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Research Article

Modeling of Viscosity and Thermal Expansion of Bioactive Glasses

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The behaviors of viscosity and thermal expansion for different compositions of bioactive glasses have been studied. The effect of phosphorous pentoxide as a second glass former in addition to silica was investigated. Consequently, the nonlinear behaviors of viscosity and thermal expansion with respect to the oxide composition have been modeled. The modeling uses published data on bioactive glass compositions with viscosity and thermal expansion. L^2-regression optimization technique has been utilized for analysis. Linear and nonlinear relations are shown to establish the viscosity and thermal expansion coefficients associated with oxide components of the glasses under study. The modeling allows the calculation of viscosity for a given temperature and, accordingly, the fusion temperature of these glasses along with the coefficient of thermal expansion. The established model relations also suggest first- and second-order phosphorus-alkali and alkaline earth oxides interaction which is reflected on the model coefficient that calculates viscosity and thermal expansion.

1. Introduction

In a review of the importance of comprehensive information on glass and melt properties both for the glass science and technology by Mazurin [1], it is shown that the number of publications per year concerning glass property measurements have decreased quite considerably after 1975. Moreover, the frequency of some quite important but labor-consuming property measurements decreases steadily. Besides that, these measurements are quite time and money consuming; thus, the specialist on glass science and technology needs to predict the glass properties via calculation of it. This task must be based on modeling methods which use experimental property data and calculate glass properties including newly designed glasses.

The changes in the composition area of glass often lead to the change of the reliable modeling, that is, different models may be needed. Finding the most reliable model is possible only by comparing the results of property calculations with experimental data for glasses belonging to a system of interest. Next, the model with a minimal root-mean-square error is selected. After that, the model is used for future calculations of glass properties. At present, this is the best way to obtain a property value that is as near to the true one as possible. This explains why modeling of glass properties is an enduring active field in glass science and technology [2].

Viscosity at given temperature and the coefficient of thermal expansion CTE for bioactive glasses are the glass properties which are focused on in this study. Bioactive glasses have the property of forming an apatite layer; thus, when the implants is coated with bioactive glass, it can chemically bond to bone [3]. However, if there is a large difference in coefficient of thermal expansions between the coating and the implant, the bioactive glass will crack resulting in incomplete coating. A second problem is that the fusion temperature is needed to be well estimated for efficient cast of the glass coating to the implant. The fusion temperature should be low enough to avoid phase transformation and degradation of the mechanical properties of the implant. Therefore, scientific efforts must be carried out to achieve glass compositions that are suitable in view of fusion temperature and coefficient of thermal expansion [4]. The glass designer intends to assemble bioactive glass with fusion temperature below 900°C to avoid possible phase

Table 1: The composition and thermal properties for reference glasses.

No.	wt% SiO_2	wt% P_2O_5	wt% Na_2O	wt% K_2O	wt% CaO	wt% MgO	Ts (K)	Tg (K)	CTE (10^{-6} °K)
1	45.0	6.0	24.5	0.0	24.5	0.0	784	830	15.1
2	44.2	6.0	23.6	6.5	12.6	7.1	722	776	15.6
3	44.2	6.0	17.0	4.6	18.0	10.2	789	833	13.0
4	44.2	6.0	10.3	2.8	23.4	13.3	800	872	11.3
5	49.8	6.0	15.5	4.2	15.6	8.9	795	833	12.2
6	52.7	6.0	17.0	4.6	12.6	7.1	803	838	12.9
7	52.7	6.0	10.3	2.8	18.0	10.2	804	881	11.5
8	54.5	6.0	12.0	4.0	15.0	8.5	821	875	11.0
9	56.5	6.0	11.0	3.0	15.0	8.5	830	882	10.8
10	61.1	6.0	10.3	2.8	12.6	7.2	837	897	10.2
11	67.7	6.0	8.3	2.2	10.1	5.7	838	917	8.8

Table 2: Reference experimental Eμ (kJ), $\ln A$, and CTE (10^{-6} °K) versus their calculated values.

