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Effects of composition on selected physical properties of SiO_2–K_2O–Na_2O glasses

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Physical properties were used to characterize a range of five, three-component glass formulations (SiO_2–K_2O–Na_2O) synthesized from spray-dried precursor powders in terms of their final bulk chemical compositions. Five specimens per composition were produced by mixing dry glass powder with methyl alcohol to form a slurry, then shaping the slurry in a cylindrical mould, using conventional methods. Specimens were fired under vacuum. Optimum firing conditions for each glass were determined by selecting holding times which produced the maximum Young's modulus. Fracture toughness, K_{IC}, values ranged from 0.92–0.99 MPa m$^{1/2}$ and Young's modulus, E, values ranged from 45.09–58.06 GPa. Linear regression analyses showed significant correlations between chemical composition and fusion temperature ($n = 5$; $P < 0.001$), opacity ($n = 5$; $P < 0.01$), specific gravity ($n = 5$; $P < 0.02$), dynamic Young's modulus ($n = 5$; $P < 0.01$) and fracture toughness ($n = 30$; $P < 0.001$). The selected physical properties were found to be very sensitive to small variations in chemical composition.

1. Introduction

The composition of glass materials for use in various biomedical applications requires a high degree of homogeneity and purity. Much greater homogeneous precursor powder compositions are possible by using a spray-drying technique than by the use of direct evaporation methods. This is particularly important when synthesizing glass from multicomponent salt solutions [1, 2].

The importance of composition for biomedical glasses is due to the fact that the chemical constituents within the glass directly affect such important properties as translucency, fusion temperature, rate of change of viscosity, abrasion resistance, leachability, thermal expansion and mechanical properties.

The addition of alkali oxides as network modifiers to form alkali silicate glasses causes a disruption of the pure silicate network resulting in a random open network. The extra oxygen provided by Na_2O and K_2O to the continuous (SiO_4) network increases the O/Si ratio in the network above its value of 2 in SiO_2, resulting in a number of non-bridging oxygens which are bonded to only one silicon atom. These "non-bridging" oxygens are charge compensated by the monovalent cations while their position in the structure remains relatively unchanged in the SiO_4 tetrahedron, although there is some weakening of the Si–O bond with increasing alkalies [3]. The weakening of the structure is associated with the fact that the coordination sphere of oxygen around alkalies includes bridging as well as non-bridging oxygen. Furthermore, the alkalies are ionically bonded with the non-bridging oxygen and thus have lower bonding energy than the covalently bonded Si–O. This behaviour would be expected to influence significantly the physical properties of the final glasses.

The present work aimed to evaluate the level of correlation between a range of physical properties and the chemical composition of synthesized SiO_2–K_2O–Na_2O glasses.

2. Experimental procedure

The investigation was carried out using five three-component (SiO_2–K_2O–Na_2O) glasses synthesized by spray drying. The chemical analysis of each glass was determined by means of atomic absorption spectrophotometry and was previously reported (Table I) [1].

2.1. Specimen fabrication

The synthesized glasses were ground to a particle size of 10 μm using an agate pestle and mortar. The glass powder was very hygroscopic and was therefore stored in an oven at 250 °C prior to fabrication. Cylindrical specimens were made by mixing 0.6 g dry glass powder with methyl alcohol (rather than water) to form a slurry. A two-part mould of 7.6 mm diameter was used to form the specimens. The mould was lined with polytetrafluoroethylene tape to prevent the sample from sticking to it and to prevent contamination. The slurry was vibrated into the mould and excess alcohol was removed by means of a dry cellulose paper. The specimen was ejected from the mould and dried overnight at 80 °C. The temperature was increased slowly at a rate of 10 °C h^{-1} in order to

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TABLE I Chemical composition of three-component glasses synthesized by spray drying [1]

