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Glass workability study and correlation of melting history, microstructure, apparent liquidus temperature, and mechanical strength

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The glass workability during the forming process has been discussed from the aspects of rheology, heat transfer, and microstructure. The rheological behaviour and heat-transfer characteristic of glass determine the workability of glass. However, the accidentally caused changes of glass structure during melting, fining and forming can affect the workability; therefore, the apparent liquidus temperature and crystal structure of bad workability glass have been studied and compared with the good workability glass. It is found that the apparent liquidus temperature study seems to be an effective method for determining the good and bad workability glasses. The results from the mechanical strengths study of the good workability glass shows evidence of microvoids of the order of 400 Å existing in the glass structure. However, there is no such evidence in the bad workability glass; therefore, it is believed that a large flaw size, or stress concentration around the inclusions existed in the bad workability glass.

1. Introduction

Glass workability is one of the most elusive terms used by glass technologists. Generally speaking, "bad workability" means that there is "something" about the glass that makes it difficult to form. Two of the most vital factors associated with glass workability are the rheological behaviour of glasses and the heat-transfer characteristic during the forming operations. Both subjects have been recently discussed [1, 2]. As is mentioned by Hsich [1, 2], in any glass forming process, characterization of the rheological behaviour of glass composition, determination of the forming machine, and an understanding of the heat transfer process are of primary importance to glass technologists. Usually, having carefully considered all three fundamental factors during glass forming, one would expect to have a good workability glass. However, some accidental causes of bad glass workability may occur in the batch house due to inadequate control of the composition of raw materials, in the glass tank due to inadequate melting and fining, and in the forehearth due to poor conditioning or undesired reboiling. The problem caused in the batch house is relatively easy to solve and prevent. The other problems caused in the glass tank or forehearth result from the improper control of heat transport, mass transport and chemical reactions.

The workability problems have been observed and discussed by Poole [3]. Although Poole has given many good observations and discussions on the glass workability problems, some of the bad workability mentioned by Poole might be caused by the limitation of keeping the same conditions of forming operations and/or heat and mass transports in glass tank and forehearth. For example, an increase in alumina and calcia or a decrease in baryta would increase the viscosity of glasses in the same temperature range; therefore without changing the forming condition (change of working temperature range or heat-transfer

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process during forming), workability problems would be created, such as causing the glass to check or split. Ryder [4] was able to eliminate these problems by adjusting the forming condition to compromise the difference in rheological behaviour due to changes in composition. He was also able to improve melting and fining by modifying the furnace design to give better heat and mass transport and thus improving the chemical reactions in the glass tank.

There are several bad workability problems which may occur in the glass melt between dissolution of glass melt and formation of glass gob. Some examples of these problems are associated with the microstructure of glass, such as melting remnants, composition cords, and seeds. These problems are caused by poor melting and fining associated with glass chemistry and/or inadequate control of heat and mass transport in the furnace. Ryder [4] has mentioned that a stress concentration is induced around the melting remnant during glass forming, which subsequently causes brittleness in glass.

Weyl and Marboe [5–7] have suggested that by producing local disorder through the formation of asymmetrical units can act as a "molecular stirrer" aiding diffusion for the improvement of glass fining and homogenizing. Their idea has been confirmed to be correct through the fact that multiple components of fining agent and/or glass composition, have a better fining and homogenizing character than the single component. The hypothesis of Weyl and Marboe is that the increase in entropy through complexity modifies all properties which involve deformation, flow, or the motion of molecules. This concept is also independently proposed by Hsich [8].

In Hsich's model, an irreversible thermodynamic fluctuation theory has been used to describe the creation of entropy through the fluctuation of the internal thermodynamic ordering parameter. Therefore, the mean square fluctuation of the ordering parameter can be used to explain the modified physical and flow properties of the glass due to the increase in entropy through complexity. Based on the concept of the frozen-in structure of the internal thermodynamic ordering parameters in a non-equilibrium system, Hsich [9, 10] is also able to explain the structural relaxation or stabilization process of the glass.