No.	$E\mu$	$E\mu$c	$\ln A$	$\ln Ac$	CTE	CTEc
1	927.5	927.2	125.9	122.8	15.1	15.1
2	681.5	679.8	97.1	85.9	15.6	15.6
3	979.0	986.6	132.9	131.7	13.0	13.2
4	637.6	636.6	79.5	79.5	11.3	11.3
5	1141.1	1106.5	156.3	149.5	12.2	12.4
6	1258.2	1279.3	172.1	175.3	12.9	12.5
7	605.7	608.7	74.3	75.3	11.5	11.0
8	872.9	870.2	111.6	114.3	11.0	11.0
9	821.7	848.8	101.8	111.1	10.8	11.0
10	923.4	905.6	117.5	119.6	10.2	10.4
11	640.4	639.8	75.6	79.9	8.8	8.9

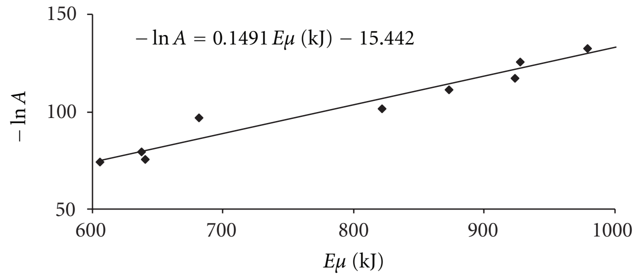

Figure 1: ln$A$ versus $E\mu$. The equation of least-squares line representing the data is also shown.

transformation of for example, Ti-alloys; also, the value CTE should be around 9.6×10^{-6} °K which should match that of Ti-alloys [5]. In addition, the trend in bioactive glass compositions is to set P_2O_5 content to 6% with high CaO content to ensure the formation of apatite layer after implantation that is responsible for the biocompatibility of the glass.

In general, viscosity and thermal expansion for bioactive glass shows nonlinear behavior with glass composition. Therefore, any proposed model should express effective composition-related terms that describe these properties for bioactive glass. Consequently, the model calculation can be used in design technology in such glass category [6].

The topic of predicting the viscosity and thermal expansion of bioactive glass is still vigorous for different sets of bioactive glass compositions [6, 7], and the modeling study based on formerly published data is still on focus in the applied ceramics community [8–10]. This work presents modeling methodology, results, and discussion of the modeled bioactive class along with the comparison on the effect of CaO and MgO content on the properties of the bioactive glass.

2. Composition-Viscosity and Thermal Expansion Model

The variation of viscosity μ with the absolute temperature T is expressed as the following [11]:

$$\mu = AT \exp\left(\frac{E\mu[J]}{RT}\right). \tag{1}$$

The parameter A is constants, R is the gas constant, and $E\mu$ is the activation energy of the viscous process.

The natural logarithm of (1) readsas the following:

$$\mathrm{Ln}\left(\frac{\mu}{T}\right) = \ln A + \frac{E\mu[J]}{RT}. \tag{2}$$

The above equation shows that $E\mu$ and $-\ln A$ are linked linearly. Accordingly, values of ln A can be calculated for a given set of viscosity μ at temperature T and $E\mu$ for a range of glass compositions.

$E\mu$ is as function of glass composition as well as the coefficient of thermal expansion CTE [12]:

$$E\mu = \sum_{i=1}^{i=n} C_i \cdot N_i \tag{3a}$$

$$\mathrm{CTE} = \sum_{i=1}^{i=n} C_{\mathrm{TE}i} \cdot N_i, \tag{3b}$$

Table 3: Coefficients C_i and C_{TEi} associated with the glass composition.

Term	wt% SiO_2	wt% P_2O_5	wt% K_2O	Wt% MgO	R_{11}	R_{12}	R_{21}	R_{22}
$E\mu$ coefficient	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
Value	39.82	−1355	−135.9	82.27	83645	−54473	−66823	44794
CTE coefficient	C_{TE1}	C_{TE2}	C_{TE3}	C_{TE4}	C_{TE5}	C_{TE6}	C_{TE7}	C_{TE8}
Value	−0.62	−7.62	−0.84	−0.37	−64.65	36.09	395.01	−309.81

N_i is the weight percentages wt% of the ith component composing the glass and C_i or C_{TEi} is the coefficient associated with the ith glass component. The terms $(C_i \cdot N_i)$ or $(C_{TEi} \cdot N_i)$ can also include nonlinear combination of more than one glass component. Finally, n represents the total number of terms.

