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Mechanical properties of silicate glasses as a function of composition

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ABSTRACT

Bulk production of silicate glasses is based around a narrow range of soda–lime–silica compositions and as a result any variation in mechanical properties with composition is normally considered to be of little interest. However, studies by a range of authors over the last 50 years or so have demonstrated some intriguing variations of properties such as toughness, brittleness and, more controversially, strength with composition. We have produced several series of alkali-mixed alkaline earth-silicate glasses and are assessing the variation of their mechanical properties with composition using both conventional indentation and nanoindentation. The nanoindentation studies are also being used to assess the effects of surface hydration on the near surface mechanical properties of these glasses. This presentation reviews the results we have obtained to date and attempts to draw out some wider conclusions concerning the compositional dependences of the mechanical properties of silicate glasses.

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1. Introduction

There is increasing interest in developing high strength glass that could be used to produce significantly lighter glass products and which would offer the possibility of novel applications for glass; such interest has been reflected in the US Glass Manufacturing Industry Council's "Strength in Glass" prize [1]. There have also been a number of imaginative structures such as the Skywalk at the Grand Canyon and the Skydeck at the Sears Tower in Chicago where people are enabled to look down great heights through glass floors. Clearly there would be significant benefits if silicate glasses could be made reliably stronger, on a scale of size larger than that of optical fibres, whilst retaining other desirable properties such as transparency.

It is therefore of interest to understand how composition affects the mechanical properties of glasses and whether there are any obvious compositional modifications that could result in higher strength glasses.

2. Experimental

38 silicate based glasses with different silica and network modifier contents were characterized as part of this work (see Table 1 for details). Some of the glasses were originally produced as part of earlier projects (the mixed alkaline earth NCMS, KBMS and KCMS glasses) whilst others were specially prepared for this work (the mixed alkali oxide NKCS, NCS and SS glasses). In all cases the glass batches were produced from high purity silica sand (Loch Aline sand, Tilcon, UK; 99.8%) and appropriate carbonates (Na₂CO₃, CaCO₃, K₂CO₃, BaCO₃, MgCO₃) (Eurolab, Omya, Harbonnieres (Via Prestons), BDH and Acros Organics respectively). In the case of the barium containing glasses (see Table 1) a small amount of barium was batched as barium sulphate (Acros Organics, extra pure) to act as a refining agent [2]; these glasses had to be fritted and remelted to produce a fully homogeneous melt. The glasses were melted in platinum crucibles in an electric furnace at 1450 °C for five hours, with one hour to achieve a batch free melt and four hours stirring with a platinum stirrer to homogenise the melt. The glasses were poured into a preheated steel mould to produce glass bars which were immediately placed into an electric annealing furnace for 1 h and then cooled to room temperature at 2 °C min⁻¹. [2].

The glass transition temperature, $T_{\rm g}$, of each composition was determined using differential scanning calorimetry (DSC7, Perkin-Elmer). Samples were heated in aluminum pans at 10 °C min⁻¹ and the onset of the first endothermic peak was used to estimate $T_{\rm g}$ (measurement error ± 2 °C). Density was measured by Archimedes principle using water as the immersion medium (measurement error ± 0.005 Mg m⁻³).

For mechanical testing the glass bars were sliced into $20 \times 20 \times 10$ mm samples using a water-cooled low-speed diamond saw. The edges of the samples were successively ground and polished using 400/800/1200 water-cooled SiC grits and 6/3/1/0.25 µm diamond pastes. All efforts were made to ensure that both edges were parallel to each other with deviation of less than 0.05 cm. After polishing, the samples were thoroughly rinsed in water, dried using a warm air blower and then re-annealed to remove any residual stresses introduced during cutting, grinding and polishing. For re-annealing the samples were heated to T_g at 2 °C min⁻¹, held at T_g for 1 h and then cooled at 1 °C min⁻¹ to room temperature. Absence of residual stresses was checked using a polariscope. Thereafter, one face of each sample was used for nanoindentation while another was used for microindentation. Surface roughnesses were assessed by tapping mode

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Table 1

Batched composition, physical and mechanical properties of the examined glasses.