As mentioned above, bad workability might occur occasionally even with the same batch composition and the same forming conditions. Therefore, it is important to characterize a difference in rheology, microstructure, or mechanical strength between good and bad workability glasses. In the characterization of the rheological behaviour, one not only needs to measure the static properties such as viscosity, but also the dynamic properties, such as creep and stress relaxation. As for the microstructure study, there are several methods, which include SAXS, TEM, and Raman scattering, which can be used for the glass structure study. Unfortunately, all of the above methods are very time consuming, and the TEM method is also frequently subject to artefacts from the replication process. Therefore, when one studies the microstructure of glass by the TEM method, one should approach it with caution and scepticism. Since characterization of the microstructure is difficult, if not impossible, by conventional means, there is a need to develop a new method which can easily characterize the different microstructures of good and bad workability glasses. The new method is to study the kinetics of the apparent liquidus temperature of the glasses. The mechanical strength of glass is also studied to determine the sources of original weakness in the glass.

2. Effect of glass microstructure on apparent liquidus temperature

Weyl and Marboe [5–7] have mentioned that different microstructures in glass will have different entropies and/or internal energies and, therefore, have different Gibbs free energies. Consequently, the driving force of diffusion, nucleation and growth is also changed. Based on this concept, it is thought that the good and bad workability glasses will have different apparent liquidus temperatures at a particular heat-treatment history. In order to perform this investigation, a 10 in. long platinum boat loaded with glass chips was put into a thermal gradient furnace for various times. The boat was made of 80% platinum–20% rhodium and had a series of holes which served to hold the glass chips, which were later studied for their devitrification products under a microscope.

The samples prepared for the experiment were made of the same composition as Plant no. 2 glass. The composition of the samples was checked by X-ray fluorescence to make sure that all samples had the same composition; if the difference in composition between the laboratory-melted and Plant no. 2 glass was larger than the experimental error limit of the X-ray fluorescence, the samples were rejected from the study. The composition of the samples was:

Oxide (%)				
SiO_2	Na_2O	CaO	K_2O	Al_2O_3
71.8	13.5	10.2	0.22	1.3
Oxide (%)				
BaO	MgO	Fe_2O_3	TiO_2	SO_3
0.18	2.5	0.041	0.014	0.26

The melting histories of laboratory-melted glasses are shown below.

Melting temperature (° F)	Melting time (h)			
	1	2	4	6
2650	– –o– –	– –+– –	– –△– –	– –□– –
2750	—o—	—+—	—△—	—□—

The results are shown in Fig. 1 using the symbols given in the above table. The apparent liquidus temperature for the good workability glass from Plant no. 2 was about 1000° C (± 3° C for different samples), and it did not change after 2 h to 5 days of heat-treatment. However, for the laboratory melted glasses, the apparent liquidus temperature depends on the melting history. If the melting temperature is high enough and the melting time is sufficient, then the apparent liquidus temperature of the laboratory-melted glass is close to the good workability glass. However, it has been found that devitrification is enhanced for an insufficiently melted glass.

For example, as is shown in Fig. 1, samples melted at 2650° F had a high apparent liquidus temperature; a glass melted at this temperature or below should tend to be a bad workability glass because it is devitrified more easily. This is probably a result of the presence of melting remnants in the glass or due to incomplete dissolution of oxides [8]. The glass melted at 2750° F showed a low liquidus temperature, close to the good workability glass from Plant no. 2 except for the sample melted for 1 h.