The final step is to explicitly express the composition-viscosity or thermal expansion model that is specific to the bioactive glass composition set under study. In this study, the effort to present such a model is enlightened by the discussion of Kuppinger and Shelby [13], that is, inspecting possible interaction between ions composing the glass which may lead to the nonlinear relations of the bioactive glass composition with $E\mu$ and CTE. In this study, phosphorous-alkali and alkaline earth effect is found. So, the suggested composition-glass property model is stated as below:

$$\begin{aligned} E\mu = {} & C_1 \cdot \text{wt\% } SiO_2 + C_2 \cdot \text{wt\% } P_2O_5 + C_3 \cdot \text{wt\% } K_2O \\ & + C_4 \cdot \text{wt\% MgO} + C_5 \cdot R_{11} + C_6 \cdot R_{12} + C_7 \cdot R_{21} \\ & + C_8 \cdot R_{22} \end{aligned} \tag{4a}$$

$$\begin{aligned} \text{CTE} = {} & C_{TE1} \cdot \text{wt\% } SiO_2 + C_{TE2} \cdot \text{wt\% } P_2O_5 \\ & + C_{TE3} \cdot \text{wt\% } K_2O + C_{TE4} \cdot \text{wt\% MgO} \\ & + C_{TE5} \cdot R_{11} + C_{TE6} \cdot R_{12} + C_{TE7} \cdot R_{21} \\ & + C_{TE8} \cdot R_{22}. \end{aligned} \tag{4b}$$

R_{11}, R_{12}, R_{21}, and R_{22} are first- and second-order functions of phosphorous-alkali and phosphorous-alkaline earth content:

$$\begin{aligned} R_{11} &= \frac{\text{wt\% } Na_2O}{\text{wt\% } P_2O_5 + \text{wt\% } Na_2O} \\ R_{21} &= \frac{\text{wt\% CaO}}{\text{wt\% } P_2O_5 + \text{wt\% CaO}} \end{aligned} \tag{5}$$

$$R_{12} = (R_{11})^2 \tag{6a}$$

$$R_{22} = (R_{21})^2. \tag{6b}$$

Equations (4a)–(6b) are the model equations presented in this study that calculate $E\mu$ and CTE as function of the glass compositions.

3. Modeling Technique

Table 1 shows published bioactive glass composition data with their thermal properties [5]. In this table, Ts represent the temperature at constant viscosity level of $\mu = 10^{6.6}$ Pa·s, which corresponds to the Littleton softening temperature. Tg represents another constant viscosity level of $\mu = 10^{12}$ Pa·s, which is in the range of the expected glass transition temperature ($\mu = 10^{11} \cdots 10^{12.3}$ Pa·s).

Utilizing (2), the two unknowns ($E\mu[kJ]$ and ln$A$) can be found by substitution of Ts and Tg in Table 1. Figure 1 is a plot of $E\mu$ against $-\ln A$ which shows linear relation connecting them. The figure also shows the equation of the least-squares line passing through the data points. The reference values of $E\mu[kJ]$ and ln$A$ found utilizing Table 1 is used together with the glass compositions in L^2-regression [14] calculations. Accordingly, calculated glass properties ($E\mu c$ and CTEc) are found as function of their composition.

The assumption of linear additive behavior is firstly examined. This assumption yields to large differences between reference experimental and calculated glass properties. These differences remain at large values even when several combinations of the wt% of oxide constituents are taken into account. The differences between the reference experimental and calculated glass properties are reduced only when phosphorous-alkali and alkaline earth effect as shown in (4a)–(6b) is taken into account. The calculations astonishingly show that the nonadditive relations are equally needed for modeling of both $E\mu$ and CTE. The final root-mean-square error for $E\mu$ and CTE calculations are 26.47 and 0.23, respectively. These are only around 2% of the reference experimental value for $E\mu$ and CTE.

