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Brittleness of glass

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Abstract

A study seeking to decrease the brittleness of glasses was carried out. The brittleness, defined as the ratio of hardness to fracture toughness, was estimated from the ratio of median crack length to the diagonal length of a deformation impression. The brittleness of various kinds of glasses in the silicate as well as borosilicate systems was investigated as a function of glass properties. The brittleness of the glasses was correlated with densities, i.e., a variation of ~1 to ~9 $\mu m^{-1/2}$ in brittleness was observed as the density varied from ~1.9 to ~2.8 g/cm^3. The brittleness of normal glasses decreased with decreasing density due to the ease of both plastic flow and densification. On the other hand, the brittleness of anomalous glasses increased with decreasing density due to the lack of plastic flow. In addition, the brittleness of normal glasses was less than that of the anomalous glasses with the same density. We also observed that a 50% decrease in brittleness resulted in an increase of crack initiation load by ~15 times.

1. Introduction

Recently, the demand for light-weight glasses [1] has been increasing for many applications such as architectural, automobile, bottle, display. Such glasses are, typically, obtained by decreasing the thickness of glass. The mechanical failure of these thin glasses is a problem in applications. Failure results from crack initiation at the glass surface and subsequent crack propagation [2]. There is, therefore, a need to improve the resistance against crack initiation.

We assume that the crack initiation of materials, especially glasses, is related to their brittleness. Hence, the catastrophic mechanical failure of glasses is attributed, in part, to its brittleness. Of course, the crack propagation cannot be ignored, but it is the crack initiation (brittleness) which triggers the reduction of strength of glass by a few orders of magnitude when compared to their theoretical strength [2].

Efforts to estimate brittleness of materials are not new. A recent report by Quinn and Quinn [3] contains some information on the previous work on the brittleness of glass. Puttick [4] considered that energy scaling, size effects are important for ductile–brittle transitions. However, a more convenient method to compare brittleness was proposed by Lawn and Marshall [5] to be the ratio of hardness to toughness (H/K_C). However, since then there have been no reports concerning the brittleness of glass as far as we are aware. Recently we [6] showed that appropriate and relatively small change of the ratio of the constituents of the soda-lime-silica glass, without changing the type of the constituents, can decrease brittleness by ~30% and increase the crack initiation load by almost a 10-fold.

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In this present work we examine: (1) a possibility of further decreasing the brittleness of glasses and (2) the effect of glass properties on the brittleness. Furthermore, to show the importance of brittleness, we study the relationship between brittleness and crack initiation loads.

2. Experimental

To understand the effect of properties on brittleness, various kinds of glasses mainly in the (Li, Na, K)$_2$O–(Mg, Ca)O–Al_2O_3–B_2O_3–SiO_2 system were studied. The glass batches were prepared by using reagent grade chemicals to obtain 500 g of glass. After weighing, the batches were continuously mixed in a mortar and pestle for 20 min. The glass batches were melted in Pt–5% Rh crucibles between 1500 and 1650°C for 1 h for initial reaction of the ingredients. The liquids were then stirred for 2 h for homogenization using a Pt–5% Rh stirrer. After the stirrer was removed, the liquids were kept in the furnace for another 1 h for refining before pouring. The liquids were poured onto a heated carbon plate to reduce breakage from thermal shock. Differential thermal analysis was performed to determine the glass transition temperatures (T_g) using a heating rate of 10°C/min. The glasses were cut, ground and polished to obtain samples of 50 mm × 50 mm × 2 mm size. The polishing was of optical lens grade quality with roughness less than 1 nm. The samples so obtained were annealed at T_g + 10°C for 1 h and then cooled to room temperature, at a cooling rate of 1°C/min.

Vickers indentations were then performed on most of the glass samples at 49 N in flowing N_2 gas to obtain median cracking in the glass samples. However, for some glasses with smaller brittleness, a 98 N load was used for indentations. From the indentation patterns, crack size, C, and contact diagonal size, a, were measured and brittleness, B (H/K_c), was estimated using Eq. (1) derived by us [6,7] from the original Lawn–Marshall formulation [5]

$$B = \gamma P^{-1/4}\left[\frac{C}{a}\right]^{3/2}. \tag{1}$$

In this equation B is brittleness in $\mu m^{-1/2}$, P is the indentation load (N) for median cracking and $\gamma = 2.39\ N^{1/4}/\mu m^{1/2}$. Other details of the measurement procedures are described in Refs. [6,7].

