

Properties of $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glasses impregnated with ethyl alcohol

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$\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glasses impregnated with up to 8.5 wt % ethanol were prepared under high pressure and hydrothermal conditions and their properties such as hardness, fracture toughness and density were measured. Both hardness and density increased initially with increasing ethanol content up to 1~2 wt % ethanol and then decreased with further increase in ethanol content, while fracture toughness decreased monotonically. This initial increase of hardness and density of ethanol-impregnated glasses is in contrast to the behaviour of glasses with high water content, which showed a steadily decreasing hardness and density with increasing water content. A structural study using IR and X-ray diffraction analyses was also made and changes in properties of glasses with increasing ethanol was related to the formation of Si—O—C bonds and the precipitation of sodium carbonate crystal.

1. Introduction

It is well known that alcohol and water in atmosphere have different influences on the mechanical properties of glasses. For example, Westwood *et al.* [1] reported that the hardness and drilling behaviour of a soda-lime glass are influenced differently by different chemical environments such as alcohols and water. R. E. Cuthrell [2] also measured the drilling rate of a borosilicate glass and found that the drilling rate was associated with the zero-zeta potential of the liquid environments. In general, glasses appear to become more brittle in alcohol environment. On the other hand, water in atmosphere is known to increase crack velocity [3], reduce strength [4] and the surface viscosity [5].

Recently, various properties of glasses with high water content [6-9] were measured. Results appear to be consistent with the effect of water in atmosphere, for example, water in glass reduces mechanical strength and viscosity (or glass transition temperature). It is expected from these observations that alcohol in glass might have similar effects to those of alcohol in atmosphere on the mechanical properties of glasses.

Recently there has been an increasing amount

of activity on alkoxide derived glasses. The alkoxide derived gel is extremely fragile and often the direct formation of a monolithic glass from the gel is difficult. Furthermore, glasses prepared by melting alkoxide-derived gel appear to be more brittle compared with the conventional glasses. These features may be attributed to the remaining alcohol in glass.

Under these circumstances, it would be useful to learn about the effect of alcohol in glasses on the mechanical properties of glasses.

Thus in this paper, ethanol-impregnated glasses were prepared under hydrothermal conditions [6] and some of their properties were investigated in order to clarify the effect of alcohol on the properties of the glasses. Specifically, hardness, fracture toughness and density of these glasses were measured and compared with those of glasses containing water.

2. Experimental procedures

$\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glass was prepared by melting reagent-grade SiO_2 and Na_2CO_3 powders in a platinum crucible in an electric furnace at 1400°C for 3 h. Impregnation of ethanol into the glass was

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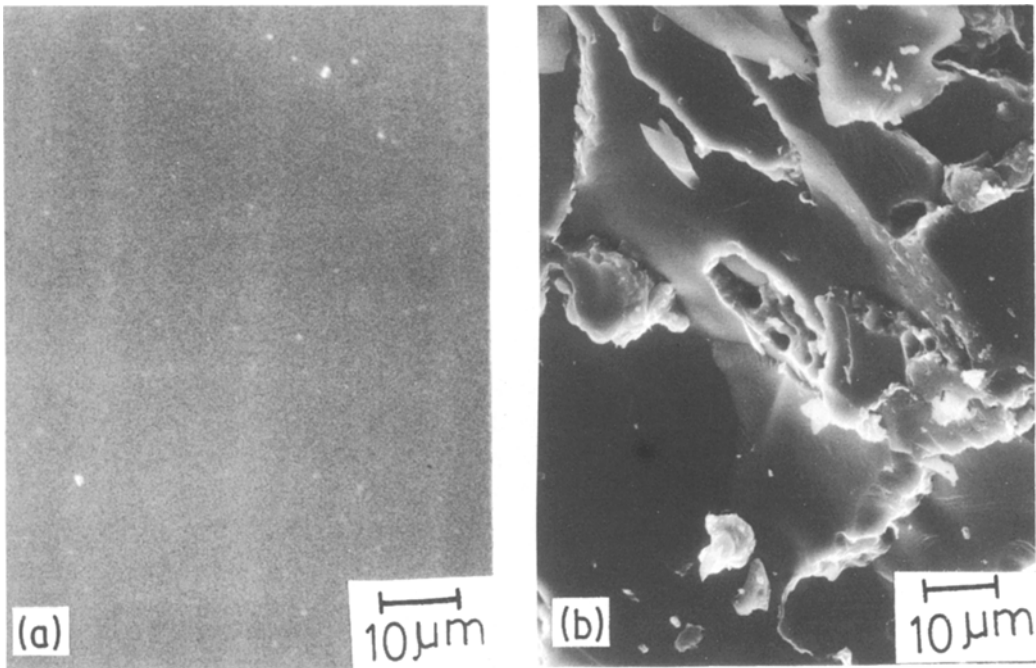