Table 2 shows the reference experimental $E\mu$, reference experimental ln A, calculated $E\mu$ via L^2-regression, calculated ln A (utilizing calculated $E\mu$ and the least-squares relation shown in Figure 1), reference experimental CTE, and calculated CTE via L^2-regression. The final coefficients C_i and C_{TEi} that obtained by L^2-regression to calculate $E\mu$ and CTE for bioactive glasses are shown in Table 3.

To find the temperature at a given viscosity value (an inverse problem), it needs to calculate $E\mu$ and ln$A$ by the above methodology, then (2) can be solved for T. This can be accomplished using any numerical technique such as the "finite step method." Finally, setting μ to 20 Pa·sec; the fusion temperature for a bioactive glass can be calculated [15].

To conclude, Figure 2 is a way to show how $E\mu$ and CTE respond to CaO and Na_2O content. $E\mu$ and CTE are calculated by setting K_2O, MgO, and Na_2O to 3, 6, and 9 wt%, respectively, and let SiO_2 varies with CaO to make total contents to 100 wt%. The same is done when varying

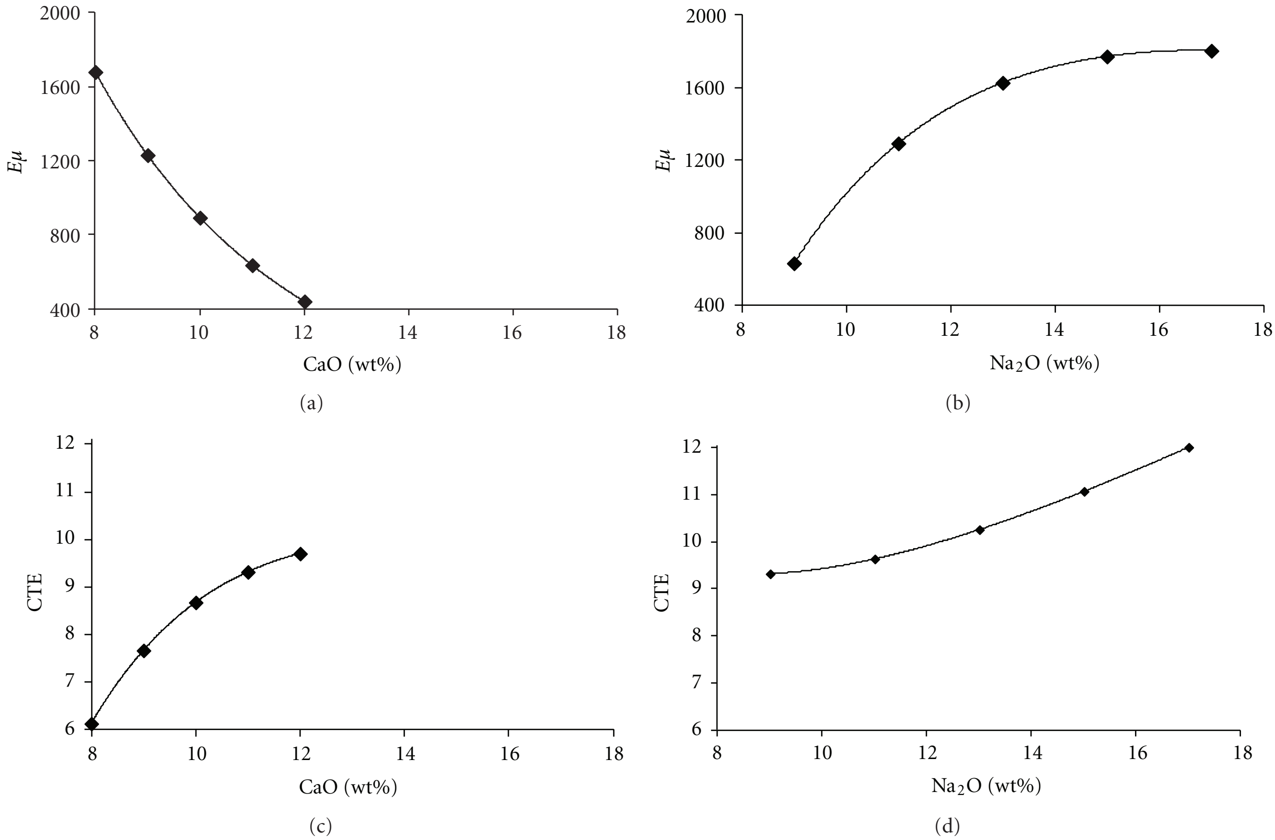

FIGURE 2: The variation of $E\mu$ and CTE with CaO and Na_2O contents. Parts (a) and (b) show the variation of $E\mu$ with CaO and Na_2O content. Parts (c) and (d) show the variation of CTE with CaO and Na_2O contents.

Na_2O by setting K_2O, MgO, and CaO to 3, 6, and 11 wt%, respectively. The figure is presented to show an example of the nonlinear behavior of $E\mu$ and CTE with CaO and Na_2O. Yet, $E\mu$ and CTE are linear with other oxide contents as shown in (4a)–(6b)

4. Discussion

Table 3 shows that SiO_2 has a trend to increase $E\mu$ and to decrease CTE. At the same time, P_2O_5 tends to decrease both $E\mu$ and CTE. MgO shows similar behavior with SiO_2; also, K_2O behaves similar to P_2O_5 with different values of their coefficients. Figure 2 describes the behavior of CaO and Na_2O more obviously. Na_2O shows a trend to increase both $E\mu$ and CTE in nonlinear manner. The effect of Na_2O is distinguished from that of K_2O although they are both alkali oxides. Similarly, Figure 2 shows that CaO is decreasing $E\mu$ and increasing CTE in nonlinear fashion. This effect of CaO is also distinguished from that of MgO although they are both alkaline earth oxides.