Crack initiation tests were performed using the same Vickers indenter [8]. The load was varied to obtain an increasing number of cracks around the indent. The crack initiation load was taken as the load at which the average number of cracks around the four corners of the indents was two. The hardness of the glasses was measured from the Vickers impressions. The loading time was 15 s and the load (100–300 g) employed for determination of Vickers hardness was less than the load at which the glasses exhibited cracking. Fracture toughness of glasses was determined by an indentation method [9] based, primarily, on the original Anstis et al. [10] formulation. Densities of the glass samples were measured using Archimedes' principle using distilled water. An optical microscope was used to obtain the micrographs of the indents to study the mode of deformation in glass below the indenter. The micrographs of the face of the indent with or without the shear lines are indicative of plastic flow or densification mode of deformation, respectively [11–14].

3. Results

The composition, brittleness, density, glass transition temperature, Vickers hardness and fracture toughness data for our samples (labeled No. 1–24) and B_2O_3-rich glass (No. 25), and 100% B_2O_3-glass taken from literature [15–17] (No. 26) are listed in Table 1, which also includes the data for some commercial glasses, e.g., soda-lime–silica (No. 27), borosilicate (Tempax [1])(No. 28), alkali alkaline earth silicate (TV-panel) (No. 29), and silica glass (No. 30) [5]. From Table 1, it can be observed that the minimum brittleness in the silicate glasses is around 4.7 $\mu m^{-1/2}$, which is about 35% less than the brittleness of the commercial soda–lime–silica glass (No. 27).

[1] Schott Glass Works borosilicate glass – almost the same as Pyrex.

Table 1
Composition (mol%) and properties of glasses in the SiO_2-and B_2O_3-based glass systems [a]

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	76	78	78	78	78	67	80	78	80	75	78	81	75	80	75
Al_2O_3		2	1	2	2			2		1	2	1			
Li_2O	14					33	20						25		
Na_2O		15	7	15	13			15	15	8		6		10	20
K_2O	10		14		2					16	15	12			
CaO				1	1			3	5		5			10	5
MgO		5		4	4			3							
Brittleness ($\mu m^{-1/2}$)	4.7	4.8	4.9	5.0	5.1	5.3	5.5	5.7	5.8	5.8	5.9	5.9	6.0	6.1	6.1
Density (g/cm^3)	2.360	2.386	2.410	2.395	2.395	2.340	2.280	2.407	2.410	2.430	2.413	2.380	2.290	2.430	2.460
T_g (°C)	410	490	455	490	515	405	550	495	500	435	510	475	485	560	490
H_v (GPa)	4.4	4.5	3.5	4.7	4.7	4.8	5.1	5.2	5.1	4.0	5.3	4.2	5.2	5.8	4.9
K_c (MPa $m^{1/2}$)	0.94	0.93	0.73	0.93	0.92	0.91	0.88	0.92	0.90	0.70	0.90	0.71	0.86	0.92	0.83

	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
SiO_2	73	78	64	78	78	75	55	75	70	30		72	84	71	100
Al_2O_3	6	2	13	2	2		21			7		1	1	1	
Na_2O	16	5	17	15	10	15	18	10	20	5		12	4	9	
K_2O		10			5					5		1		6	
CaO	5	5	6	5	5	10	6	15	10			9		SrO: 6	
MgO												5		BaO: 4	
B_2O_3										53	100		11		
Others														3	
Brittleness ($\mu m^{-1/2}$)	6.2	6.3	6.3	6.3	6.4	6.5	6.6	6.7	7.0	3.9	1.2	7.1	8.4	8.7	9.0
Density (g/cm^3)	2.461	2.422	2.488	2.421	2.421	2.480	2.532	2.500	2.520	2.140	1.860	2.500	2.230	2.760	2.200
T_g (°C)	550	515	620	525	520	530	650	585	510	400		555	560	510	
H_v (GPa)	5.9	5.5	5.9	5.8	5.7	5.5	5.9	5.7	5.5	3.3	1.7	5.4	5.5	5.6	6.2
K_c (MPa $m^{1/2}$)	0.94	0.88	0.94	0.93	0.89	0.88	0.89	0.88	0.80	0.84	1.44*	0.76	0.65*	0.64	0.70*

[a] 1–24: (Li, Na, K)$_2$O–(Mg, Ca)O–Al_2O_3–SiO_2 glasses, 25: B_2O_3-rich glass, 26: 100% B_2O_3 glass [15], 27: Commercial soda–lime–silica glass, 28: Tempax, 29: TV-panel glass and 30: silica glass. Brittleness was measured by indentation method for all glasses except No. 26 [16,17], No. 28 (K_{IC} by Chevron-notch method), and No. 30 [5]. The brittleness values of the latter glasses were calculated from H_v and $*K_{IC}$. Error in brittleness by indentation was ±0.1 $\mu m^{-1/2}$, hardness was ±0.2 GPa and fracture toughness was ±0.03 MPa $m^{1/2}$. Error in density measurements was ±0.001 g/cm^3. Error in T_g measurements was ±5°C.