Figure 1 Scanning electron micrographs of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glasses containing 0.56 wt % (a) and 8.55 wt % (b) ethanol.

carried out by the hydrothermal pressure method, which was also used by Takata *et al.* [6] to prepare glasses with high water content. The $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glass was ground to a coarse powder and loaded into thin-walled platinum tubes (5 mm diameter and 3 cm long). The desired amount of dehydrolysed pure ethanol (US Industrial Chemical Co.) was added to the tubes with a microsyringe. After being sealed by welding in a carbon arc, the welded platinum tubes were placed in cold-seal pressure vessels, in which the tubes were pressurized and heated simultaneously to about 1 kbar (10^8 Nm^{-2}) and 900°C . These conditions were maintained for about 7 h. Subsequently, the vessels were quickly cooled by blowing air until the temperature reached 400°C ; then the vessels were immersed in water while the samples were still under pressure. After depressurizing and opening the platinum tubes, glass rods were obtained. The glasses were cut using a diamond saw and were polished using diamond paste. The hardness testing was performed on both the ethanol-impregnated glasses and the water-containing glasses by using a Vickers diamond pyramid with a microhardness tester manufactured by Akashi Co. The indentations were made at room temperature in air. The Vickers diamond pyramid indenter was brought into contact with

the glass surface under a load of 200 g for 15 sec. The hardness number was determined by measuring the length of at least 10 separate crack-free indentations on each specimen surface.

Indentation fracture tests were also performed to estimate the fracture toughness of the glasses. An indenter load of 1 kg was used for the ethanol-impregnated glasses and of 1.5 kg for the ethanol-free glass which was difficult to fracture. The surface cracks extending from the impression corners were measured approximately 30 min after the load was removed.

The density was measured by Archimedes method using ethanol. Infrared (IR) spectra were measured by the KBr pellet method using a Perkin-Elmer 298 infrared spectrometer. Powder X-ray diffraction measurements were also conducted using a General Electric XRD-5 X-ray diffraction unit. The fractured surface of the samples was observed with the use of an AMR Model 1000 scanning electron microscope.

3. Results and discussion

The glasses obtained gave the characteristic appearance of glass although their colour was black. However, the glasses with high ethanol content, such as 8.55 wt %, did not show the shell-like fractured surface. In Fig. 1 scanning electron micro-

TABLE I Amount of ethanol added and weight loss on heating at 550° C for 30 min

Added ethanol (wt %)	Measured weight loss (wt %)
0.56	0.25
2.36	1.65
4.13	2.97
5.46	4.07
8.55	5.32

graphs of the fractured surface are shown for glasses containing 0.56 and 8.55 wt % ethanol, respectively. It is observed that the glass containing 0.56 wt % ethanol consists of the homogeneous single phase (Fig. 1a), whereas the glass containing 8.55 wt % ethanol consists of heterogeneous phases (Fig. 1b).