Glass	SiO_2 (%)	Na_2O (%)	K_2O (%)
6B	65.60 ± 1.49	16.89 ± 0.89	17.50 ± 0.61
8B	67.99 ± 0.43	15.61 ± 0.17	16.41 ± 0.28
9B	69.91 ± 0.85	14.87 ± 1.22	15.22 ± 0.60
10	71.50 ± 0.52	13.51 ± 0.28	14.98 ± 0.28
12	74.76 ± 0.83	12.41 ± 2.46	12.89 ± 2.29

ensure that the CH_3 groups were oxidized prior to fusion. Failure to follow this procedure resulted in the sample turning black due to entrapment of carbon. The specimens were heated at a rate of 40 °C min^{-1} under a vacuum of 1×10^{-3} torr ($\simeq 6.89\ \text{N mm}^{-2}$) from 500 °C to a temperature 50 °C below the final firing temperature and the vacuum was then released. The temperature was then raised to the final firing temperature and held for a specific time. The individual firing temperatures were determined by means of a series of preliminary firing schedules in which the glass specimens were fired at increasing temperatures in order to determine the optimum fusion temperature which did not result in an overfired specimen with loss of form. These tests were performed in a furnace with a calibrated thermocouple. Once the individual firing temperatures had been determined, a series of specimens were produced using different holding times ranging from 0–2 min at 0.5 min intervals. At the end of the heating schedule the specimens were removed and cooled under a glass beaker in order to prevent drafts from causing increased thermal stresses during cooling.

2.2. Physical property measurements

After the completion of the firing schedules, the specimen dimensions were 6.4 ± 0.1 mm diameter and 5 ± 0.1 mm length. The end surfaces of each specimen were ground flat and parallel using silicon carbide under water. The grit size was varied from 400–600 μm and the specimens were given a final polish with 6 μm diamond paste. The density of each specimen was determined by means of the water displacement technique. Three specimens for each of the firing conditions were evaluated.

2.2.1. *Opacity*

The opacity (%) was evaluated for each glass composition using a Hunter LAB Model DC 25-9 colorimeter. The main principle of this measurement is the use of the contrast ratio method which is the ratio of the reflectance of the sample combined with a white backing to that of the sample combined with a black backing [4].

2.2.2. *Dynamic Young's modulus*

The dynamic Young's modulus of each specimen was evaluated using a sonic method [5–7]. The test involved using lithium niobate crystals (cut at 36° along the *y*-axis) for transmitting and receiving the ultrasonic signal which was generated at the 10 MHz reasonant frequency. The dynamic Young's modulus was derived from the measured velocity of the longitudinal wave in the sample of known thickness and density [7]. The Poisson's ratio was estimated as 0.24 [8].

2.2.3. *Fracture toughness*

The glass specimens were sectioned in half, embedded in resin and repolished. In each of the two halves of the specimen 15 indentations were made using a Vickers indentor and a Model Mo Tukon hardness tester. A load of 4.9 N (500 g) was used with a constant rate of loading controlled by a dashpot oil brake, such that a full load was attained in 15 s. The hardness tester was calibrated using an ASTM steel block. The 4.9 N force was selected for the tests because it provided readily observable fractures at the corners of the diamond indentation. The measurement of the crack length in the glass specimens was enhanced by use of a surface dye. The fracture toughness, K_{Ic}, was calculated from the crack length, the diagonal of the indentation, the hardness, and Young's modulus of the specimen, using a formula described elsewhere [7].

3. Results

The opacity (%) of each glass composition was evaluated for a range of specimens fired at different holding times. It can be observed from Table II that the opacity was not influenced by the time of firing. However, the glass exhibited a darker colour and increased opacity as the amount of alkalies were increased. Similarly, the specific gravity of the glass was not sensitive to the time of firing (Fig. 1). However, denser glasses were obtained as the amount of alkalies (K_2O–Na_2O) were increased (Figs 1 and 2).

