Viscosity of iron rich glasses obtained from industrial wastes

A. Karamanov, R. Di Gioacchino, P. Pisciella, M. Pelino[1]

Department of Chemical Engineering and Materials, University of L'Aquila, Monteluco di Roio, 67100, Italy

A. Hreglich

Stazione Sprimentale Del Vetro, Murano-Venezia 30141, Italy

Viscosity–temperature (V–T) curves for two iron rich glass compositions, named G1 and G2, made from various industrial wastes were obtained by using dilatometry and rotational viscosimeter. The experimental V–T curves are compared with the theoretically estimated values by the Gehlholff–Thomass and Bottinga–Weill models. Investigated compositions showed a large forming temperature interval and a high tendency to crystallise which influences the viscosity. For low crystallisation rate, the experimental V–T curve of G1 glass is in good agreement with the values obtained by theoretical methods. When spontaneous crystallisation takes place in G2 composition the experimental results are higher than the prediction of the models. The activation energies for viscous flow, E_η, resulted as 421 kJ/mol for G1 in the glass transformation range and 311 and 378 kJ/mol for G1 and G2, respectively, in the melting region.

The temperature dependence of viscosity, η, has a fundamental meaning for glass science and technology. The viscosity temperature (V–T) curve of each composition is characterised by the temperatures at which the viscosity corresponds to a number of 'fixed points' or standard viscosity values.[1–5]

The first 'fixed' point at high temperature corresponds to a viscosity of 10^2 dPa s and is named 'melting' point. However, in the actual glass industry, melting and refining are usually carried out at lower viscosity values in order to reduce the melting time.

The forming, i.e. blowing, pressing, rolling, etc., occur in the 10^3–10^9 dPa s viscosity region; the correct interval depends on the shaping method because each glass forming technology requires a certain viscosity range.

Glasses are defined as 'short' and 'long' according to the temperature interval between viscosity values of 10^4 and 10^8 dPa s. The shorter the temperature interval the shorter is the glass. The forming and shaping of 'long' glasses is easier and allows working at lower temperatures while the 'short' glasses become rigid faster favouring automatised production processes. The 'fixed' points relative to this interval are the working point (10^4 dPa s) and the Littleton softening point ($10^{7.8}$ dPa s).

In order to prevent undesirable crystallisation the working temperature must be above the liquidus curve. This requirement is very important in the case of glass ceramic production or, in general, for compositions with high crystallisation tendency.[5–7] It is found that some shaping methods cannot be used for certain glass ceramic compositions.

The annealing of glass articles is limited by upper and lower annealing temperatures. The upper annealing temperature corresponds to a viscosity of 10^{13} dPa s which is 10–20°C higher than the glass transformation temperature, T_g, corresponding to a viscosity value of $\sim 10^{13.3}$ dPa s. The lower annealing temperature is defined as 'strain point', the temperature below which the glass is considered as a solid and elastic material ($\sim 10^{14.5}$ dPa s). The dilatometric softening point, T_S, which corresponds to viscosity of $\sim 10^{11.3}$ dPa s is the last low temperature 'fixed' point.

For the temperature interval between T_g and the melting point, the V–T curve is usually calculated by the Vogel–Fulcher–Tamman (VFT) equation[1–5]

$$\log(\eta) = A + \frac{B}{(T - T_0)} \qquad (1)$$

where A, B and T_0 are constants depending on the glass

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[1] Author to whom correspondence should be addressed. (e-mail: pelino@ing.univaq.it)

composition. To solve the VFT equation at least three measurements at three different viscosities must be carried out; they are usually the glass transition, T_g, the Littleton softening point and melting points, respectively.

For glass forming melts the value of the activation energy for viscous flow, E_η, is a function of temperature. In the glass transformation range, E_η varies between 350 and 700 kJ/mol depending on the glass composition, i.e. the higher the percentage of glass formers the higher the value of the activation energy.[1,4,8] By increasing the temperature the melt structure becomes less 'bonded' and with more 'cavities'; as a result E_η decreases. Usually, in the melting region, the activation energy for viscous flow is 2–3 times lower than the values in the glass transformation region ranging between 100 and 300 kJ/mol.