The weight loss of glasses after heating at 550° C for 30 min is shown in Table I along with the ethanol contents calculated from the quantity of ethanol sealed in the platinum tube. It is seen that in ethanol-impregnated glasses approximately one-third of the weight of ethanol added remained after heating at 550° C. This behaviour is markedly different from the water-containing glasses in which water is completely evaporated at 550° C. On heating at higher temperatures, a further weight loss of ethanol-impregnated samples took place, gradually accompanied by the change of the specimen colour to grey or white. These phenomena suggest that ethanol reacted with glasses under hydrothermal conditions to result in the formation of new chemical bonds, although a part of ethanol might have been burnt to carbon.

The Vickers hardness of ethanol-impregnated glasses is shown in Fig. 2 together with the Vickers hardness of glasses containing water. In the glasses containing water, the Vickers hardness decreased monotonically with increasing water content. These results are consistent with the Knoop hardness measured by Takata *et al.* [7], who explained that the dissolved water produces a looser silica network structure which in turn gives a decrease in hardness.

On the other hand, in the ethanol-impregnated glasses the change of hardness with ethanol content is markedly different from that of water-containing glasses. Hardness increases initially with increasing ethanol content to a maximum at 1~2 wt % ethanol and decreases with further increase in ethanol content. The hardness of glasses containing more than about 5 wt % ethanol is lower than that of original dry glass.

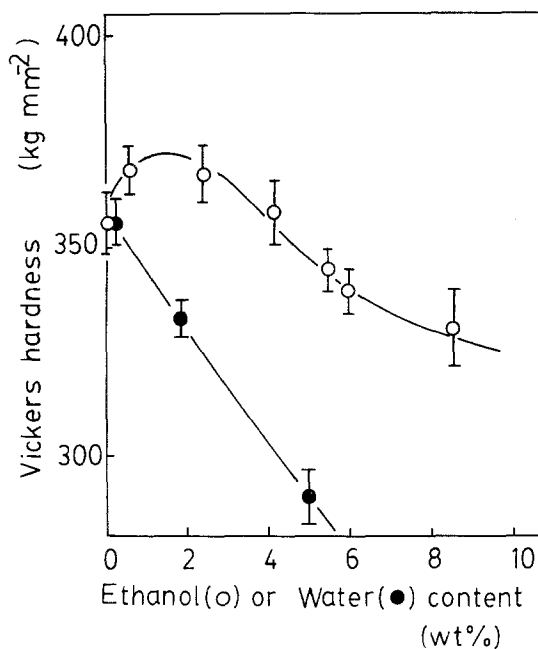


Figure 2 Vickers hardness of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glasses as a function of ethanol or water content. Error bars indicate \pm one standard deviation.

It is known that Vickers indentation testing can also be used to characterize the fracture behaviour of glasses [10–13]. The fracture toughness (K_c) of glasses is related to both the extent of surface traces (C) of well-developed cracks growing from the corners of the Vickers indentation and applied load (P) by the following formula: $KK_c = P/C^{3/2}\pi^{3/2} \tan \psi$, where ψ is the half-angle of the indenter, i.e. 68° and K is an empirical constant. Fig. 3 shows $P/C^{3/2}\pi^{3/2} \tan \psi$ values, which are proportional to the fracture toughness

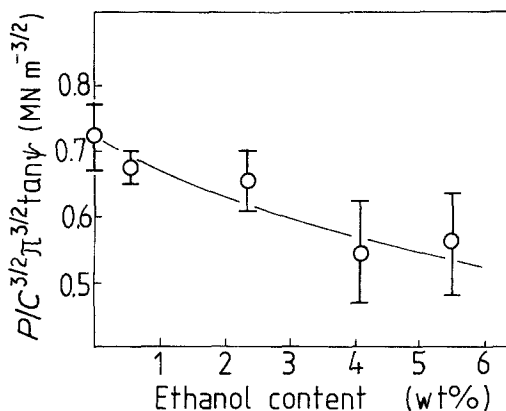


Figure 3 Plot of fracture toughness ($P/C^{3/2}\pi^{3/2} \tan \psi$) of $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glasses against ethanol content. Error bars indicate \pm one standard deviation.