Glass	Sample	Batch composition, mol%						$T_{\rm g}$	ρ	H _V	K _{Ic}	$E_{\rm r}'$
Series	number	SiO ₂	Na ₂ O	CaO	K ₂ O	MgO	BaO	°C	Mg/m ³	GPa	$MN m^{-3/2}$	GPa
NCMS	1	75	15	10		0		549	2.480	4.91 ± 0.06	0.72 ± 0.01	79 ± 5
	2	75	15	7.5		2.5		538	2.451	4.80 ± 0.07	0.74 ± 0.01	77 ± 3
	3	75	15	6.25		3.75		532	2.462	4.74 ± 0.06	0.76 ± 0.02	78 ± 2
	4	75	15	5		5		531	2.441	4.77 ± 0.04	0.77 ± 0.02	78 ± 3
	5	75	15	4.5		5.5		531	2.440	4.80 ± 0.02	0.79 ± 0.01	78 ± 2
	6	75	15	3.75		6.25		530	2.446	4.69 ± 0.03	0.86 ± 0.01	77 ± 3
	7	75	15	3		7		528	2.431	4.57 ± 0.07	0.90 ± 0.02	76 ± 4
	8	75	15	2.5		7.5		526	2.429	4.59 ± 0.07	0.93 ± 0.04	76 ± 3
	9	75	15	0		10		530	2.392	4.44 ± 0.08	1.07 ± 0.05	72 ± 4
KBMS	1	70			20	7.5	2.5	550	2.523	4.05 ± 0.06	1.03 ± 0.01	64 ± 4
	2	70			20	6.25	3.75	538	2.549	4.06 ± 0.06	1.02 ± 0.04	64 ± 2
	3	70			20	5	5	577	2.601	4.01 ± 0.05	0.91 ± 0.02	64 ± 2
	4	70			20	4.5	5.5	536	2.619	4.04 ± 0.05	0.80 ± 0.02	66 ± 2
	5	70			20	3.75	6.25	538	2.647	4.08 ± 0.04	0.78 ± 0.03	66 ± 3
	6	70			20	2.5	7.5	534	2.694	4.07 ± 0.02	0.76 ± 0.01	66 ± 2
	7	70			20	0	10	525	2.769	4.02 ± 0.07	0.64 ± 0.01	70 ± 2
KCMS	1	65		10	25	0		577	2.528	4.35 ± 0.02	0.64 ± 0.01	76 ± 5
	2	65		7.5	25	2.5		561	2.511	4.24 ± 0.06	0.66 ± 0.01	71 ± 7
	3	65		5.5	25	4.5		558	2.491	4.27 ± 0.01	0.72 ± 0.03	72 ± 5
	4	65		2.5	25	7.5		547	2.477	3.99 ± 0.02	0.82 ± 0.02	67 ± 9
NKCS65	1	65	0	15	20			539	2.544	4.81 ± 0.02	0.67 ± 0.01	76 ± 2
	2	65	4	15	16			576	2.559	5.10 ± 0.09	0.65 ± 0.01	80 ± 3
	3	65	8	15	12			557	2.565	5.35 ± 0.02	0.63 ± 0.01	84 ± 2
	4	65	10	15	10			545	2.568	5.39 ± 0.05	0.62 ± 0.01	85 ± 2
	5	65	12	15	8			539	2.565	5.40 ± 0.05	0.61 ± 0.01	85 ± 2
	6	65	16	15	4			543	2.571	5.38 ± 0.04	0.70 ± 0.01	87 ± 3
	7	65	20	15	0			556	2.583	5.25 ± 0.05	0.73 ± 0.01	87 ± 3
NKCS75	1	75	0	10	15			554	2.460	4.58 ± 0.02	0.75 ± 0.02	74 ± 2
	2	75	3	10	12			583	2.466	4.86 ± 0.03	0.69 ± 0.01	79 ± 2
	3	75	6	10	9			566	2.466	5.06 ± 0.02	0.69 ± 0.01	82 ± 2
	4	75	7.5	10	7.5			560	2.477	5.03 ± 0.08	0.68 ± 0.01	81 ± 3
	5	75	9	10	6			554	2.478	5.01 ± 0.06	0.61 ± 0.01	79 ± 2
	6	75	12	10	3			551	2.472	5.03 ± 0.02	0.59 ± 0.01	82 ± 2
	7	75	15	10	0			557	2.476	4.82 ± 0.04	0.64 ± 0.01	91 ± 2
NCS	1	70	15	15				590	2.592	5.63 ± 0.11	0.68 ± 0.03	81 ± 3
	2	66.7	25	8.3				523	2.531	4.90 ± 0.03	0.74 ± 0.02	81 ± 6
	3	66.7	16.7	16.7				599	2.581	5.52 ± 0.04	0.70 ± 0.03	97 + 6
NS		66.7	33.3					468	2.493	4.01 ± 0.07	0.97 ± 0.02	78 + 4
Error								±5	± 0.005			

atomic force microscopy (AFM, Veeco) on a $10 \times 10\,\mu m$ area and did not exceed 2 nm.