The crystal structures were identified as wollastonite and tridymite. Occasionally, cristobalite and devitrite were also observed in the samples. As mentioned by Holland and Preston [10], for most commercial bottle glass compositions, the primary crystalline phase should be devitrite; however, devitrite is capable of decomposing to give wollastonite, which is why wollastonite was found as a primary crystalline phase in this study. Two different crystalline structures of silica were also found in this study. Although cristobalite is metastable below 1470° C in the bottle glass composition [12, 13], it may persist for long periods even below 1100° C. How-

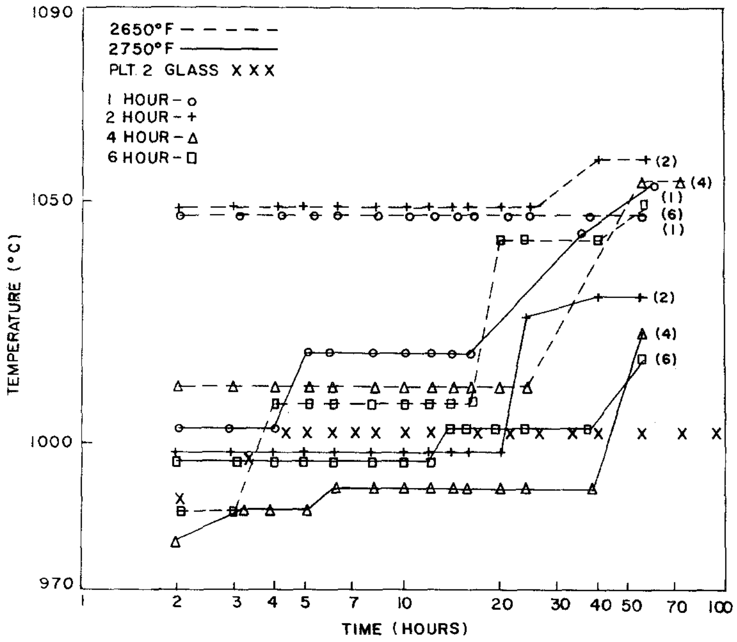

Figure 1 Apparent liquidus temperature versus heat-treatment time.

ever, the natural form of silica to be expected in this study would be tridymite.

The result of this study is as expected. When glasses are insufficiently melted, the melting remnants or inhomogeneity in the glass will change the Gibbs free energy; therefore, the driving force for the devitrification of glass is also changed by the accompanying changes of thermodynamic parameters and kinetics in the glass system. The insufficiently melted glass shows a larger devitrified temperature range and higher apparent liquidus temperature than the good workability glass. As one knows, a poorly designed glass tank and/or too high a glass pulling rate might create a bad workability glass due to a poorly melted glass caused by undesired heat and mass flow patterns in the glass tank [14, 15]. This study shows that poorly melted glass is not only easy to devitrify but also devitrifies at a high temperature range. Consequently, the stress concentration around the inclusion may embrittle the glass during formation.

3. Sources of original weakness of glass and evidence of microvoids in glass fibre

It is well known that the ultimate strength of a material should be about one-fifth of the Young's modulus. For a typical soda-lime–silica glass, the Young's modulus is about 10^7 psi*; therefore, its ultimate strength should be about 2×10^6 psi. However, the accepted safe-design strength for engineering purposes is far below this value, being of the order of 10^4 psi. The reduction of the mechanical strength in glass traditionally has been blamed on surface damage due to handling, chemical environment, weathering and ageing; for this reason, some of the data on the mechanical strength tests of glasses appearing in the literature might only present the high strength part of the data because the low values of the data have been neglected because of assumptions that the result is caused by bad samples. However, Ernsberger [16, 17] has shown complete data of a strength test from pristine samples, as indicated in Fig. 2. The data show a bimodal distribution, a low-strength peak around 10^5 psi and a high-strength peak near 3×10^5 psi.

The breaking stength of a good container glass under four-point testing is shown in Fig. 3. The samples were prepared by remelting bottle glass at 2650° F for $\frac{1}{2}$ h, and then transferring it to the fibre drawing furnace at 2050° F for 1 h before drawing. The diameter of fibre was 0.075 to 0.090 in. The pristine samples without HF treatment showed a bimodal strength distribution, similar to the results shown by Ernsberger [16, 17] with a low-strength peak around 10^5 psi and a a high-strength peak near 3×10^5 psi; and the low-strength peak is more dominant in the distribution. However, the samples with 2% HF treatment show a dominant peak near 3×10^5 psi. This is because the sharp tip of the flaws on the glass surface are rounded off by treatment in HF. Therefore, after samples have been treated in HF, the dominant strength peak should be around the value which is equivalent to the original flaw size of the glass. As from the results of this study, one can conclude that there are two types of flaws in the glass