The dynamic Young's moduli for the different glass compositions as a function of holding time are shown in Fig. 3. Glass formulations 6B, 8B, 9B were not sensitive to the time of firing. Glass 10 appeared to exhibited a plateau between the 1, 1.5 and 2 min firing; this followed an initial slope (regression analysis, $r = 0.988$) occurring for firing times of 0, 0.5 and 1 min. In contrast, Glass 12, which had the least amount of alkalies, did not exhibit a plateau during incremental firings up to 2 min. The mean values of the above parameters for Glasses 6B, 8B, 9B and 10 were calculated from the plateau region and correlated with the predetermined glass chemical composition [1]. In the case of Glass 12 the value for Young's modulus was obtained from the regression equation. The values for Young's modulus for the five glasses are shown in Table III. The values for Young's modulus for the four glasses excluding Glass 12 were analysed by a Student–Newman–Keuls test which indicated that materials 6B, 8B, 9B, and 10 were all significantly different at the 0.99 level of confidence.

The mean fracture toughness values analysed by a Student–Newman–Keuls rank order test (SNK) for the five three-component glass compositions are shown in Table IV, ranked from highest to lowest.

TABLE II Opacity (%) of five three-component glasses synthesized by spray drying

Holding time (min)	Opacity (%)				
	Glass 12 760 °C	Glass 10 732 °C	Glass 9B 718 °C	Glass 8B 704 °C	Glass 6B 691 °C
0	29.26 35.69	64.26	57.52	75.28 77.30	94.91
0.5	27.81 27.62	46.94	63.01	84.35	96.44
1.0	23.06 25.08	67.95 53.67	48.67	68.90	98.79
1.5	27.91 29.16	53.08	50.17 58.83	79.39	98.07
2.0	28.45 34.93	60.40	69.02 57.66	70.94	102.62
Mean ± S.D.	28.90 ± 3.88	57.72 ± 7.83	58.6 ± 6.86	76.03 ± 5.65	98.17 ± 2.91
Coefficient of variation	13.43%	13.62%	11.70%	7.43%	2.96%

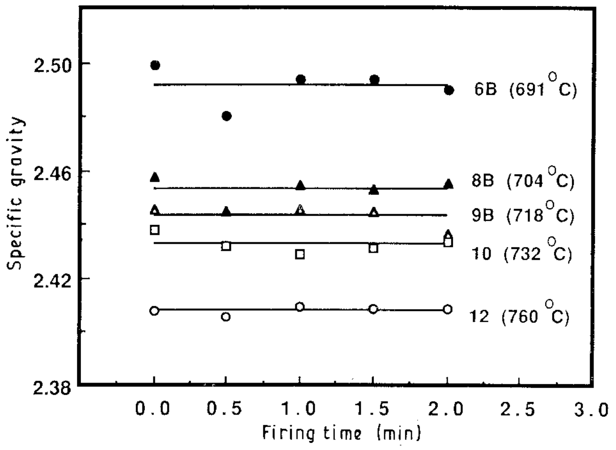

Figure 1 Specific gravity versus holding time for five three-component glass materials.

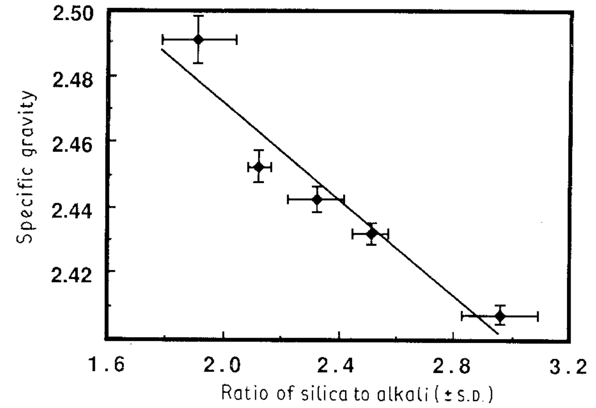

Figure 2 Specific gravity as a function of the ratio of silica to alkali in the glass composition. $r = -0.954$, $t = 5.511$, $p < 0.02$.

This analysis indicated three significantly different groups of fracture toughness values at the 0.95 level of confidence for the five glasses.

Linear regression analyses were performed on the mean specific gravity, firing temperature, per cent opacity, dynamic Young's modulus and fracture toughness relative to the ratio of silica to alkali in the five glass compositions (Figs 2 and 4–7). These analyses were all significant at $p < 0.01$.