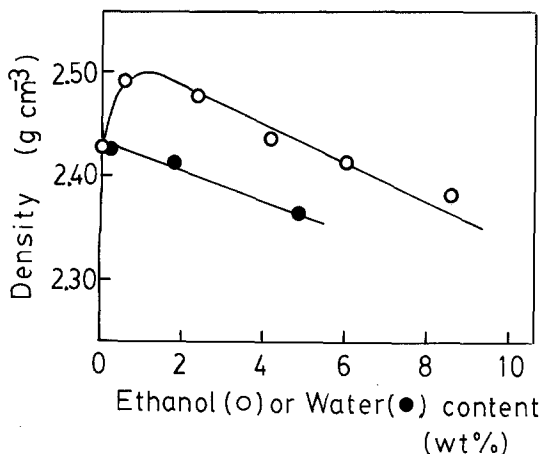


Figure 4 Density of $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glasses as a function of ethanol or water content.

as a function of the ethanol content. It can be seen that the fracture toughness decreases with increasing ethanol content.

In Fig. 4 the density is plotted as a function of ethanol content or water content in glass. The changes of density with the ethanol content and the water content appear quite similar to those of Vickers hardness. Ethanol and water show a decidedly different effect on the properties of glasses (cf. Figs. 2 and 4). Water in glasses with high water content was found to be in the form of molecular water as well as in the hydroxyl state connected to silicon. It was reported [7, 14, 15] that the concentration of molecular water increased continuously with increasing water content, which resulted in decreases in both hardness and density. On the other hand, ethanol is decomposed into methyl, carboxyl and hydroxyl groups by oxidation [16] and this reaction is considered to have taken place under high temperature and high pressure.

To examine the effect of ethanol on the glass structure, the IR spectra were measured, see Fig. 5. The bands around 1060 and 800 cm^{-1} are assigned to a stretching vibration of the Si—O—Si bond and bending modes of the O—Si—O bond, respectively [17]. In the IR spectra of ethanol-impregnated glasses a strong absorption peak at 960 cm^{-1} is seen. This band was observed even after heating at 550° C for 30 min. It is also reported that a Si—O bond combined with a strong polarizing cation such as Ti^{4+} [18] or B^{3+} ion [19] gives the absorption peak around 960 cm^{-1} . From these results, the absorption band observed at 960 cm^{-1} can be attributed to the Si—O stretching mode

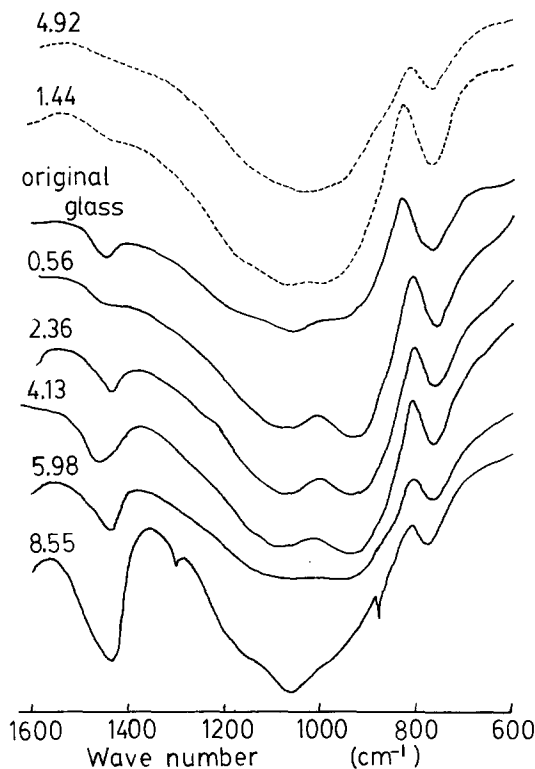


Figure 5 IR spectra of $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glasses containing ethanol (solid lines) or water (broken lines). Numbers indicate ethanol or water content (wt %).