For relatively short temperature intervals the value E_η can be evaluated through the Boltzman equation

$$\eta = K\exp(E_\eta/RT) \qquad (2)$$

In the present work the V–T curves for two iron rich glass compositions made from various industrial wastes are obtained by using dilatometry and a rotational viscosimeter. The experimental V–T curves are compared with the theoretically estimated values by the Gehlhoff & Thomass[9] and Bottinga & Weill[10] models. The first approach evaluates the temperature corresponding to different fixed viscosity values between 10^3 and 10^{13} dPa s. The second one is developed to calculate the viscosity of magmatic iron rich melts in the 1200–1600°C temperature range.

The activation energies for viscous flow, E_η, for the low and high temperature regions are also evaluated and discussed.

Experimental

Two iron rich glasses were obtained using the following industrial wastes: (1) jarosite (JAR), an iron rich hazardous mud coming from the hydro-metallurgical production of zinc; (2) electric arc furnace baghouse dust (EAFD), a waste by-product from the steelmaking process; (3) granite scraps (GS); and (4) glass cullet (GC).

The batch of first glass, G1, was prepared by mixing calcined jarosite, glass cullet and granite scraps in a ratio 30/40/30. The batch of second glass, G2, was obtained by mixing electric arc furnace dust, glass cullet and sand in the ratio 45/35/20. The glasses were melted at temperatures of 1400°C in a super kanthal electric furnace using corundum crucibles for 2 h. The melt was

Table 1. *Chemical compositions of the wastes and corresponding glasses (wt%)*

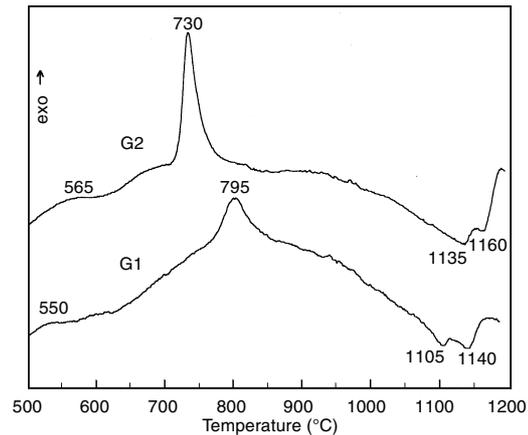|	Jar	GS	GC	EAFD	G1	G2
SiO_2	3·7	70·2	72·5	5·9	52·9	46·9
Al_2O_3	0·3	12·1	0·5	0·7	4·1	0·4
Cr_2O_3	–	–	–	1·1	–	0·5
Fe_2O_3	49·3	1·6	0·1	52·8	24·1	25·7
CaO	0·1	5·2	8·7	7·5	5·2	6·5
MgO	0·2	0·6	4·0	5·2	1·8	3·9
MnO	–	–	–	5·3	–	2·5
ZnO	5·6	–	–	13·8	2·7	6·5
PbO	3·6	–	–	0·5	1·7	0·2
Na_2O	–	2·9	13·4	0·9	6·4	5·7
K_2O	–	3·3	0·2	1·0	1·1	0·7
LOI	37·2	4·1	–	5·1	–	–

Figure 1. *DTA traces of G1 and G2 glass compositions*

poured into a stainless steel mould, annealed and then cut into specimens for subsequent thermal treatment.

The chemical analyses of the wastes and of the corresponding glasses were carried out by a Spectra-Xepos EDXRF instrument equipped with a 50 W Rh anode x-ray tube. The results, expressed as wt% of the oxides, are shown in Table 1.

The crystallisation behaviour of the glasses was estimated by differential thermal analysis (DTA) using 'Netzsch STA 409' apparatus. 100 mg bulk samples were heat treated in temperature interval 20–1200°C at a heating rate of 20°C/min.

The glass transformation temperature, T_g and the dilatometric softening point, T_s, were obtained using a 'Netzsch 402 ED' differential dilatometer. In these experiments, prismatic samples of size $3\times3\times25$ mm^3 were treated at heating rates of 3, 5 10 and 20°C/min between room temperature and 700°C.

