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VISCOSITY OF LEAD BISMUTH GALLATE GLASSES CONTAINING MINOR ADDITION OF SILICA AND GERMANIA

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Abstract

Heavy metal oxide glasses with and without minor additions of Silica and Germania in the system PbO-Bi2O3-Ga2O3 have been prepared which have potential applications for infrared fibres. Viscosity measurements using penetration viscometry were first carried out on sample of glass No. 711 provided by National Bureau of Standards (NBS) over a range of 107 to 1010 Pa.s and is in accordance with NBS data having mean error of 1.35% using modified-Nemilov equation. The viscosity of glasses studied fell sharply about three orders of magnitude in a temperature interval of less than 45°C. The results are discussed in relation to activation energy for viscous flow and also fragility of the melts is compared.

Keywords: Metal oxide glass, infrared fibre, viscometry, activation energy

1. Introduction

The way in which the viscosity of a glass melt varies with temperature is one of the important factors for understanding forming and annealing processes. In the heavy metal oxide glass systems, the rod-in-tube method is the favoured processing technique for pulling fibres. For this reason, the core and the clad of the preform should have similar processing viscosities in the temperature range of softening point of the glass. The softening temperature corresponds to a viscosity of around 106.6 Pa.s [1]. For the lead bismuth gallate glass system, Dumbaugh [2] first reported the steep viscosity/ temperature curve and short range between the glass transformation and beginning of crystallization temperature. On the other hand, silica based melts are excellent glass formers having high shear viscosities at liquidus temperatures, and the viscosity increases gradually with declining temperature. Heavy metal oxide melts have a comparatively low viscosity at the liquidus temperature which rises rapidly to high values in a short temperature range up to fairly close to transformation temperature (in Kelvin) of glass (Tg). Looking at it from a different viewpoint, upon heating above Tg, viscosities of silicate melts remain rather high over a considerable range of

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temperature, whereas heavy metal oxide melts drop at a more rapidly. This viscosity/temperature behaviour not only provides poor workability but also increases the tendency to denitrify. The viscosity of lead bismuth gallate glass melts (57.21 PbO - 25.02 Bi2O3 - 17.77 Ga2O3 in mol %) has been measured [1] by using parallel plate Viscometry and up to 15 mol % silica was added to the base glass composition.

According to Lapp et.al, in this region Arrhenius behaviour is exhibited by the viscosities of the glasses. It was considered that activation energy for viscous flow would decrease with the addition of silica, i.e., reduce the gradient of the temperature/viscosity curve. However it was found that, if any, there was a little effect in decreasing the activation energy with increasing the silica content of the glass. The activation energies of their base glass (57.21 PbO - 25.02 Bi2O3 - 17.77 Ga2O3 in mol %) and with additions of up to 15 mol % silica to the base glass for viscous flow were close to 628 kJ/mole. One of the best fitting empirical formulae describing the viscosity of a glass as a function of temperature is that suggested by G. S. Fulcher [3].

H. R. Lillie [4] made a most remarkable contribution to this subject when he proved that the viscosity of glass melts, within and close to the transformation range, is a function of time, because in the annealing range the attainment of an equilibrium glass structure is time dependent. Lillie critically evaluated glass melt viscosities at the annealing and the strain points. An interesting approach to the mathematical treatment of the temperature dependence of viscosity has been chosen [5]. It was found that the changes of viscosity with temperature for glasses of widely different compositions become very similar when one plots the logarithm of the viscosity against Tg/T instead of against 1/T. For example, the low melting BeF2 and the high melting SiO2 were compared on the same basis or, as physical chemist's term, in "corresponding states".

By plotting log η against Tg/T, the temperature of each glass is measured in effectively different units. For silica, Oldekop used a much smaller unit than for beryllium fluoride. This interpretation of the viscosity of glass melts suggests that whatever the mechanism of viscous flow may be for silica at 1500°C, this also must be the mechanism for BeF2 at 300°C. This model agrees where the structure of a liquid changes so as to resemble more of a molecular liquid when the temperature is raised. An atomistic interpretation [6] of the viscosity of Na2O -RO-xSiO2 glass melts (where R = Pb or Sr) showed that PbO substitution for SrO not only lowers the viscosity but also increases its temperature coefficient and hence also activation energies of viscous flow. This is due to the fact that the more polarizable electron cloud of Pb2+ can adjust itself more readily to an asymmetrical environment than can the less polarizable electron cloud of the same charge and similar size.