Nanoindentation measurements were made on a Hysitron Triboscope® nanoindenter (Hysitron Inc., Minneapolis, USA) mounted on a Dimension 3100 (Veeco Digital Instruments, Santa Barbara, CA, USA) nanoscope and equipped with a three-sided pyramidal (Berkovich) diamond tip (half-included angle of 70.3°). Before nanoindentation tests the as prepared samples were rinsed with absolute ethanol to remove any dirt. Nanoindentation data were collected at 24 ± 1 °C with a relative humidity of 60-80%, using an automated 8×8 array of indents (5 s loading, 5 s hold and 5 s unloading cycle) with 10 µm distance between indents on both x and y axes. Prior to the measurements, drift correction of the transducer was accomplished by running a 0.1 µN test with a 20 s hold at peak load and measuring displacement drift during this hold time. During such a test, the displacement was measured as a function of time and the remainder of the test was corrected by the measured drift rate (typical drift rate did not exceed 0.1 nm/s). A conventional Oliver and Pharr analysis of the nanoindentation data was used to obtain the reduced modulus, E_r ,

$$\frac{1}{E_{\rm r}} = \frac{1 - \nu_{\rm g}^2}{E_{\rm g}} + \frac{1 - \nu_{\rm i}^2}{E_{\rm i}} \tag{1}$$

where E_g , E_i and ν_g , ν_i and the Young's moduli and Poisson's ratios of the glass and the indenter respectively. For diamond $E_i = 1141$ GPa

and $v_i = 0.07$ hence the plane strain modulus of the glass, E'_{g} is given by

$$E'_{\rm g} = \frac{E_{\rm g}}{1 - \nu_{\rm g}^2} = 1 \left| \left(\frac{1}{E_{\rm r}} - 8.721 \times 10^{-4} \right) \right|$$
(2)

where both E_r and E_g are in GPa.

Microhardness, indentation fracture toughness and brittleness were measured using a Mitutoyo HM-101 microhardness indenter equipped with a Vickers indenter. Loads varying from 0.05 to 1 kg were used. Ten indents, of 15 s hold time, were made for each load. Vickers hardness, H_V , was calculated using

$$H_{\rm V} = \frac{1.8544P}{d^2} \tag{3}$$

where *P* is the applied load and *d* is the mean length of the two indent diagonals. After indentation, samples were stored in a desiccator for 24 h to allow relief of the residual stresses. The total length of the cracks, 2*c*, emanating from the corners of the indents was measured using an optical microscope (Polyvar), which was calibrated using a reference grid accurate to 0.2%. $K_{\rm lc}$ values were then calculated using the relationship given by Evans and Charles [3]

$$K_{\rm lc} = \frac{0.0824P}{c^{3/2}} \tag{4}$$

which has been shown to give results more consistent with conventional fracture toughness tests than other suggested relationships [4]. Brittleness values were calculated from the measured H_V and K_{Ic} values using

$$B = \frac{H_{\rm V}}{K_{\rm lc}} = \frac{22.505c^{3/2}}{d^2} \tag{5}$$

3. Results and discussion

Values of H_V and K_{Ic} measured by microindentation and E'_r measured by nanoindentation along with density and T_g values for all the glasses studied are given in Table 1.

Plots of hardness, toughness and plane strain modulus versus the potassia fraction of the total alkali oxide content for the two mixed alkali oxide NKCS glass series along with some literature hardness and toughness data for $20(Na_2O + K_2O)$ 10CaO 60SiO₂ glasses [5] for comparative purposes are given in Fig. 1. It can be seen that the hardness curves for all three glass series show a small maximum at an intermediate (mixed alkali) composition (Fig. 1a). Although related features are seen in the toughness and brittleness curves (Fig. 1b and c) the NKCS65 glasses give results that are closer to those for the 20 (Na₂O + K₂O) 10CaO 70SiO₂ glasses (labelled JGK data) than the NKCS75 glasses. The NKCS65 glasses and the 20(Na₂O + K₂O) 10CaO 60SiO₂ glasses have the same total alkali oxide contents although their silica and calcia contents are different; this may suggest that the total alkali oxide content is important in determining the exact behaviour

of hardness, toughness and brittleness as a function of composition in potassia–soda–calcia–silica glasses. Unlike the small maximum seen at intermediate compositions in the hardness curves the plane strain moduli for the NKCS glasses decrease with increasing potassia content (Fig. 1d; equivalent data for the $20(Na_2O + K_2O)$ 10CaO 60SiO₂ glasses is not given in Ref. [5]). The difference in behaviour between modulus and toughness is surprising in that one would expect hardness to also be affected by the increasing presence of a larger, softer ion, whereas it would appear that the packing of dissimilar alkalis has at least as great an effect on hardness for these glass compositions.