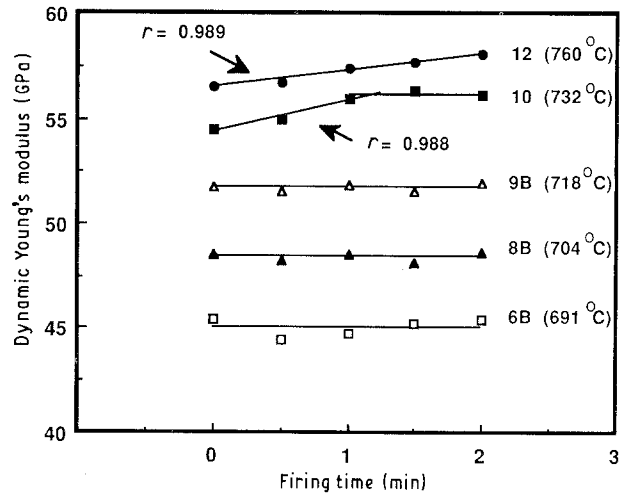

Figure 3 Dynamic Young's modulus as a function of holding time.

TABLE III Young's modulus of five three-component glasses synthesized by spray drying

Glass	Firing temperature (°C)	Young's modulus (GPa ± S.D.)
12	760	57.27[a]
10	732	56.12 ± 0.21
9B	708	51.74 ± 0.18
8B	704	48.39 ± 0.18
6B	691	45.09 ± 0.47
(Level of confidence 0.99)		

[a] Value from the regression equation.

TABLE IV Student–Newman–Keuls rank test comparing the fracture toughness, K_{Ic}, in three-component glasses synthesized by spray drying. The values linked by a brace are not significantly different at the 0.95 level of confidence

Glass	Firing temperature (°C)	K_{Ic} (MPa m$^{1/2}$)
12	760	0.99 ± 0.03
10	732	0.96 ± 0.03
9B	708	0.95 ± 0.03
8B	704	0.94 ± 0.04
6B	691	0.92 ± 0.03
(Level of confidence 0.95)		

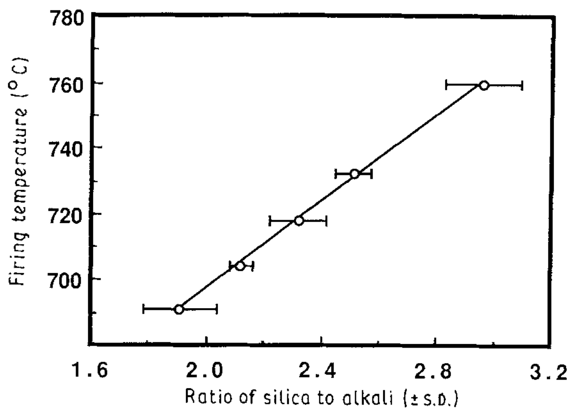

Figure 4 Firing temperature as a function of the ratio of silica to alkali in the glass composition. $r = 0.9995$, $t = 54.752$, $p < 0.001$.

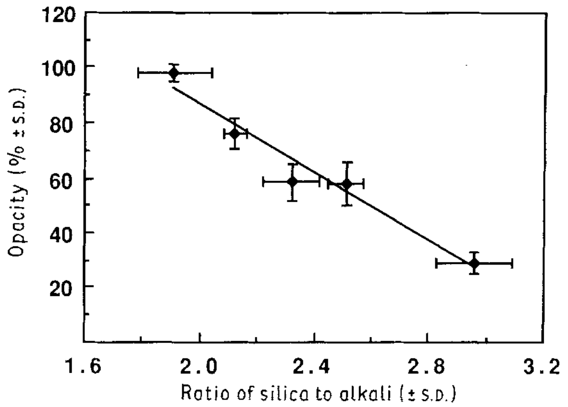

Figure 5 Opacity as a function of the ratio of silica to alkali in the glass composition. $r = -0.976$, $t = 7.763$, $p < 0.01$.

