

EFFECT OF DISSOLVED WATER ON PHYSICAL PROPERTIES OF SODA-LIME-SILICATE GLASSES

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ABSTRACT

Dissolved gases in glass melts are known to influence properties of the melts as well as the resulting glass and dissolved water is thought to be one of the most influential of all the dissolved gases. In this work, the effect of vacuum processing and the ensuing changes in dissolved water concentration on various physical properties of soda-lime-silica glasses were studied. Glass melts with varying dissolved water concentration were prepared by melting frit at atmospheric and sub-atmospheric (≈ 100 torr) pressures at 1450°C . The physical properties of these melts and the resulting glasses were determined by rotating spindle viscometry, beam bending viscometry, and spectroscopy. The densities of the glass samples were also determined. Results from these experiments are discussed in relation to prior work in the field and the implications of changes in properties on the glass making process are discussed.

INTRODUCTION

The presence of dissolved gases and their influence on properties of soda-lime-silica, as well as other silicate melts and glasses, is well known and characterized in detail [1–10]. A common route by which gases are introduced in glasses is through batch constituents, which may contain both physically adsorbed and chemically bonded gases. For example, both limestone (CaCO_3) and soda ash (Na_2CO_3), commonly used in the synthesis of soda-lime-silica glasses, release CO_2 during melting of the glass batch. Much of this gas escapes the melt in the form of bubbles during melting and fining, but some can remain dissolved in the melt. Depending on the raw materials used, many other gases can be present in a soda-lime-silica melt including H_2O , SO_2 , O_2 , NO , and NO_2 . These gases may also remain in the resulting solidified glass. When the glass melt is subject to sub-atmospheric pressure or vacuum, the dissolved gas concentration is expected to change. Consequently, the physical and chemical properties of glasses obtained from vacuum-processed melts can be expected to be different from corresponding glasses obtained from atmospheric or ambient melts. Variations in atmosphere surrounding the melt, particularly in the oxygen content, could also influence the properties of glasses from vacuum-processed melts.

Several earlier reports have discussed the influence of vacuum processing on the properties of silicate glasses. For instance, Fenstermacher et al. [2] measured the dissolved water concentration and viscosity of soda-lime silicate glasses obtained from glass batches melted at both ambient pressure and under vacuum. They found that the softening point of glass samples resulting from vacuum melting can be as much as 5°C higher than the glasses obtained from ambient melts and attributed this difference to the lower dissolved water content in the vacuum melt samples. Similarly, Graff and Badger [9] measured the viscosity of glasses (presumably soda-lime silicates) obtained from melts subject to vacuum, as well as those saturated with carbon dioxide and water, and found that, at a given temperature, the samples from vacuum

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melts generally had higher viscosities than those from saturated melts. Sproull and Rindone [11] melted lithium-potassium silicates under vacuum and found that fibers drawn from these vacuum melts have lower strength, by as much as 25%, than those produced from ambient melts. They attributed the reduction in strength to a heterogeneous microstructure brought about by low levels of oxygen in the atmosphere surrounding the melt under vacuum.

Most of this early work focused primarily on a specific property of the glass, such as viscosity or mechanical strength. However a more thorough and comprehensive investigation of the effects of vacuum processing on various properties of soda-lime silica glasses and melts is lacking. To address this gap, viscosity, density, Fourier transform infrared (FTIR) and ultraviolet (UV)-Visible (Vis) transmission spectra of soda-lime silicate glasses obtained from vacuum melts were measured in the present study. These data were compared with the corresponding properties of glasses produced by standard practice, i.e. from melts prepared at atmospheric pressure. Any difference in properties between the two sets of glasses was explained in context of differences in dissolved water concentration and/or processing glass under an oxygen-deficient atmosphere. It should be pointed out that although many different gases can be dissolved in a silicate glass, the focus of this work was limited to water, *because water is thought to be the dominant species among dissolved gases in soda-lime-silica glasses* [12].

The central finding of this work was that vacuum processing has a measureable impact on the viscosity and UV-Vis transmission spectra of a soda-lime-silica glass. Specifically, at viscosities corresponding to melting and gob formation, the temperatures of vacuum processed melt can differ by about 10°C from the ambient melt. This result is consistent with those previously reported by others and can be attributed to the lower dissolved water concentration in the vacuum melt [2]. The dominant wavelength in the UV-Vis transmission spectrum of the vacuum processed flint glass is found to shift to lower values compared to a standard flint glass. Changes in redox brought about by the vacuum processing may have some bearing on this result. However, the density of the glass was not effected by vacuum processing. Mechanical properties, critical from an end use viewpoint, have not been characterized here and remain a topic for future work.