In the high temperature region the viscosity was measured by a rotational, Searle type viscosimeter at the Stazione Sperimentale del Vetro (Venice, Italy). The measurements were made at 1200, 1240, 1280 and 1320°C according to the ISO/DIS/7884/2 standard.[11]

Results and discussion

DTA plots of the investigated glasses are reported in Figure 1. The T_g temperatures of G1 and G2 compositions occurs at 550 and 565°C, respectively. The formation of crystalline phases is highlighted by the occurrence of single exothermal peaks. For G1 the peak is in the region of 770–830°C with a maximum at 795°C. For G2 the exo-effect is sharper and its maximum is at a lower temperature, 730°C, which indicates a higher crystallisation rate. The melting endo-peaks highlight that two phases melt at different temperatures in both samples. It was previously highlighted that in similar glasses two different crystal phases, magnetite and pyroxene, are formed.[12] For G1 the temperatures of the endo-peaks are at 1105 and 1140°C while for G2 they are at 1135 and 1160°C, respectively; the differences in the liquidus temperatures depend on the glass composition.

The higher crystallisation tendency of G2 was also confirmed by XRD analysis of the parent glasses. The spectrum of G1, quenched in the stainless steel mould,
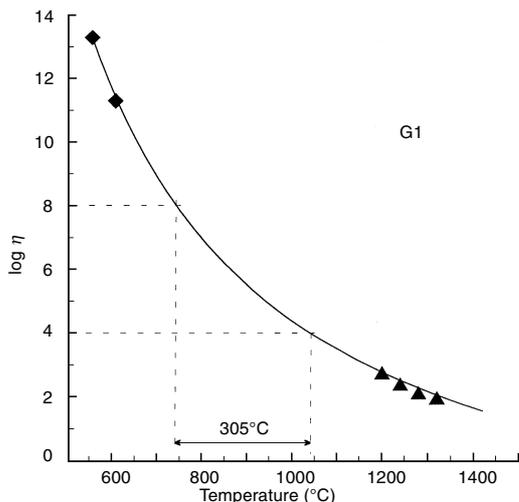
Figure 2. *Experimental viscosity points and the corresponding VFT curve for G1 composition*
◆ dilatometry ▲ rotational viscosimetry

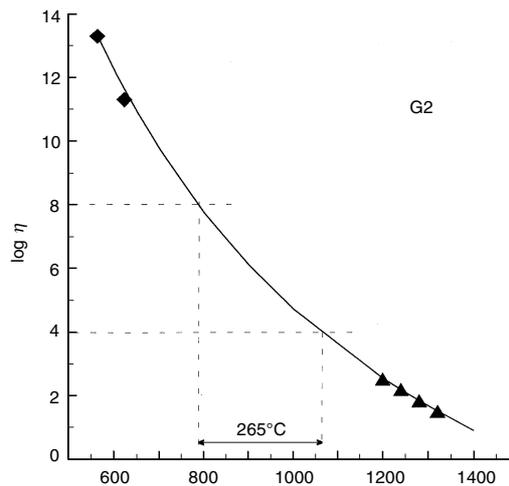**Figure 3**. *Experimental viscosity points and the corresponding VFT curve for G2 composition*
◆ dilatometry ▲ rotational viscosimetry

shows an amorphous halo with low intensity traces of magnetite formation. These traces have a very wide 'path' and could be related to a liquid–liquid separation with the presence of an iron rich phase with not well arranged magnetite structure.[12] At the same time the XRD spectrum of G2 composition, quenched in the stainless steel mould and in water shows the presence of about 6–8 and 2–4% magnetite spinel, respectively. Detailed results on the crystalline structure of heat treated glasses have been presented elsewhere.[12]

The viscosity data were obtained by dilatometry, at low temperature where no crystallisation occurs, and by a rotational viscosimeter at temperatures higher than the liquidus. Due to the high crystallisation rate the measurements of the Littleton softening point resulted in being unmeaningful in similar compositions;[7] alternative methods, such as measuring the change of shape of pressed glass powder samples in heating microscopy would not give reliable results either.[13]

The experimental viscosity values for both glasses obtained by dilatometry and viscosimeter are summarised in Table 2. The VFT curves were evaluated by using the results for the glass transition temperature, T_g, and the dilatometric softening point, T_s, obtained at 3°C/min heating rate and viscosity measured at 1200 and 1320°C. Figures 2 and 3 report the experimental points and corresponding VFT curve as function of temperature, for G1 and G2, respectively.

By comparing the two viscosity curves it appears that G1 has lower T_g and T_s but higher viscosity in the

melting region than G2. The temperature interval related to the 10^4–10^8 viscosity range is 305°C for G1 and 265°C for G2. Therefore both compositions can be theoretically considered 'long' glasses, however crystallisation takes place in this temperature range.