Plots of hardness, toughness and plane strain modulus versus the magnesia fraction of the total mixed alkaline earth oxide content for the three mixed alkaline earth oxide glass series (NCMS, KBMS and KCMS glasses) are given in Fig. 2. Electron probe microanalysis data were available for these glasses and thus the exact ratios along the horizontal axis differ from the batched values. All three glass series show similar behaviour with hardness, modulus and brittleness decreasing with increasing magnesia content whilst toughness increases with increasing magnesia content. The increase in toughness is most marked whilst the variation of the other properties with composition is smaller. Due to measurement errors it is difficult to assess whether there is a significant decrease in modulus with increasing magnesia, however it is clear that in these glass series replacing larger and presumably softer alkaline earth ions (calcium or barium) by smaller magnesium ions does not lead to an increase in modulus which is unlike the behaviour seen in the mixed alkali oxide glass series (see Fig. 1d). A decrease in modulus associated with an increase in fractional free volume and an associated decrease in density has been reported by Pedone et al. [6] in simulated



Fig. 1. Mechanical properties versus the potassia fraction of the total alkali oxide content for the mixed alkali oxide NKCS65 and NKCS75 glasses along with some data for 20(Na₂O + K₂O) 10CaO 60SiO₂ glasses (JGK data) [5]; a) microindentation hardness; b) indentation toughness; c) brittleness and d) plane strain modulus. Lines drawn as a guide for the eye.



Fig. 2. Mechanical properties versus the magnesia fraction of the total alkaline earth oxide content for the mixed alkaline earth oxide NCMS, KBMS and KCMS glasses; a) microindentation hardness; b) indentation toughness; c) brittleness and d) plane strain modulus. Lines drawn as a guide for the eye.

soda-calcia-magnesia-silica glasses; this change was attributed to magnesia tending to adopt a network former role whilst calcia is a network modifier.

The ranking of the hardness of the mixed alkaline earth oxide glass series generally follows NCMS>KCMS>KBMS. The differences in silica content between these glass series makes it difficult to be definitive as to the causes of this ranking order, however it is clear that the ranking order does not simply follow silica content as the glass series that contains two large ions (namely KBMS) has the lowest hardness despite having a greater silica content than the KCMS series. Meanwhile the ranking order for toughness implies that whilst glasses with larger ions may show greater resistance to fracture (KBMS>NCMS) silica content is also important as the glass series with the lowest silica content overall has the lowest resistance to fracture.

The trends seen in Figs. 1 and 2 indicate that the relationships between mechanical properties and composition are far from



Fig. 3. Brittleness versus density for the glasses studied here along with the data of Sehgal and Ito [7]. The dashed lines are the fits to the data given by Sehgal and Ito [7].



Fig. 4. Mechanical properties versus the molar ratio of (calcia + baria) to silica for all of the glasses considered here; a) microindentation hardness; b) indentation toughness; c) brittleness and d) plane strain modulus.

straightforward. However in trying to identify glasses with improved mechanical properties it is clearly desirable to identify some general trends. Sehgal and Ito suggested that brittleness scales with density [7] and thus Fig. 3 shows the glasses from the current study along with the data of Sehgal and Ito. Although some similarity in trend is seen it is clear that the data obtained in the current work do not follow exactly the same pattern as that seen by Sehgal and Ito although there is a general tendency within any particular glass series for brittleness to increase with density. However the brittleness of the KBMS glasses is much lower than their density would suggest if the trend seen by Sehgal and Ito is of universal applicability, although other work [8] shows that the durability of these glasses is relatively low and thus they would not be ideal for most applications.