Glass melts having high temperature coefficients of viscosity results in a glass being "short", i.e. it has a short working range. "Long" glasses are characterized by a comparatively small temperature coefficient of viscosity. The change of viscosity with temperature of many glass systems can be described by an S-Shaped curve [5]. Temperature coefficient is low at lower temperatures at which the viscosity can be measured. At high temperatures the viscosity is also rather insensitive to temperature changes. At the beginning of Tg, the viscosity of glasses decreases rather sharply on heating. This is the region where the temperature coefficient of viscosity is high. The reason for this is that above Tg the thermal expansivity of the "glass" increases which causes all binding forces to decrease. Tg marks the beginning of structural changes which lead to a greater disproportion of the binding forces, hence the temperature coefficients of glasses reach their maximum value above Tg. The aim of the present work is to verify the quick and precise technique of penetration viscometry using commercial thermal mechanical analyzer in a heavy metal oxide glass system.

2. Experimental Work

Cylindrical specimens having diameter between 9-10 mm and 3 mm deep were made from a K2O-PbO-SiO2 standard reference glass number 711 provided by the NBS (National Bureau of Standards). Each specimen was polished to 3 micron surface finish and faces ground such that these became parallel having with allowance of ± 0.05 mm. Polished specimen was positioned at the top of platinum foil in the chamber of Dupont 943 thermal mechanical analyzer. As shown in Figure 1, a flat based cylindrical indenter having 1 mm base diameter, which has been fabricated from Nimonic 105 (a high temperature Ni-Co-Cr alloy reinforced with Mo, Al, and Ti), was put on the end of a cylindrical shaped silica probe of the analyzer to support it between surface of polished specimen and probe [7].

The offset probe mass was loaded by apposite weights ranging from 1-100 grams. The probe's position was set to zero µm at the specimen surface. To attain the required temperature, the analyzer chamber was heated in active nitrogen atmosphere (0.2dm3/min), usually at the rate of 10 K/min. Heating at the rate of 100 K/min to a temperature 40 K lower than the requisite level and then at the rate of 10 K/min, to attain the required temperature was found to give good results and saved time. The isothermal diffusion was gauged as function of time. Once a linear diffusion rate was achieved, measurements were taken between 15 and 45 minutes.

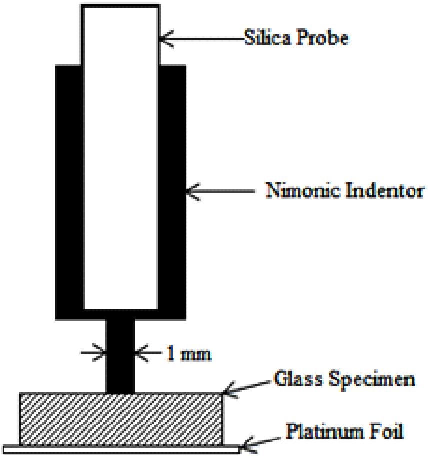

Figure 1. Schematic of accessory kit used in the penetration technique.

3. Results and Discussion

A characteristic plot of depth of isothermal penetration vs. time is demonstrated by Figure 2 where OA is instantaneous elastic section, AB is the delayed elastic section and the BC is the viscous section with steady state rate of penetration. Since the zero micron setting was adjusted at room temperature, at first indenter responded to thermal expansion of specimen to the range of glass transformation. In the transformation range temperature, the theological response of glass melt is explained by Watanabe [8] in simple physical terms of three consecutive systems:

- An early immediate elastic deformation
- Delayed elastic strain so that melts respond viscoelastically
- Finally pure viscous relaxation

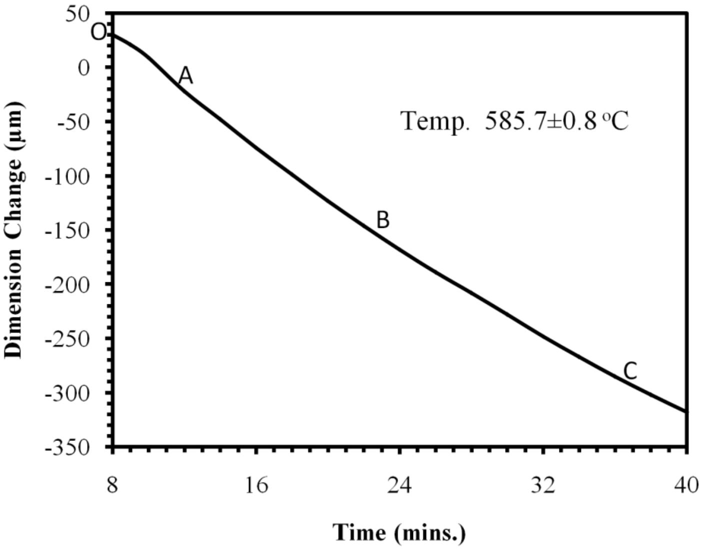

Figure 2. Analogue output of TMA presenting depth of the indicator against time (NBS standard glass # 711 with 2.0 gram of load at 585.7± 0.8 °C).