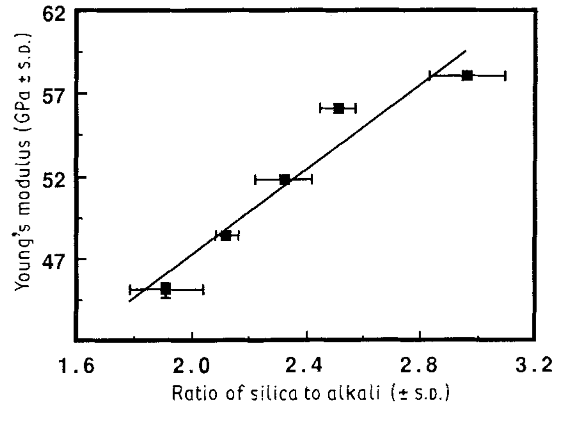

Figure 6 Dynamic Young's modulus as a function of the ratio of silica to alkali in the glass composition. $r = 0.960$, $t = 5.938$, $p < 0.01$.

Multiple linear regression analyses were also performed for the firing temperature, per cent opacity, specific gravity, dynamic Young's modulus, and fracture toughness versus composition. The equations for these analyses are given below.

The equation for predicting the firing temperature (F.T.) from the chemical composition is

$$\begin{aligned} \text{F.T.} &= 20\,892.517 - 199.397(\%\text{SiO}_2) \\ &\quad - 209.503(\%\text{K}_2\text{O}) - 204.629(\%\text{Na}_2\text{O}) \end{aligned} \tag{1}$$

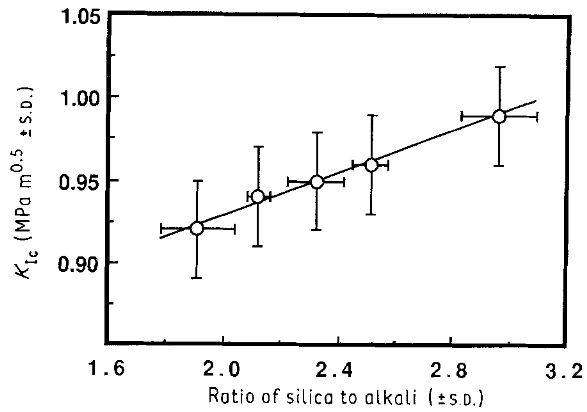

Figure 7 Fracture toughness, K_{Ic}, as a function of the ratio of silica to alkali in the glass composition. $r = 0.995$, $t = 17.255$, $p < 0.001$.

The correlation coefficients for firing temperature versus composition were

$\%\text{SiO}_2$: $r = 0.995$ $t = 17.255$ $p < 0.001$
$\%\text{K}_2\text{O}$: $r = -0.989$ $t = 11.581$ $p < 0.01$
$\%\text{Na}_2\text{O}$: $r = -0.985$ $t = 9.887$ $p < 0.01$

The equation for predicting the per cent opacity from the chemical composition is

$$\begin{aligned} \%\ \text{opacity} &= 26\,124.616 - 262.818(\%\text{SiO}_2) \\ &\quad - 250.620(\%\text{K}_2\text{O}) - 260.579(\%\text{Na}_2\text{O}) \end{aligned} \tag{2}$$

The correlation coefficients for per cent opacity versus composition were

$\%\text{SiO}_2$: $r = -0.987$ $t = 10.637$ $p < 0.010$
$\%\text{K}_2\text{O}$: $r = 0.994$ $t = 15.740$ $p < 0.001$
$\%\text{Na}_2\text{O}$: $r = 0.963$ $t = 6.189$ $p < 0.010$

The equation for predicting the specific gravity (S.G.) from chemical composition

$$\begin{aligned} \text{S.G.} &= 82.037 - 0.798(\%\text{SiO}_2) \\ &\quad - 0.797(\%\text{K}_2\text{O}) - 0.783(\%\text{Na}_2\text{O}) \end{aligned} \tag{3}$$

The correlation coefficients for specific gravity versus composition were

$\%\text{SiO}_2$: $r = -0.976$ $t = 7.763$ $p < 0.01$
$\%\text{K}_2\text{O}$: $r = 0.964$ $t = 6.279$ $p < 0.01$
$\%\text{Na}_2\text{O}$: $r = 0.971$ $t = 7.035$ $p < 0.01$