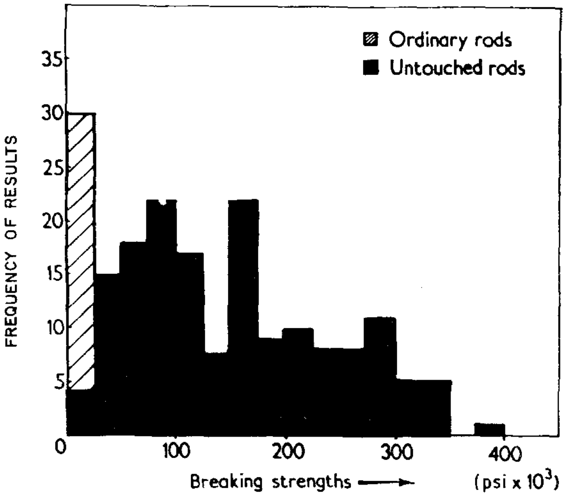

Figure 2 Comparison of the strength of "ordinary" and "untouched" 8 mm diameter rods (after Proctor [17]).

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*10^3 psi = 6.89 N mm^{-2}.

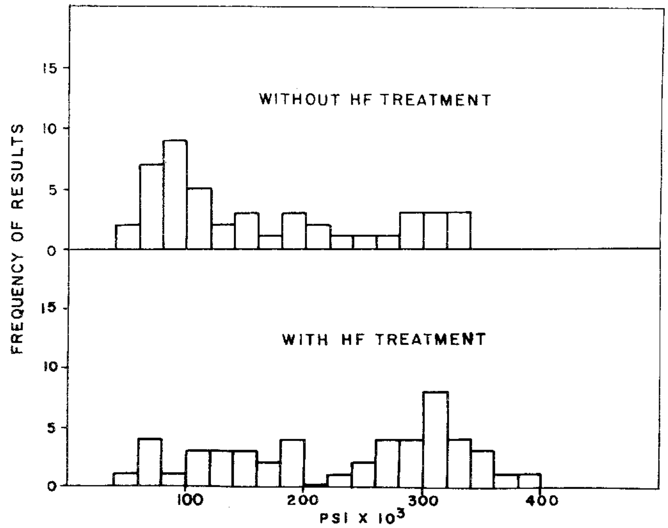

Figure 3 Comparison of the strength of container glass with and without HF treatment.

samples. One type of flaw is due to an accident, causing surface damage during the sample's preparation, such as happens during fibre drawing, sample handling, high humidity environment, etc. The other type of flaw is due to the intrinsic microvoids dispersed in the glass. The high-strength peak at a value near 3 x 10^5 psi presents a flaw size equivalent to intrinsic microvoids in the glass. From Griffith's law, the equation of fracture can be written as:

$$\sigma_f = \left(\frac{2\gamma E}{\pi a}\right) \qquad (1)$$

where σ_f is the critical fracture strength, γ is the fracture surface energy, E Young's modulus, and a is the half-length of the crack. Using the values from Wiederhorn [18] for the soda-lime–silica glass, $E = 7 \times 10^{11}$ dyn cm^{-2} = 10^7 psi, and $\gamma = 4 \times 10^3$ erg cm^{-2}. From Equation 1, to have a critical fracture strength near the value of 3 x 10^5 psi, the flaw size must be around 400 Å. This finding is coincidental with the results of the study of glassy polymers; by using SAXS experiments, Zborzhil *et al.* [19] also found that microvoids with sizes between 200 Å and 300 Å existed in the different glassy polymers.