In order to assess the reliability of this method in our laboratory, measurements were carried out on a NBS lead silica glass No. 711 [9]. Results are compared with the NBS derived Vogel Fulcher equation for this glass i.e.;

$$\text{Log10}\ (\eta\ /\ \text{Pa.s}) = -2.621+4254.649/\ (T-152.1)$$

Errors in measured viscosities in comparison with the Vogel-Fulcher values generally become unacceptable outside the range log10 (η/Pa.s) = 107-1010. Viscosities calculated using Kokovkin equation within this range gave good agreement with Vogel-Fulcher values and the mean error was 1.82% within a maximum error of 3.25%.

The Nemilov equation [10] was modified in the current study to get viscosity values close to Vogel-Fulcher fit and is here given by;

$\eta=$

The above equation improved the fit to Vogel-Fulcher equation with mean error of 1.35% and maximum error of 3.09%.

The glass compositions studied in the present work for viscosity measurements are given Table 1. All the data points in Figure 3 were obtained using the modified Nemilov equation.

Table1. Batch composition of glasses studied in the present work (in mol %).

Glass	PbO	Bi_2O_3	Ga_2O_3	SiO_2	GeO_2
Base Glass	50	30	20	-	-
Batch 1	48	28.8	19.2	4	-
Batch 2	46	27.6	18.4	8	-
Batch 3	41	24.6	16.4	-	17.9

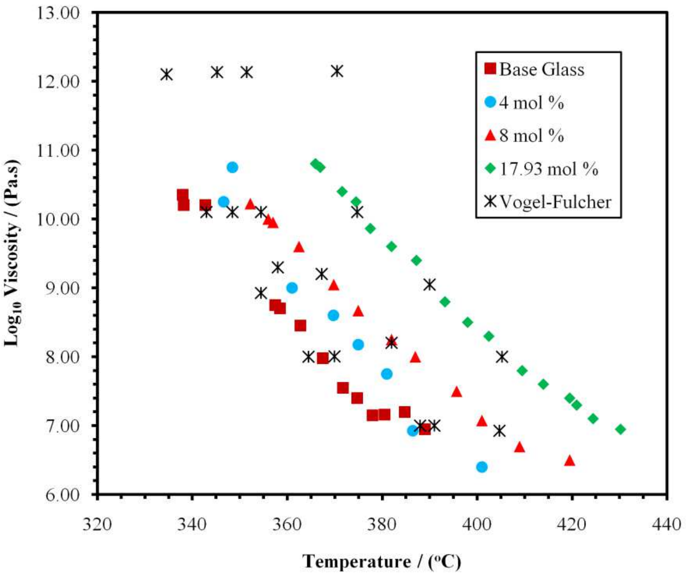

Figure 3. The graph between Log_{10} Viscosity (Pa.s) and temperature (^{o}C) for base glass composition, 17.93 mol% germania glass, 4 mol% and 8 mol% silica glass.

The log10 (η/Pa.s) vs. temperature (°C) curves show that the viscosity falls sharply in a temperature interval of less than 45 degrees Celsius through over nearly three orders of magnitude (from around 1010 to 107). In the case of the lead silicate NBS 711 standard glass the same interval was around 106 °C. This clearly demonstrates that the heavy metal oxide glasses have relatively much lower viscosities at their liquidus temperature as compared to silicate melts and stay fairly soft till they are near Tg, the point at which the viscosity increases rapidly. This behaviour can be seen in Figure 3 for base glass, 4 and 8 mol% silica glasses and 17.93 mol% germanium glass. Values of activation energy Eη are an indication of the type of structure present within the glass. Strongly bonded silica has Eη equal to 119.5 kJ/mole [11], while the comparatively more disordered structure of NBS 711 glass has, Eη equal to 322 kJ/mole.

At the start of this work, it was considered that by adding silica and germania to the base glass composition will lead to reduction in the activation energy for viscous flow, i.e. reduction in the gradient of the viscosity/temperature curves. However, as seen in Table 2, activation energy was surprisingly increased when silica contents of glass were increased.

Table 2: Calculated values of activation energy for different glass compositions from 10^7 to 10^{10} Pas.