The aforementioned different type of contribution for both Na_2O and CaO to the viscosity and thermal expansion compared with that of K_2O and MgO, respectively, may be understood in view of that Na2O and CaO content is generally higher than that of K_2O and MgO in the bioactive glass as seen in Table 1. Consequently, large ion concentration of Na and Ca give a chance for P-Na and P-Ca interactions. These interactions are seen in a way that P_2O_5 is modifying the role of Na_2O and CaO to that observed in Figure 2 and reflected formally in (9)–(12). Nevertheless, those interactions on a relatively low-concentration level of K_2O and MgO do not influence the properties apparently. This explanation is illuminated by the discussion of Kuppinger and Shelby [13] that suggest short range ion-ion interaction in the glass medium that yields nonlinear relations of glass viscosity and thermal expansion with the oxide content. They study sodium potassium borate glasses with high sodium and potassium oxides contents which led to ion-ion interaction between the alkali ions. Nevertheless, in this study the high sodium and calcium oxide contents do not led to mutual interaction between them, but phosphorous-alkali and alkaline earth interaction takes place. The acidic nature of P_2O_5 may explain the interaction with alkali and alkaline earth oxides of the basic nature.

It is worth to mention that multilayer coating is one of the experimental experiences to avoid crack generation which originates from CTE mismatch [7]. However, multilayer coating may lead to other problems such as thick coating. As a direct application of the modeling presented in this study, a bioactive glass can be designed with suitable fusion temperature and CTE passing up lengthy experiments and cost.

5. Conclusions

(1) Model relations of viscosity and thermal expansion with bioactive glass compositions have been obtained. The model allows the predictions of viscosity and thermal expansion for bioactive glass necessary in the field of glass science and technology.

(2) The model relations are discussed for the nonlinear behavior of viscosity and thermal expansion (deviation from additivity) with Na_2O and CaO content. It is suggested that the deviation from additivity originates from short-range interaction between alkali and alkaline earth ions with phosphorus as formally presented in the model.

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