The equation for predicting the dynamic Young's modulus, E, from the chemical composition was

$$\begin{aligned} E &= 4071.072 - 39.753(\%\text{SiO}_2) \\ &\quad - 39.375(\%\text{K}_2\text{O}) - 43.151(\%\text{Na}_2\text{O}) \end{aligned} \tag{4}$$

The correlation coefficients for dynamic modulus, E, versus composition were

$\%\text{SiO}_2$: $r = 0.978$ $t = 8.120$ $p < 0.01$
$\%\text{K}_2\text{O}$: $r = -0.946$ $t = 5.055$ $p < 0.02$
$\%\text{Na}_2\text{O}$: $r = -0.993$ $t = 14.562$ $p < 0.001$

The equation for predicting the fracture toughness, K_{Ic}, from the chemical composition was

$$K_{Ic} = 0.175(\%SiO_2) + 0.166(\%K_2O) + 0.170(\%Na_2O) - 16.348 \quad (5)$$

The correlation coefficients for fracture toughness, K_{Ic}, versus composition were

$\%SiO_2$: $r = 0.995$ $t = 17.255$ $p < 0.001$

$\%K_2O$: $r = -0.994$ $t = 15.740$ $p < 0.001$

$\%Na_2O$: $r = -0.980$ $t = 8.530$ $p < 0.010$

The limits of the above equations are:

$$65.60 - 1.49\% \leqslant SiO_2 \leqslant 74.76 + 0.83\%$$
$$12.83 - 2.29\% \leqslant K_2O \leqslant 17.50 + 0.61\%$$
$$12.41 - 2.46\% \leqslant Na_2O \leqslant 16.89 + 0.89\%$$

4. Discussion

4.1. Specific gravity

It is reported by Kreidl [3], that the density of binary alkali silicate glasses increases generally with increasing alkali contents as the space in the loose $(SiO_4)^{4-}$ network becomes filled. Similar behaviour has been observed in the present investigation for the five three-component synthesized glasses. The regression analyses indicated an excellent correlation between the chemical composition of these glasses and the specific gravity (S.G.) ($p < 0.01$).

4.2. Colour and opacity

The five three-component synthesized glasses were not chemically stable in an aqueous environment because they were very hygroscopic. An early attempt at producing cylindrical specimens using distilled water to form the slurry was found to cause the glass to become opaque [9]. The reason for this behaviour was attributed to water reacting with the alkali in the glass, forming an alkali hydroxide. The alkali hydroxides may not be fully decomposed at the firing temperature of the glass specimens, thus causing the internal pores to be retained within the glass. As a result, white opaque specimens were produced when water was used. The opacity was due to the difference between the refractive index of the glass and that of the pores. On the other hand, when methyl alcohol was used to form the slurry prior to firing the green specimens, clear translucent glass was obtained at the highest silica level (74.8%), while black opaque glass resulted when the amount of alkalies reached a value of 35%. It is reported by Morrison and Boyd [10] that acidic alcohols could react with alkali metals to form hydrogen gas. Furthermore, methyl alcohol is classified as the strongest acid in the alcohol series. It seems in the present investigation that methyl alcohol might have reacted with the alkali in the glass thus forming alkali methoxide and a release of hydrogen. The methyl group is usually released by heating the specimens slowly from room temperature up to about 500 °C. However, if the glass particles sinter at a temperature lower than 500 °C, the methyl group and subsequent carbon will be trapped within the glass, thus causing the black colouration. This behaviour was observed in the composition (6B) which contained the highest amount of alkali. The black colour observed in these glasses also significantly affected the translucency. The regression analyses indicated an excellent correlation between the chemical composition of the five three-component glasses and opacity ($p < 0.01$).