Glass Name	Activation Energy (kJ/Mole)
NBS 711 Glass	322
Base Glass	563
17.93 Mole % Germania Glass	651
4 Mole % Silica Glass	607
8 Mole % Silica Glass	620

The 17.93 mol % germania glass gave the highest value of activation energy of all which implies that this glass possesses most disordered structure. It must be noted that the addition of silica and germania resulted in shifting the viscosity/temperature curves to higher temperatures. Angell [12] has shown that when log10 viscosity data is plotted on a reduced inverse (absolute) temperature scale, it is likely to get insight on the comparative relaxation time of the melt presuming that this is evident in the shear viscosity of the liquid. Within this logical basis, silica glass melts lie down at the extreme of behaviour. The solid vitreous silica has three dimensional covalent networks which are extremely strong and mutually supporting. The liquid shows roughly Arrhenian deviation of structural relaxation time above Tg which is evident in almost linearly scaled viscosity graph and is known as a strong liquid. Germania glass melts have similar behaviour. Whereas ZBLAN shows clearly non-Arrhenian or delicate behaviour, since melt is mainly ionic, rather poorly bonded and being multi component posses a variety of bond strengths. Figure 4 shows the results for the of base glass, 4 mol % silica glass, 8 mol % silica glass, 17.93 mol % germania glass and the NBS 711 glass on a scaled-viscosity graph where Tg is taken as a temperature where viscosity is equal to 1012 Pa.s [13]. This was obtained by an extrapolation of the TMA η/T data.

Figure 4 also shows that additions of 17.93 mol % germania and 8 mol % silica lead to nearly similar fragility curves hence suggestive of similarities of structure. Whereas the base glass show less fragile behaviour as compared to 4 mol % silica glass.

As the fragility is proportional to inverse absolute temperature then it should also be proportional to the activation energy for viscous flow. In this study, less fragile glasses i.e., 8 mol % silica and 17.93 mol % germania glasses have higher values of activation energies, which contradicts the above discussion. This contradiction may be because of two reasons;

a) Due to the errors at higher viscosities, the measured Tg at 1012 Pa.s is not very accurate when calculated from the Vogel-Fulcher fit.

b) There could be some other factors to be considered in measuring fragility behaviour.

It has been suggested [14] that log10 (η/Pa.s) versus Tg/T plots should be considered for discussing quick setting (short glasses) and slow setting (long glasses) glasses rather than as a measure of fragility.

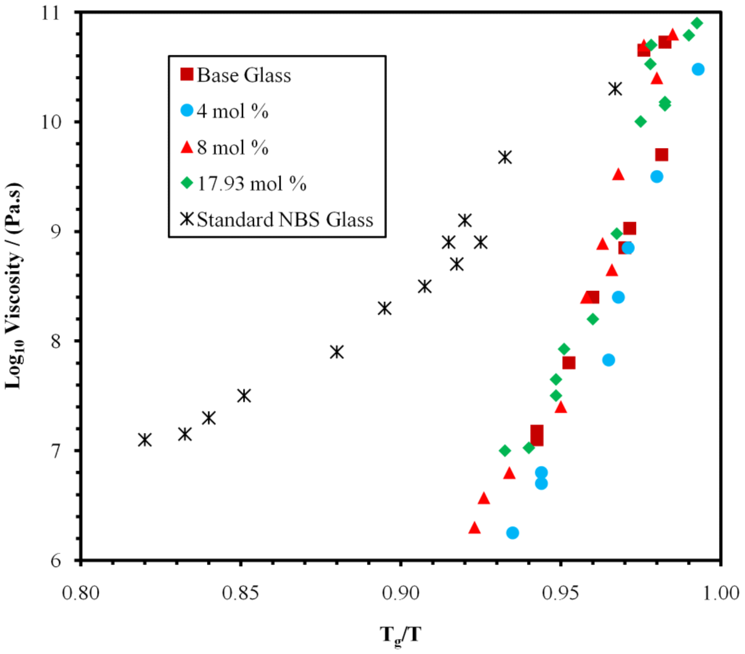

Figure 4. Log$_{10}$ Viscosity versus reduced temperature (T_g/T) curves for NBS standard glass, base glass, 17.93 mol% germania glass and 4 mol% and 8 mol% silica glasses.

4. Conclusions

Low temperature viscosity measurements have been carried out on a NBS glass No. 711 over a range of Log(η/Pa.s) = 107- 1010 and show excellent agreement with NBS data having a mean error of 1.35% when using the modified - Nemilov equation. Viscosity measurements were performed on samples of the base glass and with minor additions of silica and germania. The viscosity of the glass studied falls sharply in a temperature interval of less than 45°C by nearly three orders of magnitude. For the lead silicate NBS 711 standard glass the interval required for the same fall in viscosity was around 106 degrees Celsius. The addition of silica and gemania simply moved the viscosity temperature curves to elevated temperatures and also results in increase in the activation energy for viscous flow.

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