EXPERIMENTAL METHODS

Details of sample preparation and data collection methods are provided in this section. Note that x-ray fluorescence (XRF) measurements were carried out to establish composition of a vacuum processed glass sample. Within experimental error, the composition of this sample was found to be similar to a sample prepared by standard methods. Hence, except for their dissolved gas content, both kinds of glasses are treated to be of similar chemical composition in this work.

Batching and melting

Soda-lime-silica glass frit was prepared by melting batch materials in an electric furnace at ambient pressure. Raw materials from bulk suppliers were used in preparing glass batches of nominal composition, in mass fraction, 73.7% SiO₂ - 13.6% Na₂O - 11.3% CaO - 1.4% Al₂O₃. The frit was then melted for 2.5 h in an evacuated furnace, where the pressure was maintained between 13.3 kPa and 17.3 kPa. This is referred to as “vacuum-processed glass”. The frit was also melted in ambient, i.e. at 101.3 kPa, for 2.5 h to obtain glass samples that are representative of glasses produced by existing commercial practices. This is the “ambient-processed glass”.

FTIR, UV-Vis transmission, and density measurements

Samples for FTIR experiments were prepared as described above by first melting ≈300 g of frit at 1450°C for 2.5 h either in ambient or in vacuum. These melts were then poured onto a

room temperature metal plate and pressed into discs. The discs were annealed at 550°C for 10 min and subsequently slow cooled to room temperature. They were then cut to size (3.81 cm diameter) using a core drill and polished on both sides. The polished discs were placed in an FTIR spectrometer sample chamber and purged with nitrogen gas for 15 min before collecting absorption spectra. A background scan was also collected with an empty sample chamber after a fifteen minute purge with nitrogen gas. Absorption spectra were used to calculate the dissolved water concentration in glass samples as will be described in the results section below.

Glass prisms measuring 35 mm × 35 mm × 13 mm for UV-Vis transmission were also prepared from the melts used for producing the FTIR samples. A small section, roughly 2 mm thick, was cut from the 35 mm × 13 mm face of the prism using a diamond saw. The cut faces were ground and polished to a mirror finish. A UV-Vis spectrophotometer was used for the transmission measurements.

Density measurements were carried out on crushed glass pieces obtained from the same sample set as used for FTIR and UV-Vis spectroscopy measurements by the Archimedes method. Deionized water with a few drops of surfactant was used as the weighing medium. A wire mesh, hung from a support frame connected to a balance, was used to suspend the samples in the water. A thermometer was clipped to the water beaker to continuously monitor the water bath temperature. Six glass samples were used from two different batches at each condition, vacuum and ambient processing, for the density measurement.

Viscosity

Viscosity measurements were carried out by two different methods. A rotating spindle viscometer was used to measure viscosities in the (10^1 - 10^4) Pa·s range, whereas a beam bending viscometer was used for measurements in the (10^8 - 10^{13}) Pa·s range. Combining data from these two measurement series, viscosity of the glass in the (10^1 - 10^{13}) Pa·s range was obtained by interpolation.

For the rotating spindle viscometer experiments, approximately 320 g of frit was melted in a platinum crucible for 2.5 h at 1450 °C in the viscometer furnace. The furnace temperature was then set to desired value and the rotating viscometer spindle was lowered into the melt. The torque experienced by the spindle was measured and noted at defined time intervals. The viscosity of the melt was calculated from the measured torque and spindle RPM and plotted as a function of time. A steady state value of this measurement provided the viscosity of the melt at that temperature. This process was repeated for different temperatures. The procedure for the vacuum processed samples was slightly different. Approximately 320 g of frit was melted in a platinum crucible for about 2.5 h at 1450°C in a laboratory furnace evacuated to between 13.3 kPa and 17.3 kPa. After the 2.5 h melting the crucible was transferred to the viscometer furnace. Viscosity measurements were then carried out using the procedure described above for the ambient sample.