bonded with carbon to form the Si—O—C group. Increase in hardness with increasing ethanol content is related to the intensity of the absorption band at 960 cm^{-1} . This suggests that the formation of the Si—O—C bond in the glass structure results in the increase in hardness. For ethanol contents greater than about 4 wt %, however, it is observed that both a decrease in intensity of the band at 960 cm^{-1} and an increase in that at 1440 cm^{-1} occur with increasing ethanol content. Furthermore, an additional sharp absorption band is seen at 880 cm^{-1} in the spectra of the sample containing 8.55 wt % ethanol. The absorption bands at 1440 and 880 cm^{-1} which are associated with the C=O bond [20] indicate the precipitation of carbonate in glass.

Fig. 6 shows the X-ray diffraction patterns of the powdered specimens. Patterns of glasses containing small amounts of ethanol are completely amorphous. However, in the glasses containing a large amount of ethanol, a crystalline phase appears which can be identified as sodium carbonate. Thus both IR spectroanalysis and X-ray diffraction analysis indicate the presence of

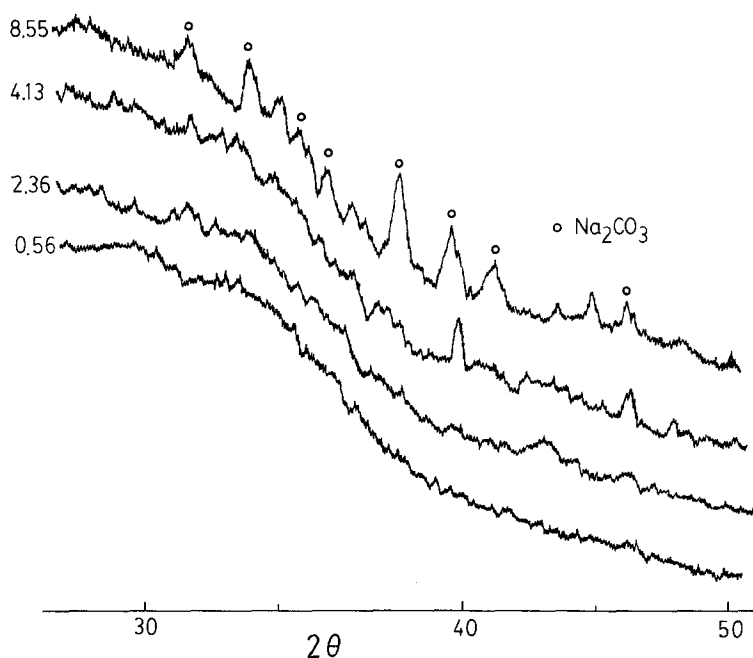


Figure 6 Powder X-ray diffraction patterns of ethanol-impregnated $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ glasses. Numbers indicate ethanol content (wt %).

sodium carbonate in glasses impregnated with a high concentration of ethanol.

The sodium carbonate can be formed on the surface of a glass [21] with poor chemical durability. And it might be suggested that the present observation of the sodium carbonate is also due to the glass-atmosphere water reaction. The fact that the sodium carbonate observed here is not the result of the glass surface-water reaction but exists in the bulk of the present glasses was confirmed by observing the similar X-ray diffraction patterns obtained using a bulk specimen containing 8.55 wt % ethanol. It appears that the precipitation of sodium carbonate crystal having low hardness causes the reduction in overall hardness of the sample at higher ethanol content glasses.

4. Conclusion

The glasses became more brittle when impregnated with ethanol. This was consistent with the behaviour of glasses in atmosphere containing alcohol and in contrast to the behaviour of glasses containing water.

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