The scattering intensity due to the submicrocracks from the SAXS experiment is written as [19]:

$$I(\theta) = AI_0 \frac{NV^2}{b} \exp\left[-\frac{\pi a^2 \theta^2}{3\lambda^2}\right] \qquad (2)$$

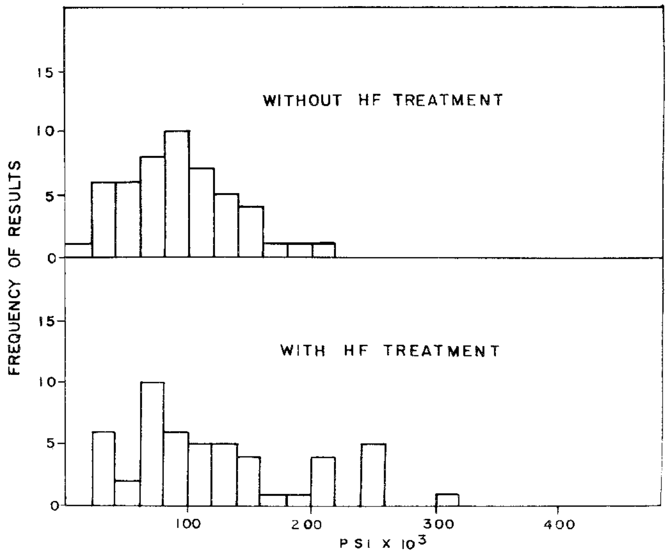

Figure 4 Mechanical strength of insufficiently melted glass.

where A is the instrument constant, I_0 is the intensity of the incident wave, a and b are the radii of major and minor axis of the crack, N is the crack concentration, V is the volume of sample crack, and λ is the wavelength of the incident wave. As can be seen from Equation 2, the SAXS method is more sensitive than the methods of acoustic wave or laser light scattering for detecting of submicrocracks because of the short wavelength of X-rays.

The results of the mechanical strength test from the insufficiently melted samples are shown in Fig. 4. The samples were prepared by melting a glass batch with the same composition as the container glass at 2650° F for 2 h, and then transferring it to the fibre drawing furnace at 2050° F for 1 h before drawing. The data show that the strength peak due to the intrinsic microvoids in glass is not well-developed. So the strength distribution of the sample with only 2 h melting time at 2650° F is much lower than the glass sample having sufficient melting time and a high enough melting temperature. This result is consistent with the results from the apparent liquidus temperature study. Because the container glass composition melts at 2650° F in less than 4 h, it has a tendency not to have a well-developed glass structure due to melting remnants and/or composition inhomogeniety (such as incomplete dissolution of mixed oxides [8]) in the glass. However, when the samples are prepared at a melting temperature of 2750° F over more than 4 h, the results of the breaking strength test are very similar to those from the good plant glass, as shown in Fig. 3.

4. Microstructure study by Raman scattering

The structure of the glass with various melting times and different sand size distributions was studied by Raman scattering experiments. Two kinds of glass batches were prepared for this study. One batch was prepared from the container glass composition with 50% −40/+ 50 mesh and 50% −30/+ 40 mesh of sand sizes; the other batch was prepared from 50% −40/+ 50 mesh and 50% −50/+ 60 mesh sand sizes. The samples were prepared in the optical grade glasses by bubbling nitrogen gas and by melting at 2750° F. The melting times for the samples in each batch were 45 min, 2 h, and 6 h. The Raman spectra of the small and large sand size glass samples are shown in Fig. 5 as (A) and (B) respectively.