In case of beam bending viscometer experiments, samples were prepared from melts conducted by heating about 200 g of frit at 1450 °C for 2.5 h in platinum crucibles. The melting was either in vacuum or at ambient pressure. After 2.5 h soak, the melts were poured into rectangular cavities measuring 90 mm × 50 mm × 10 mm. The plates were machined into beams measuring 55 mm × 4 mm × 4 mm and then loaded, one at a time, into a beam bending viscometer for measuring the viscosity. Measurements were carried out in accordance with ASTM standard C-598. Both sets of viscosity measurements were repeated on two different batches of material, with the average of each measurement reported below.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectroscopy was used in this work to quantify the concentration of dissolved H₂O. The FTIR absorption spectra of ambient and vacuum processed glass samples are shown in Figure 1. Bands at about 2800 and 3500 cm⁻¹, that are generally attributed to OH groups [3], are clearly visible. Absorption in ambient processed glass samples is found to be generally higher than in the vacuum processed samples due to the higher dissolved water content. The relationship between infrared absorption and dissolved water concentration C_i, is given by the Beer-Lambert equation:

$$C_i = \frac{A_i}{\rho \cdot t \cdot \epsilon_i}$$

where A_i is the absorption of ith band, ρ is density, t is thickness, and ε_i is the absorption coefficient corresponding to the ith band of the sample. The band corresponding to 2800 cm⁻¹ was used to calculate the concentration of the dissolved water. Behrens and Stuke [13] have shown that the practical molar absorption coefficient corresponding to this band is independent of the dissolved water concentration in soda-lime-silica glasses. Hence this band was used instead of the more commonly used 4500 cm⁻¹, 5200 cm⁻¹, or the 3550 cm⁻¹ bands. The practical molar absorption coefficient for the 2800 cm⁻¹ band was taken from Behrens and Stuke [13] as 50.8 l·mol⁻¹·cm⁻¹.

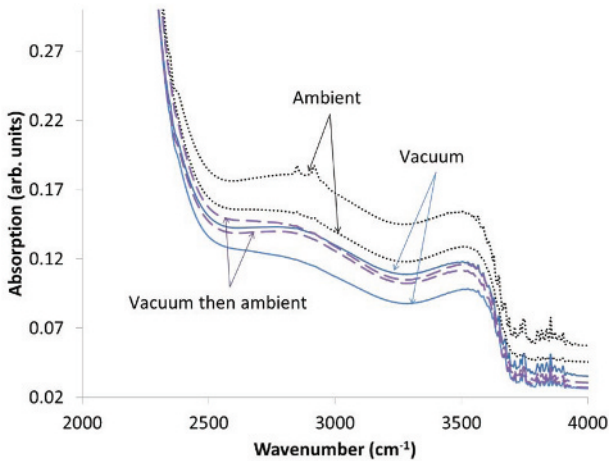


Figure 1. Infrared absorption spectra of ambient and vacuum processed glass samples. Also shown are the absorption spectra from samples that have been vacuum processed and subsequently melted under ambient conditions. Note that the spectra of these samples is similar to those of vacuum processed samples.

Assuming a density of $2.5 \times 10^3 \text{ kg/m}^3$, the dissolved water concentration (in mass fraction) calculated using Eq. (1) was found to be $0.0237 \pm 0.0027\%$ in the ambient processed glass and $0.0194 \pm 0.0015\%$ in the vacuum processed glass. The density of both ambient and vacuum processed glasses was assumed to be the same for this calculation. This assumption is reasonable as will be shown below. The dissolved water concentration values obtained in this work are in reasonable agreement with those found by Fenstermacher et al. [2] and by Jewell et al. [3].

Infrared absorption spectra were also collected from glass samples obtained by re-melting vacuum processed glass in ambient (for 2.5 h). The absorption spectra of the vacuum processed glass and vacuum processed then ambient melted glass were found to be similar. This result suggests that once water has been extracted from the glass, melting under ambient conditions subsequently has little effect on the dissolved water concentration, at least within the time scale of the experiments. This result provides confidence in asserting that the measurements of physical properties of vacuum processed glasses, which are carried out under ambient conditions, are representative of the true properties of the vacuum processed glass.

Viscosity

Results from the viscosity experiments are shown in Figure 2. The data from the ambient and vacuum processed samples can be approximated by the Fulcher equation $\log \eta = A + B/(T - T_0)$, where η is the viscosity, T is the temperature, and A , B , and T_0 are constants, which are used as fitting parameters. Although it appears that the viscosities of the two kinds of glasses is similar, a close observation reveals systematic differences.

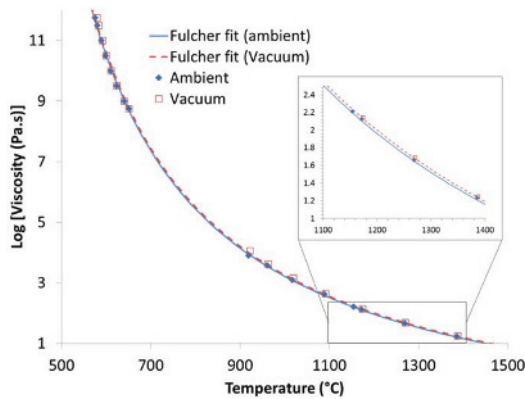


Figure 2. Viscosity versus temperature of ambient- and vacuum-processed glasses. A least squares fit to the data gave the parameters of the Fulcher equation. The resulting curves are shown as lines.

