Original Paper

Some aspects of the workability of glass melts

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Criteria are given for the isothermal or isochomal workability of glass melts and discussed by means of a schematic example which is based on numerous measurements. A thesis for a simple connection of this kind of workability is presented and examined by means of so far existing measurements. The isothermal or isochomal workability, which becomes more important with increasing deformation rate, is in contrast to the non-isothermal or athermal workability. The differences are based on certain connections between the stiffness, the relaxation modulus of a glass melt, its high-temperature fracture strength and the value of the quantity B in the Vogel-Fulcher-Tammann (VFT) equation if the constants are evaluated from a measurement of the whole viscosity-temperature range, from $10^{1.5}$ to 10^{12} Pa s.

Einige Aspekte der Verarbeitbarkeit von Glasschmelzen

Es werden einige Kriterien für die isotherme oder isochome Verarbeitbarkeit von Glasschmelzen gegeben, die an Hand eines schematischen Beispiels, das auf zahlreichen Messungen basiert, diskutiert werden. Eine These bezüglich eines einfachen Zusammenhangs dieser Art der Verarbeitbarkeit wird gegeben und an Hand bisher vorliegender Messungen geprüft. Diese isotherme oder isochome Verarbeitbarkeit, die um so mehr an Bedeutung gewinnt, je größer die Verformungsgeschwindigkeit wird, steht im Gegensatz zur nichtisothermen bzw. athermischen Verarbeitbarkeit. Die Unterschiede basieren auf bestimmten Zusammenhängen zwischen der Steifigkeit, dem Relaxationsmodul, der Hochtemperaturfestigkeit und der Größe B aus der Vogel-Fulcher-Tammann (VFT)-Gleichung, wenn die Konstanten der VFT-Gleichung aus Messungen über den gesamten Viskositäts-Temperaturbereich von $10^{1.5}$ bis 10^{12} Pa s ermittelt worden sind.

1. Introduction and definition

The conception on workability of glass melts may be based on different points of view. Frequently it is based on the viscosity-temperature behaviour in such a way that the temperature range of a certain viscosity range is considered [1 and 2].

Another point of view is to consider the high-temperature (ht)-fracture strength as the lowest temperature limit of workability having in mind that this limit depends on the practical deformation and deformation rate which in turn depends on temperature. In the latter case, however, this connection is not known and still up to now a matter of empiricism.

In order to treat this problem it seems to be necessary at first to reduce the conception workability to the isothermal and/or isochomal workability, because otherwise further complex influencing parameters and criteria have to be introduced.

For the isothermal workability of a glass melt some fundamental criteria can be given such as ht-fracture strength, relaxation behaviour and stiffness of a glass melt which may be comprised by the conception brittleness of a melt and which is described and discussed extensively in [3]. With respect to that a connection was found in that way that a "brittle" melt is characterised by a high relaxation modulus, which is equivalent to a high stiffness, and a low ht-fracture strength. Further on, the viscosity-temperature relation plays an important part, not only for the non-isothermal but also for the isothermal workability. The question is what happens if a slight change in viscosity takes place by the influence of minor components such as OH^- content, vaporisation of alkali oxide or even changes in redox ratio of polyvalent ions. Such a viscosity change or shift also influences the brittleness behaviour at the same temperature. Thus, for a very exact comparison of the stiffness of two glass melts not only the isothermal conditions but also the isochomal (equal viscosities) conditions have to be considered and therefore, it may be important in special cases to distinguish additionally between isothermal and isochomal workability.

Another point is the viscosity- and load-dependent non-Newtonian flow behaviour (viscosity decrease) which, however, is very similar for all investigated silicate glass melts and which is reported in [4], but which is very different between silicate and e.g. phosphate or borate glass melts [5].