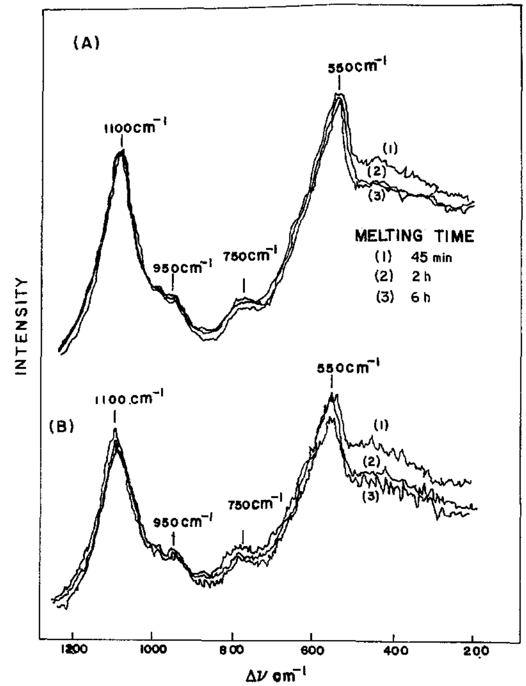

Figure 5 Raman spectra of soda-lime–silicate glasses with different melting times.

The spectra of all six samples show four typical Raman lines of soda-lime–silicate glass [20–22]. These four peaks of Raman lines are: 1100 cm^{-1} attributed to the bond-stretching vibration four-bridging oxygens of SiO_4; 555 cm^{-1} attributed to the bending vibration of the one non-bridging oxygen of SiO_4; 950 cm^{-1} attributed to the bond-stretching vibration of two non-bridging oxygens of SiO_4; and 775 cm^{-1} attributed to the subsidiary of four-bridging oxygens of SiO_4. However, in both batches, the spectra of the samples melted for only 45 min show a distinct difference from the spectra of the other samples with long melting times. The Raman intensities are greater in the spectra of those samples only melted for 45 min in the range 200 to 500 cm^{-1}. The extra intensity seems to result from the incomplete reactions of the step-dissolutions of the mixed oxides [8] and/or from the melting remnants. Therefore, this extra intensity seems to be attributable to the structure of a strong broad band at 440 cm^{-1} of vitreous silica [23, 24], or the low frequency peaks of metasilicate and disilicate [25]. It seems that there is no significant difference in the spectra between the samples of two different sand size distributions. Although a Raman hump around 440 cm^{-1} is clearly shown in both 45 min melted samples, further investigation is needed to determine whether this extra intensity is due to melting remnants or due to incomplete dissolution reaction of vitreous silica.

5. Conclusions

The correlations of melting history, microstructure, apparent liquidus temperature, and mechanical strength of glass are discussed in order to shed some light on glass workability. The study shows that a good workability glass has high breaking strength and a low and narrow range of apparent liquidus temperature. Bad workability or an insufficiently melted glass shows that the devitrification process has been enhanced by changing the entropy and/or internal energy of the glass system due to the inhomogeneity or inclusions in the glass. The evidence of inhomogeneity and/or inclusions in a bad workability glass has also been confirmed by a Raman scattering study in which an extra Raman band has been found. It is also concluded that there are two sources of original weakness in the glass: accidental surface damage and intrinsic microvoids. The size of the microvoids is of the order of 400 Å.

In conclusion, for studying glass workability, one must first characterize the rheological behaviour of the glass [1] and understand the heat-transfer characteristic during glass moulding [2]. Then, one also needs to know that having accidentally caused changes in the microstructure of glass during melting, fining and forming might affect the rheology, heat transfer, and mechanical strength of glass during forming. Therefore, the three most important behaviours of glass in studying good and bad workability glasses are as follows:

(1) rheological behaviour – although the rheological behaviour might be different between good and bad workability glasses, their static viscosities can be the same in some temperature ranges. Therefore, it is also important to study dynamic properties, such as dynamic viscosity, stress relaxation and structural relaxation;

(2) heat-transport characteristic – since the skin temperature of glass is of vital importance during glass formation, it is necessary to check the skin temperature of parison and the temperature profile of the blank mould when bad workability occurs during glass formation, as some of the workability problems might be caused by improper control of heat transfer during this process;

(3) microstructure – there are many methods, such as TEM, SAXS, and Raman scattering, which can be used for the study of glass microstructure. Unfortunately, as mentioned above, these experiments are very time consuming and costly; therefore, it is thought that studying the apparent liquidus temperature and crystal structure of glass through devitrification in a temperature gradient furnace, seems to be very useful for studying bad workability in glass.

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