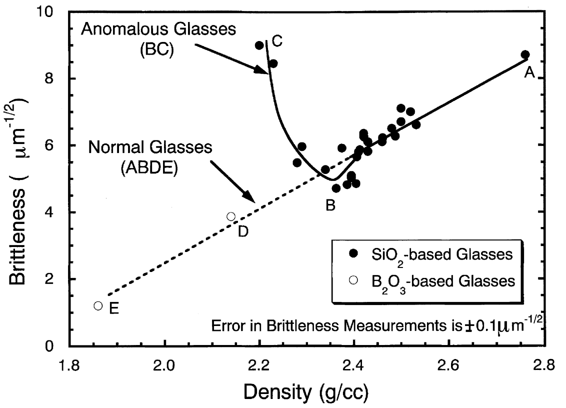

Fig. 1. Brittleness versus density for glasses in the SiO_2-and B_2O_3-based glasses.(ABC: SiO_2-based glasses, DE: B_2O_3-based glasses). Lines are drawn as guides for the eye.

The brittleness data listed in Table 1 were then plotted against density, as shown in Fig. 1. For simplicity, we define two types of glass systems, (1) SiO_2-based glasses, in which the main network former is silica, and (2) B_2O_3-based glasses, in which the main network former is B_2O_3. In Table 1, glasses Nos. 25 and 26 are B_2O_3-based glasses and the rest are SiO_2-based. In Fig. 1, in the region *ABC*, which comprises SiO_2-based glasses, there is a minimum in the brittleness versus density at around a density of 2.4 g/cm^3. The SiO_2-based glasses with densities approaching that of silica glass ($B \rightarrow C$) are considered to be anomalous glasses as reported by Kurkjian et al. [18] and evidently have larger brittlenesses. Therefore, these glasses deviate from the trend for the other compositions. We label these samples anomalous in Fig. 1. However, in the region *DE*, which comprises the B_2O_3-based normal glasses, the brittleness monotonically decreases with decreasing density. It, therefore, appears that the decrease in brittleness is linear with density for normal glasses (the region ABDE). Furthermore, the smallest brittleness for oxide glasses is, maybe, that for 100% B_2O_3 glass (No. 26). For this glass the reported density and brittleness are 1.86 g/cm^3 [15] and 1.20 μm$^{-1/2}$ (from hardness [16] and fracture toughness [17] data), respectively.

Fig. 2 shows the micrographs of the indents made at 9.8 N load on silica glass (No. 30) (anomalous), normal glasses Nos. 29, 5 and 25. The presence of shear lines, which are indicative of plastic flow, can be observed for the normal glasses, whereas silica glass (No. 30) does not have shear lines. The morphology that is obtained in the face of the indent is due to cracking, as observed by Kurkjian et al. [14].

It was also found as shown in Table 1 that near the minimum of brittleness (Fig. 1) in silica-based glasses, neglecting some scatter, hardness was less and fracture toughness was larger.

The crack initiation process was studied for six samples, i.e., samples Nos. 5, 6, 8, 22, 25 and 27. The results of the crack initiation load versus brittleness are plotted in Fig. 3. We assert that as the brittleness decreases the crack initiation load increases. From Fig. 3, we show that an almost 50% decrease of brittleness results in almost 15 times increase in crack initiation load.

4. Discussion

From Fig. 1, in the case of SiO_2-based glasses, the brittleness has a minimum between the density of 2.3 and 2.4 g/cm^3 for SiO_2-based glasses (ABC).

It was observed by Arora et al. [11], Hagan [12,13] and Kurkjian et al. [14] that normal and anomalous glasses had differing indent morphologies at room temperature. Normal soda–lime–silica glass showed shear lines due to plastic flow and the absence of shear lines in anomalous silica glass was due to the absence of plastic flow. Silica glass, therefore, showed deformation due to densification. However, the previous reports [11–14] did not explain the effect of modes of deformation on the brittleness of glass.

We believe that brittleness is dependent on densification and plastic flow modes of deformation before crack initiation. Fig. 1 also describes the effect of types of deformation on the brittleness of glasses. In an attempt to discuss the minimum in brittleness versus density, we consider three cases: (1) small density case (density < 2.4 g/cm^3) (2) large density case (density > 2.4 g/cm^3) and (3) intermediate case (density ~2.4 g/cm^3).

