shows the experimental data for compositions A1–A16 and the line described by Equation 2. The figure also shows experimental data for eight

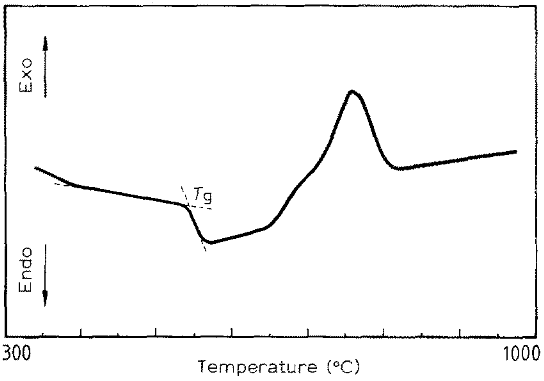

Figure 1 DTA curve for glass A9. The glass transition temperature is seen as a downward shift in the base line followed by the establishment of a new base line. T_g was determined as indicated.

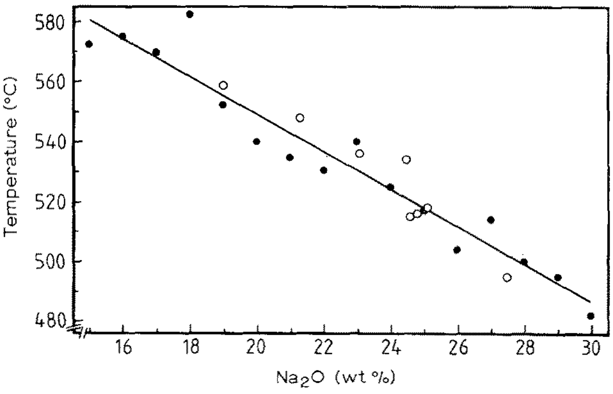

Figure 2 T_g as a function of Na_2O-content for the A-series (●) and the B-series (○). The line corresponds to Equation 2 which was developed on basis of the A-series. The T_g for glasses in the B-series are only indicated for comparison.

TABLE III Glass composition by synthesis (wt %). These compositions were studied for comparison with the glasses in Table I and as a reliability check

Sample	Glass	Na_2O	CaO	P_2O_5	B_2O_3	Al_2O_3	SiO_2
B1	S48.2P2.3	25.13	18.19	2.31	2.82	3.31	48.24
B2	S56.7P4.6	19.00	15.83	4.61	2.25	1.64	56.70
B3	S56.7P6.8	24.59	8.90	6.76	2.21	0.81	56.73
B4	S51.2P7.3	23.10	12.30	7.30	3.30	2.10	51.20
B5	S49.9P8.6	21.30	16.60	8.60	0.20	3.30	49.90
B6	S57.0P5.3	27.50	10.20	5.30	0.00	0.00	57.00
B7	S53.8P7.3	24.80	9.90	7.30	3.00	1.20	53.80
B8	45S5	24.50	24.50	6.00	0.00	0.00	45.00

TABLE IV Glass transition temperatures for glasses in the B-series determined by DTA and estimated by Equations 1 and 2

Sample	Exp.	Eq. 1	Eq. 2
B1	518	509	520
B2	559	549	555
B3	515	510	520
B4	536	515	530
B5	548	549	541
B6	495	506	502
B7	516	504	519
B8	534	534	521

glasses (B1–B8), which were studied as a check of the reliability of the models, but which were not included in the development of the models. The compositions of these glasses are given in Table III. Composition B8 corresponds to the well-known Bioglass^R 45S5 developed by Hench [1]. Experimentally determined as well as computed T_g for the B-series are given in Table IV.

For all glasses (A- and B-series) it can be seen that there is a fairly good agreement between the T_g estimated with the two models and the determined T_g. Equation 2 gives a better prediction for the B-series. Thus, Equation 2 is probably as accurate as Equation 1, although the fit to the experimental data in the A-series is somewhat better for Equation 1. The models are useful for estimating annealing, sintering and firing temperatures of given glass compositions as well as for developing glasses by optimization of the composition. It should, however, be borne in mind that the models only describe T_g within the compositional ranges that were used in developing them (cf. Table I). However, since both equations are linear, they might with due care be used for a limited extrapolation outside the given ranges.

4. Conclusions

The glass transition temperatures for glass compositions in or near the bioactive region in the system SiO_2–Na_2O–CaO–P_2O_5–Al_2O_3–B_2O_3 were determined by DTA. The compositional dependence of T_g can be described phenomenologically. Two equations were developed but, as a rule of thumb, T_g for bioactive glasses can be said to be linearly dependent on the Na_2O content in the glass. The higher the Na_2O content, the lower the T_g. Compositional alterations not including Na_2O affects T_g little in comparison with changes in the Na_2O content.

References

1. L. L. HENCH, R. J. SPLINTER, W. C. ALLEN and T. K. GREENLEE, *J. Biomed. Mater. Res.* **5** (1972) 117.
2. T. WESTERLUND, L. HATAKKA and K. H. KARLSSON, *J. Amer. Ceram. Soc.* **66** (1983) 574.
3. Ö. H. ANDERSSON, K. H. KARLSSON, K. KANGASNIEMI and A. YLI-URPO, *Glastech. Ber.* **61** (1988) 300.
4. Ö. H. ANDERSSON, G. LIU, K. H. KARLSSON, L. NIEMI, J. MIETTINEN and J. JUHANOJA, *J. Mater. Sci.: Mater. Med.* **1** (1990) 219.
5. I. KANGASNIEMI, K. DE GROOT, J. WOLKE, Ö. H. ANDERSSON, Z. LUKLINSKA, J. G. M. BECHT, M. LAKKISTO and A. YLI-URPO, *ibid.*, in print.
6. D. C. MONTGOMERY, "Design and analysis of experiments", 2nd Edn (Wiley, New York, 1984).

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