There is some evidence that the network forming alkaline earth oxides calcia and baria affect the overall properties. Fig. 4 shows the mechanical property data for all the glasses considered in this study plotted versus the molar ratio of (calcia + baria) to silica. The toughness data show a clear trend whereby for all data series the fracture toughness falls onto one curve showing decreasing toughness with increasing (calcia + baria)/silica molar ratio up to a value of about 0.15. Above this the fracture toughness shows little variation with increasing (calcia + baria)/silica molar ratio (Fig. 4b). There is some evidence of a related trend in brittleness (Fig. 4c) although the agreement between different glass series is less marked whereas the same level of data reduction is not seen with hardness and modulus (Fig. 4a and d). It would therefore seem that increased fracture toughness is favoured by the absence of larger, more immobile alkaline earth ions. This may be because immobile species make it more difficult to form a "plastic" zone around the crack tip (such a zone must be present even in highly brittle materials as otherwise the stresses would be infinite at the crack tip). The size of such a zone is linked with the ease of atomic rearrangement, and as pointed out by an anonymous referee of this paper, in glasses involving modifiers this would easier if mobile species enable bridging and non-bridging oxygen bonds to be more readily exchanged. It is also worth noting that one of us (RJH) has previously suggested that diffusional ion exchange processes involve mobile alkali ions may also be implicated in defect formation in glasses [9]. This would seem to be an area



Fig. 5. Indentation fracture toughness versus plane strain modulus for all the glass series studied.



Fig. 6. Hardness versus plane strain fracture toughness a) current work - all glass series and b) data taken from SciGlass Version 5.0 [14].

worthy of further study and some interesting insight into the importance of mobile species on mechanical properties could potentially be gained by studying lithia containing glasses.

Alternatively various papers have implied that increasing the modulus of glasses is desirable in that it will enable lead to weight reduction because thinner sections will be required for a given stiffness (see, for example [10,11]). However glass strength also has to be a concern and Makashima and Mackenzie [12] suggest that high modulus glasses will give high strength fibres. Unfortunately because strength depends on flaw size it is specimen/component property and the well known fracture mechanics relationship

$$K_{\rm lc} = C\sigma_f \sqrt{\pi a} \tag{6}$$

where C is a geometric constant indicates that for a given flaw size, a, a higher fracture toughness will result in a higher fracture strength, $\sigma_{\rm f}$. In addition the conventional fracture mechanics rationalisation of the models of Griffith and Irwin states that

$$K_{\rm lc} = \sqrt{2E_g' \gamma_e} \tag{7}$$

where γ is the elastic surface energy (see, for example, [13]). However it is clear from Fig. 5 that for the glasses studied here the fracture toughness tends to decrease as the square root of the plane strain modulus increases. From other perspectives this result is not surprising in that increasing hardness usually correlates with increasing modulus as shown in Fig. 6 for both the glasses studied here and data taken from the SciGlass database [14]; it is well known that harder materials tend to be more brittle i.e. they tend to have lower fracture toughness values. Thus increasing modulus may desirable from one perspective but disadvantageous from others.

It is worthy of note that for ductile materials with much higher fracture toughnesses the surface energy term in Eq. (7) is modified by the inclusion of a plastic energy term, γ_{p} , so that we have

$$K_{\rm lc} = \sqrt{2E' (\gamma_e + \gamma_p)}.$$
(8)

It is this possibility of plastic deformation that is responsible for the high fracture toughness of metals; if this energy absorption mechanism did not exist then the toughness of metals would not be so different from that of brittle materials such as glasses. Therefore to reduce the flaw sensitivity of glasses we actually need to find ways of increasing the energy absorption of glasses prior to failure and the relatively small changes in moduli, hardness and toughness with composition seen here and elsewhere, although interesting, are of limited value in obtaining consistently stronger bulk glass although, as discussed above, some benefit in toughness may possibly be gained by ensuring modifier species present are relatively mobile (this may, of course, have a detrimental effect on other properties such as chemical durability).

4. Conclusions

Mechanical properties as a function of composition have been studied for 38 silicate glasses. For the two mixed alkali glasses studied hardness goes through a maximum at an intermediate (mixed alkali composition) whilst toughness goes through a minimum and plane strain modulus simply decreases with increasing potassia content. All three of the mixed alkaline earth glass series studied show similar behaviour with hardness, modulus and brittleness decreasing with increasing magnesia content whilst toughness increases with increasing magnesia content. There is also some evidence that the presence of relatively immobile alkaline earth species, up to a molar ratio compared to silica of 0.15 leads to a reduction in fracture toughness. Although these trends within series could not be simply correlated to other structural parameters they do suggest that the relative mobility of network modifiers may have some effect on the mechanical properties of glasses and this area is worthy of further study. The results also highlight the fact that increasing the modulus results in lower fracture toughness; thus an increase in glass stiffness may well result in a reduction in glass strength as the flaw sensitivity will be increased. To reduce the flaw sensitivity of glasses the energy absorption of glasses prior to failure needs to be increased and the relatively small changes in moduli, hardness and toughness with composition seen here and elsewhere, although interesting, are therefore of limited value in obtaining consistently stronger bulk glass.

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