The results obtained by the Gehlholff–Thomass[9] and Bottinga–Weill[10] methods for G1 and G2 melts are presented in Figures 4 and 5, respectively, together with the corresponding VFT curves (solid line) determined from the experimental data.

For G1 glass the experimental curve is in close agreement with the values obtained with both methods while for G2 the VFT curve shows higher viscosity than the calculated values especially in the working region. This difference can be attributed to the spontaneous crystallisation taking place in G2 composition and resulting in a rising of the V–T curve.

The activation energy of viscous flow, E_η, was evaluated for the glass transition range and the melting re-
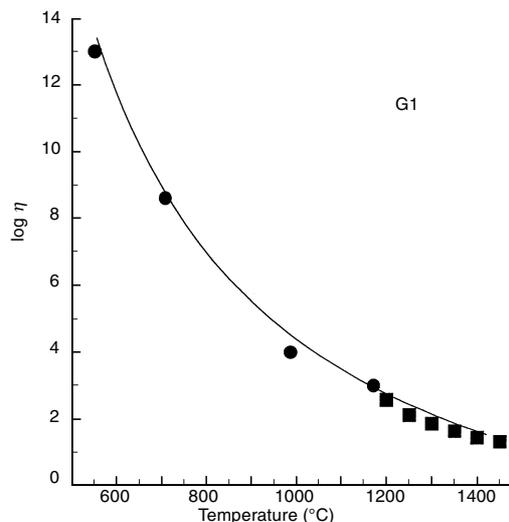
Table 2. *Experimental viscosity values by dilatometry and rotation viscosimetry for G1 and G2 compositions*

G1		G2	
T (°C)	log(η)	T (°C)	log(η)
554	13·3	560	13·3
605	11·3	620	11·3
1200	2·75	1200	2·51
1240	2·40	1240	2·18
1280	2·13	1280	1·82
1320	1·97	1320	1·49

Figure 4. *Viscosity values obtained by the Gehlholff–Thomass[9] and Bottinga–Weill[10] methods compared with the VFT curve for G1 composition (solid line)*
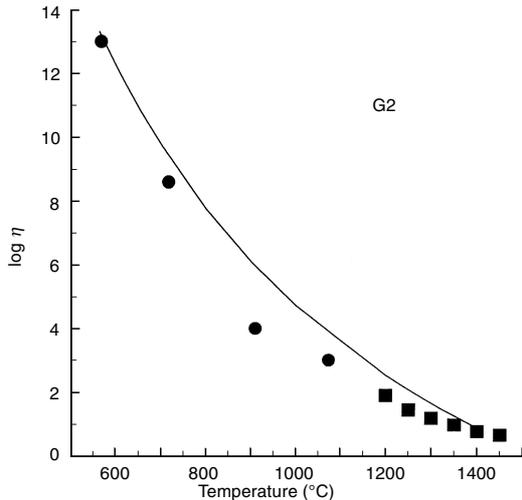● Gehlholff & Thomass ■ Bottinga & Weill

Figure 5. *Viscosity values obtained by the Gehlholff–Thomass[9] and Bottinga–Weill[10] methods compared with the* VFT *curve for G2 composition (solid line)*
● Gehlholff & Thomass   ■ Bottinga & Weill

Figure 7. *Bartenev equation, Equation (3), plot and corresponding* E_η *value for G1 composition*

gion. In order to calculate E_η in the glass transition range, dilatometric measurements at different heating rates, ϕ, were made. In these experiments only the G1 composition was used due to the presence of crystal phase in G2 samples. E_η was evaluated by the Bartenev equation[1,2] in the form

$$\phi = A\exp(E_\eta/RT_g) \qquad (3)$$

The plot of $\ln(\phi)$ versus R/T_g is a straight line whose slope corresponds to E_η.

The experimental dilatometric curves and the corresponding plot obtained by Equation (3) are shown on Figures 6 and 7, respectively. The obtained value of E_η, 421 kJ/mol is relatively low compared, for example, with the E_η value of 580–590 kJ/mol in the glass transformation range of window glass.[1] This result can be justified by the low percentage of network formers ($SiO_2+Al_2O_3$) in the investigated composition.