Small density case (*density < 2.4 g/cm^3*). As an example of small density case, we consider silica glass which has a density of about 2.2 g/cm^3. From

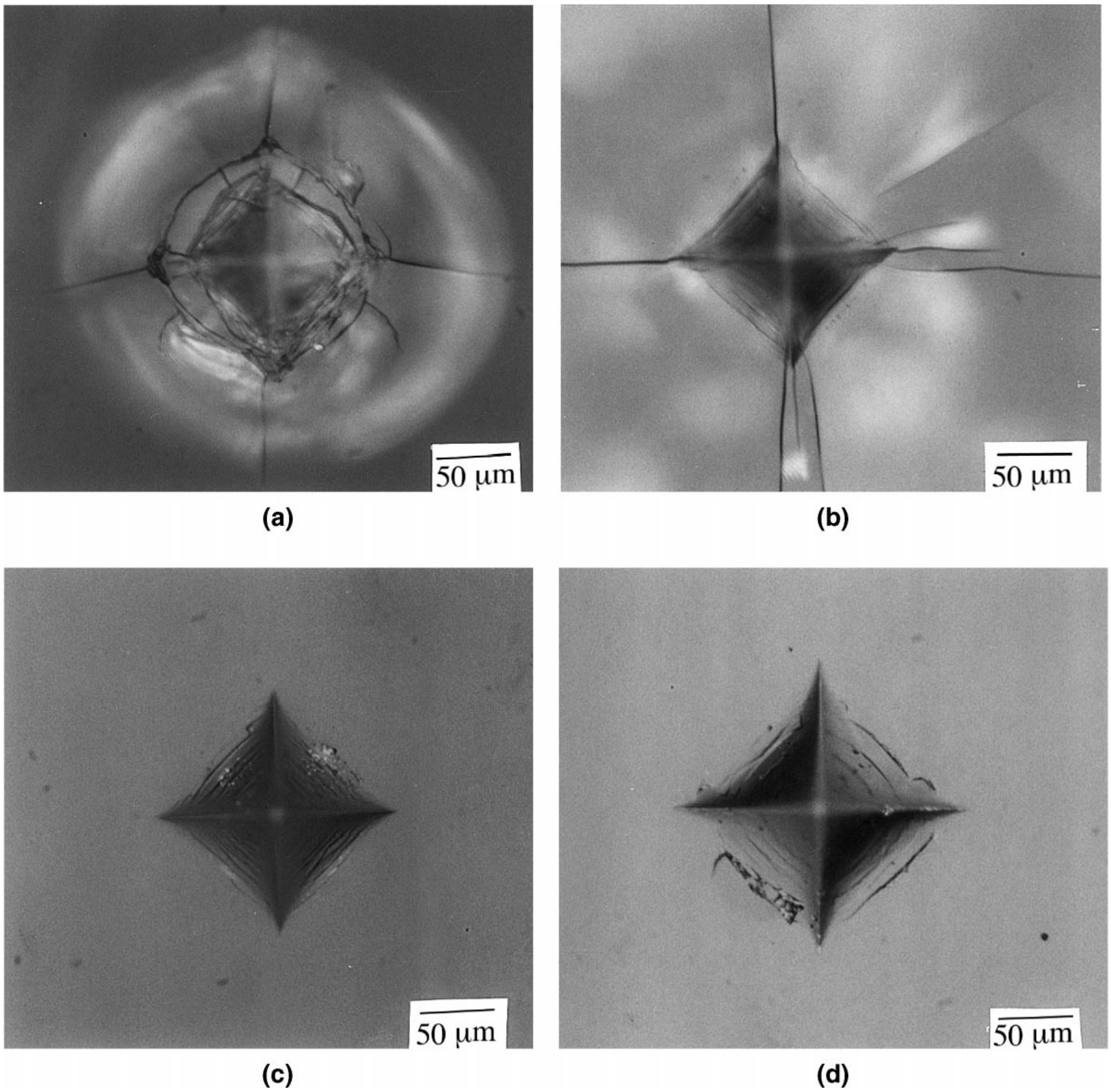

Fig. 2. Optical Micrographs of Glasses (a) No. 30, (b) No. 29, (c) No. 5 and (d) No. 25.