In

Table 1, temperatures corresponding to some viscosities of interest in glass manufacturing operations are listed for both ambient-processed and vacuum-processed glass. In general, the temperature corresponding to a particular viscosity is higher for vacuum-processed glass than for a comparable ambient-processed glass. The difference between the temperatures is largest at low viscosities and becomes smaller as the viscosity increases.

The softening point, defined as the temperature corresponding to a viscosity of $10^{6.65}$ Pa·s, is about three degrees higher in vacuum processed glass (735°C) compared to the ambient processed glass (732°C). The gob temperature, corresponding to a viscosity of 10^2 Pa·s, is 1192°C for the ambient processed glass and 1200°C for the vacuum processed glass. An 8°C difference in gob temperatures may necessitate changes in production practices. Hence this result should be carefully considered when evaluating the use of vacuum or sub-atmospheric pressures in glass melting.

The increased viscosity of vacuum processed glass compared to ambient processed glass at a given temperature can be explained by the decrease in the dissolved water content. As the dissolved water content reduces, the glass network becomes more cross-linked and the viscosity increases. If the water is only dissolved chemically, i.e. as OH species, then the isokom temperatures corresponding to lower viscosities are more influenced, as observed in this work and that of Fenstermacher et al. [2]. Stuke et al. have shown that below 0.5 wt%, water is dissolved primarily in the form of OH groups in soda-lime-silica glasses. When the water is dissolved primarily as H₂O molecules, as is the case above 3 wt%, then the low temperature viscosity may be more influenced. This is observed in Del Gaudio et al.'s work [14], in which they developed a parametric model to predict viscosity of soda-lime-silica glasses of different dissolved water concentrations. This model predicts that the viscosity difference between float glasses of different dissolved water concentrations should be greatest at low temperatures. The reason for such prediction may be that their parametric model is developed for glasses with larger dissolved water concentrations, where the water is thought to exist primarily as H₂O molecules and not as OH species. It should also be pointed out that Jewell et al. [3] have found similar trends in viscosity as those reported here and by Fenstermacher et al. [2].

Table 1. Temperatures of the ambient- and vacuum-processed glasses corresponding to a specific viscosity value.

Log[Viscosity (Pa·s)]	Temperature (°C)	
	Ambient-processed	Vacuum-processed
1	1451	1461
2	1192	1200
6.65	732	735
11	588	590
12.4	560	562

UV-Vis transmission

In terms of visual appearance, the ambient and vacuum processed glasses were found to be similar. However, subtle differences were noticed in their transmission spectra. The transmission spectra were collected on rectangular parallelepiped samples over a wide spectrum of wavelengths, ranging from 300 nm to 1100 nm. Results from the transmission experiments are shown in Figure 3, where normalized transmission is plotted against the wavelength of incident light. Solid lines represent data collected from vacuum processed glass and dashed lines from ambient processed glass. The transmission data were normalized by dividing the absolute transmission by the transmission at most intense wavelength. The wavelength corresponding to the maximum transmission (a value of 1 on the curve) is referred to as dominant wavelengths in this work. The dominant wavelength between 520 nm and 590 nm in the vacuum processed samples ranged slightly lower than the ambient processed samples, where the dominant wavelength ranged between 560 nm and 590 nm as shown in the inset in Figure 3.

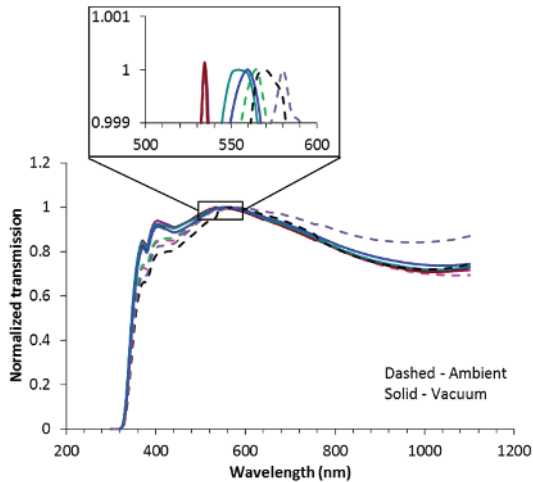


Figure 3. Transmission spectra of ambient and vacuum processed glasses. Absolute transmission was divided by the maximum transmission to obtain the normalized data.