4.3. Firing temperature

The present five three-component glasses were synthesized by spray drying [1] and melted at 1100 °C. This compares with a temperature of ≈ 1400 °C which would be required for conventional synthesis methods. The lower fusion temperature observed in the present study is due to the higher degree of homogeneity and the lower diffusion path of chemical constituents within these glasses. Increasing the amount of alkalies caused further disruption of the network [3] resulting in a reduction in the viscosity of the melt and thus a decrease in the firing temperature. The regression analyses indicated an excellent correlation between the chemical composition of the glass and the firing temperature ($p < 0.01$). The dynamic Young's modulus measurement proved to be valuable in the determination of the optimum firing conditions for the various glass compositions. The behaviour of Glass 12, which had the lowest alkali content, did not produce a plateau for Young's modulus versus holding time even after a period of 2 min at the designated firing temperature. This suggests that a longer holding time is required at 760 °C, or a higher firing temperature for this glass formulation.

4.4. Dynamic modulus of elasticity

The dynamic sonic technique proved to be an extremely valuable tool for the determination of elastic properties. The sonic data were characterized by a very low coefficient of variation for Young's modulus of elasticity. The free "volume" within the structure of glass associated with the inability of silicate tetrahedral groups to pack closely together may explain in part the variation of the dynamic modulus with alkali content for the five three-component synthesized glasses. In attempting to relate chemical compositions to dynamic modulus some consideration of the relative packing density of the various cations may be necessary. The ability and effectiveness with which specific cations can locate and fill the space within the open glass network structure may well play a significant role in determining the Young's modulus values.

Soga and Anderson [11] have previously noted the extraordinary sensitivity of elastic modulus to packing density. They calculated that for the same bulk modulus, glasses have almost 20% more free volume than the corresponding crystalline structure. The presence of K^+ which is $\approx 37\%$ larger than Na^+ may be significant. Alternatively, a specific combined packing density mixture of the two alkalies may influence the dynamic Young's modulus measurements.

A second factor could be associated with the variation of Young's modulus with composition. Increasing the alkali content in the silicate network will increase the concentration of non-bridging oxygens, thus resulting in some weakening of the Si–O bond [3]. This weakening is due to the coordination sphere of oxygen around alkali which includes bridging as well as non-bridging oxygens. Furthermore, the alkalies are ionically bonded with the non-bridging oxygen, which have a lower bonding energy than the covalent Si–O bond. According to Van Vlack [12], the values of Young's modulus are directly related to the interatomic bonding energy. The net result of the decrease of the modulus value with the increase in the alkali content could be associated, in part, with the relative packing density, the weakening of the Si–O bond, and the higher concentration of ionic bonds within the glass network. The regression analyses indicated an excellent correlation between the chemical composition of the glasses and the dynamic Young's modulus ($p < 0.01$).

4.5. Fracture toughness

The indentation fracture toughness, K_{Ic}, of the three-component synthesized glasses was found to be influenced by chemical composition. This parameter was increased by 8% when the alkali content in these glasses was reduced by 9%. Although the present study covered only a small range of chemical compositions, the data clearly showed a trend in K_{Ic} produced by compositional changes. The interpretation of the above trend can be explained in a similar fashion to the discussion presented for the dynamic modulus. The regression analyses indicated excellent correlation between the chemical composition of these glasses and the fracture toughness ($p < 0.01$). Although the percentage difference in K_{Ic} value was small, between one formulation and the other, the SKN analysis was able to separate the five different compositions into three significant groups at the 0.95 level of confidence.

5. Conclusions

1. The physical techniques that have been applied in the present study of the five three-component glasses were found to demonstrate clearly the influence of compositional change on the firing temperature, the level of opacity, the specific gravity, the dynamic modulus, and the fracture toughness. Highly significant correlations were obtained between the chemical composition and physical properties of the three simple component synthesized glasses.

2. The net result of the increase in opacity values with higher alkali content may be attributed to the carbon resulting from CH_3 groups which are retained in the glass during specimen fabrication as a result of lower fusion temperatures.

3. The decrease in dynamic Young's modulus and fracture toughness values with higher alkali content is believed to be associated with the relative packing density, the weakening of the Si–O network, and the higher concentration of ionic bonds within the glass network.

4. The multiple linear regression analyses will enable prediction of physical properties of future synthesized biomedical glasses within the specified range of chemical composition examined in this work.

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