For the high temperature region E_η was evaluated using the experimental data by rotational viscosimeter. The plot obtained by applying the Boltzman relation, Equation (2) is shown in Figure 8. In this case, the E_η values, 311 and 378 kJ/mol for G1 and G2 respectively
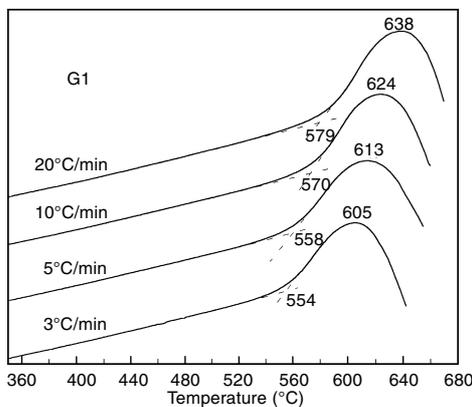
are relatively high, about 2 times higher then the E_η value of 180–190 kJ/mol for window glass in the same viscosity interval.[1] Also the E_η for G2 is higher than for G1 notwithstanding that G2 shows lower viscosity in this temperature region.

These anomalies can be explained by the high immiscibility of the parent melts. Liquid–liquid separation, at temperatures higher than liquidus, is typical of the iron rich glass forming melts; several iron oxides containing silicate systems have critical temperature of immiscibility higher then 1500°C.[14,15] The amount of iron rich phase due to liquid–liquid separation grows with increasing the percentage iron oxides in the composition and with temperature decreasing. This leads to a rise of the apparent viscosity of the melt and influences the slope of the V–T curve, i.e. the value of E_η.

Liquid–liquid separation was highlighted by measuring the behaviour of the viscosity as a function of time at 1200°C. The plots are shown in Figure 9. It is evident that the viscosity does not reach an equilibrium value even after 30–40 min holding time for both G1 and G2 melts while in similar experiments carried out on compositions without immiscibility, the equilibrium value was reached in 2–3 min. In fact the in-
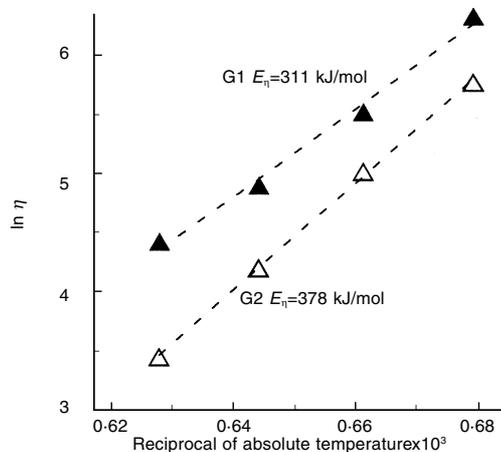

Figure 6. *Dilatometric curves for G1 composition obtained at different heating rates*

Figure 8. *Boltzman equation, Equation (2), plots and corresponding* E_η *values for G1 and G2 compositions*
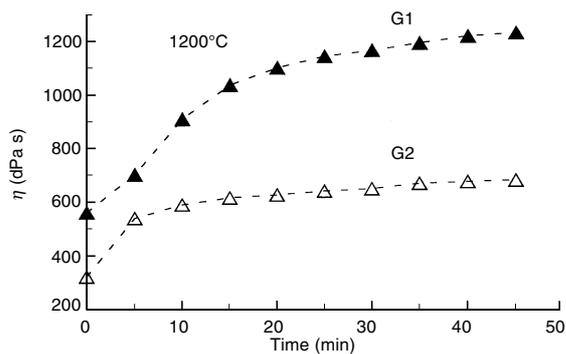
Figure 9. *Variation of viscosity as a function of time for G1 and G2 compositions at 1200°C*

ternational standard procedure for the determination of viscosity by rotation viscosimeter[11] highlights that the results may be influenced if phase transformation takes place during the measuring and suggests as right viscosity value, the one obtained after few minutes at constant temperature.

Conclusion

The iron rich compositions investigated in the present study show a large forming temperature interval and can be defined as 'long' glasses. However, the high tendency to crystallise in the working temperature range influences the viscosity and the evaluation of the fixed points.

For low crystallisation rate the V–T curve can be estimated by different methods: the Gehlholff–Thomass in the glass forming range and the Bottinga–Weill in the melting region. When spontaneous crystallisation takes place, the experimental results give values higher than the models or expected.

Above the liquidus the viscosity is influenced by the liquid–liquid separation which leads to an increasing of the activation energy of viscous flow. The calculated E_η for the melting region has a value approximately double the expected one.

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