The reason that a shift in the dominant wavelength of vacuum processed glasses is observed may lie in the fact that these glasses were processed under reduced amounts of oxygen compared to the ambient processed glass. This lower oxygen content may lead to higher FeO in vacuum processed glasses and hence a shift of the dominant wavelength to lower values. Some support for this argument is found in the UV-Vis transmission spectra of the glasses shown in Figure 3. Strong absorption below 370 nm is generally attributed to Fe^{3+} , which is found to be more prominent in the ambient processed glasses than the vacuum processed glasses. In other words, the lower amount of Fe^{3+} in the vacuum processed glasses lowers the absorption below 370 nm and shifts the dominant wavelength to lower values. Weyl ([15], see page 105) discusses similar changes in absorption spectra observed by Andresen-Kraft [16] in sodium trisilicate ($\text{Na}_2\text{O}\cdot 3\text{SiO}_2$) glasses of varying iron compositions. Andresen-Kraft found that when a large amount of iron is added to the glass, majority of iron exists in the $3+$ or Fe_2O_3 state and the glass has a greenish-brown color. On the other hand, at low iron content, some FeO is present and leads to a light green colored glass, suggesting a shift in the dominant wavelength.

If the shift in dominant wavelength is truly due to the changes in redox, it would then follow that the 2.5 h melting done in ambient/vacuum was long enough to cause oxygen to diffuse through the melts and alter the redox equilibrium. Goldman and Gupta [17] have shown that $\text{Fe}^{2+}/\text{Fe}^{3+}$ decreases by about a factor of 3 over a three hour period in a calcium aluminum borosilicate glass melt subjected to oxidation. Oxygen diffusion coefficient in this melt was found to be on the order of 10^{-7} , which is similar to that expected in a soda-lime-silica melt [18]. Hence it is plausible that the reverse effect can be expected when a glass is melted in an oxygen deprived environment. The change in $\text{Fe}^{2+}/\text{Fe}^{3+}$ was not determined in this work and remains a subject for future studies.

Density

The variation in the concentration of dissolved gases due to vacuum processing may be expected to result in changes in density of the glass specimen. While the density of vacuum-

processed glass was found to be slightly lower than the ambient-processed glass, as seen in Figure 4, the difference was smaller than the error in measurement. The average density (over twelve different measurements) in both cases was found to be 2.50 ± 0.03 g/cc. Fenstermacher et al. [2], reported a similar result. It should be noted that Shelby [19] found the density of a silica glass to vary as much as 0.15% when the dissolved water concentration changed from 0 to 800 ppm by weight. However, the changes in dissolved water concentration in the glasses studied here were much smaller and the expected change, if any, in density would be smaller than the error in measurement.

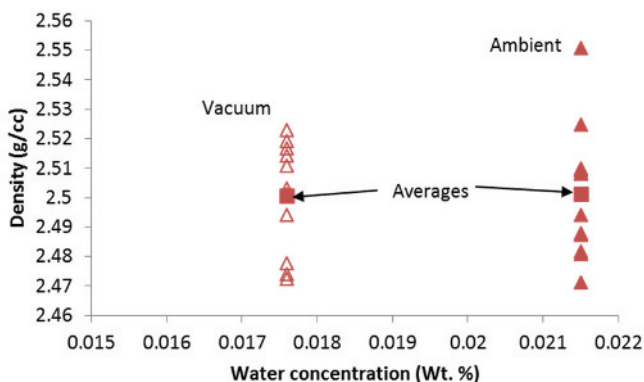


Figure 4. Density of ambient (open symbols) and vacuum (filled symbols) processed glass samples as a function of dissolved water concentration.

CONCLUSION

Vacuum processing and the ensuing changes in dissolved water concentration are found to have some effect on the viscosity and transmission spectra of soda-lime-silicate glasses. Specifically, the temperature corresponding to viscosities in the 10^1 – 10^3 range can increase by up to 10°C as the dissolved water concentration decreases from 0.0237% to 0.0194%. Such a change (in absolute terms) may necessitate minor changes to glass manufacturing operations and hence should be monitored when vacuum processing or other methods impact water content in the melt are employed. The dominant wavelength in the optical transmission spectra is also found to shift to lower wavelengths in glass samples with a lower dissolved water content. On the other hand, the concentration of dissolved water or the vacuum process has minimal influence on the density of the glass samples.

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