Fig. 2(a), as shown by Arora et al. [11], Hagan [12,13] and Kurkjian et al. [14], in our study we did not detect evidence of shear lines which are indicative of plastic flow. Hence, due to a lack of plastic flow the brittleness is large (9.0 $\mu m^{-1/2}$) when compared with the minimum of brittleness (4.7 $\mu m^{-1/2}$) from Fig. 1.

Large density case (*density* > *2.4 g/cm*^{3}). As an example of large density case, consider sample No. 29 which has a density of around 2.76 g/cm^3. Although, from Fig. 2(b), which shows the shear lines in the glass No. 29, plastic flow is possible, but, owing to its density, densification in this sample is difficult. Thus the brittleness is around 8.7 $\mu m^{-1/2}$ which is a larger brittleness than the minimum of brittleness (4.7 $\mu m^{-1/2}$).

Intermediate case (*density* ∼*2.4 g/cm*^{3}). As an example of intermediate density case, consider

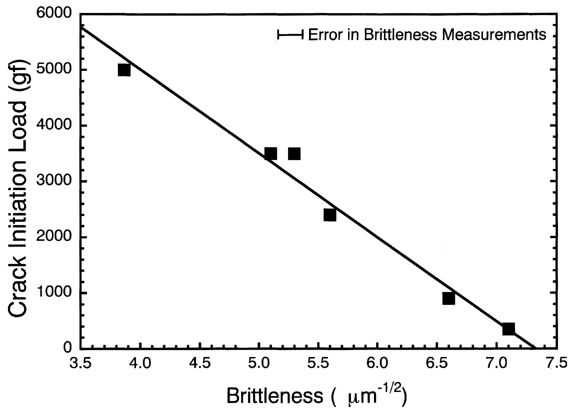

Fig. 3. Effect of brittleness on crack-initiation load. The load was varied in steps of 50, 100, 200, 300, 500, 1000, 2000, 5000 and 10 000 g loads. The line is drawn as a guide for the eye.

sample No. 5. The density of sample No. 5, which is near *B* of the curve *ABC* in Fig. 1, is between the densities of samples Nos. 29 and 30. Therefore, the more open structure (No. 5) may allow more densification as compared to sample No. 29 and the more modifiers in this structure (No. 5) will allow more plastic flow as compared with sample No. 30. For an evidence of the latter flow, refer to Fig. 2(c) for the evidence of extensive shear lines (plastic flow) in sample No. 5. Hence, we expect that the small brittleness of glasses of type No. 5, is due to both the ease of densification and plastic flow.

The ease of densification and plastic flow may result in a smaller observed hardness (larger deformation) near the minimum of brittleness as shown in Table 1. The ease of deformation near the minimum may help to release the strain energy under the indenter and result in an observed increase of fracture toughness (Table 1).

Until now we considered silica-based glasses and showed that the samples with density less than about 2.4 g/cm^3 have larger brittleness. However, there are some B_2O_3 containing glasses with larger B_2O_3 contents [19] and 100% B_2O_3 glass which have densities less than 2.2 g/cm^3 (density of silica glass), yet the brittleness of these glasses is extremely small as shown in Fig. 1. For example, the brittleness of 100% B_2O_3 sample is only about 1.2 μm$^{-1/2}$ [16,17]. We assume the reason for such brittleness is the network structure in 100% B_2O_3 glasses. It is well known [20] that B_2O_3 glasses have BO_3 triangles/boroxol group-like structure which can have slip [20] or these groups can move by sliding and hence cause plastic flow. Also, we can confirm such evidence of plastic flow from Fig. 2(d), the larger B_2O_3 content sample (No. 25) contained more shear lines as compared with other samples.

On the basis of these results, we conclude that the presence of densification and plastic deformation maybe important for reducing brittleness, for at least the SiO_2-based system, as shown in Fig. 1. We also conclude from Fig. 1 that the brittleness of all normal glasses decreased with decreasing density.

From Fig. 3, the glasses with smaller brittleness had larger crack initiation loads. A connection between crack initiation load and brittleness can be explained by the basic definition of these two terms. The study of crack initiation load involves the measurements of maximum load for deformation of a material before it fractures and brittleness [5] is a relative susceptibility of a material to two competing mechanical responses, deformation and fracture. Therefore, the measurement of crack initiation load, which involves a ductile–brittle transition from deformation without cracking at smaller loads to cracking at larger loads, is actually a manifestation of the competition of deformation and fracture, i.e., brittleness. Hence, we believe that a material with smaller brittleness will have a larger crack initiation load. On this basis, brittleness is a very important and practical mechanical parameter. We expect that such glasses with smaller brittleness or larger intrinsic scratch-resistance may have greater strength and longer life-times.

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