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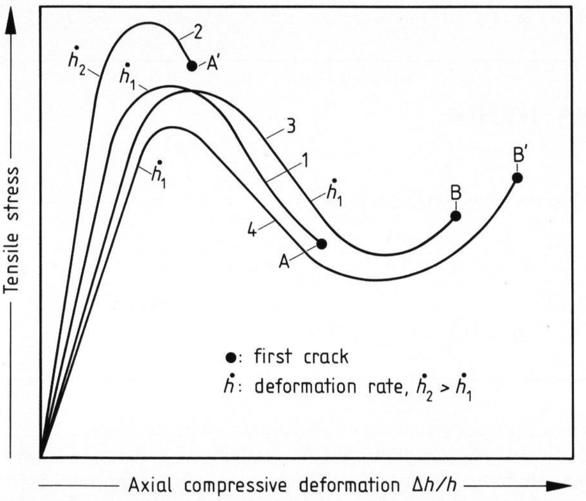

Figure 1. Schematic diagrams of tensile stress versus axial compressive deformation of cylindrical glass samples for various deformation rates $\dot{h}_2 > \dot{h}_1$ and glass melts (see text) with first cracks at different stress and strain values within the viscous flow range.

The connection of the mentioned influences is presented in the schematic diagrams of figure 1 in which the equatorial tensile stress of the cylinder compression experiments is demonstrated as a function of the degree of compression until the first ht crack occurs under various conditions [3]. Curve 1 illustrates the stress course for a deformation rate $\dot{h}_1$. The crack-free passage of higher stresses at the beginning of the experiment than that which leads to the ht crack (A) was interpreted in [3] with a load-dependent anisotropic structural change of the glass melt and is in close connection to the load-dependent relaxation behaviour [5]. At a higher deformation rate $\dot{h}_2 > \dot{h}_1$ curve 2 will be obtained for which the steeper slope indicates a higher relaxation modulus producing the first crack (A′) at a higher stress but at a lower deformation. If again the lower deformation rate $\dot{h}_1$ is applied, two cases may be considered for two different workability conditions:

First, at the same temperature curve 3 will be produced by a melt with a lower viscosity, that means with a reduction in stresses and relaxation modulus and with that a reduced stiffness of the melt. The consequence is a ht crack (B) at higher stress and higher deformation values than in the case of curve 1.

Second, at the same temperature curve 4 will be produced by a melt with the same viscosity but with a different (lowest) stress-deformation slope and therefore, with the lowest relaxation modulus and with a larger ht-fracture strength (B′) than that of curve 3 at the highest degree of deformation.

The second case is obtained by a more suitable composition of the glass melt in contrast to the first case. Changes in composition have produced so far changes in the relaxation modulus and ht-fracture strength up to 300 % at isochomal conditions [3].

2. Distinction between athermal (non-isothermal) and isothermal workability

In order to determine the workability of a concrete glass melt in the manner as described in section 1. a considerable effort of measuring is necessary. Thus, the question arises whether easier criteria exist.

2.1. Practical criterion for estimating the athermal (non-isothermal) workability

A first point of attachment for the concept athermal workability may be seen in the VFT equation

$$\lg \eta_0 = A + B / (T - T_0) \qquad (1)$$

in which the quantity B may be regarded approximately as a temperature-independent activation energy of viscous flow in contrast to the "real" activation energy E_η, based on the Boltzmann relation:

$$\lg \eta_0 = \lg \eta_{00} + E_\eta / (k\,T\,2.3) \qquad (2)$$

in which E_η is clearly temperature-dependent:

$$E_\eta = 2.3\,k\,T\,(C + B / (T - T_0)) = E_\eta(T) \qquad (3)$$

with $C = A - \lg \eta_{00}$ being temperature-independent as well as the quantity B. With respect to all interpretations and opinions about the physical meaning of the activation energy nevertheless the quantity B contains obviously some overall information about the structure of melts as was shown also for polymers in [6].

Looking at the results from [3] which concern the relaxation behaviour, stiffness, ht-fracture strength and brittleness and not least the structure and its change with temperature and load a connection to the B value seems also to exist. The simple suggestion is as follows: If the constants A, B and T_0 of the VFT equation are determined over a viscosity-temperature range as large as possible, say from $\lg \eta_0 = 12$ to 1.5 (η_0 in Pa s) in an exact manner, the quantity B should serve as a rough relative measure for the non-isothermal workability of a glass melt in comparison to another melt. In such a way the influence of single components of the melt composition may be estimated by determining the influence on B. This can be done either experimentally or, if receivable, from the so-called specific factors for calculating the constants of the VFT equation after Lakatos et al. [7]. A comprehensive collection of those data are given in [8].

The conclusion is that a good athermal (non-isothermal) workability is connected with a "long" glass melt or with a large B value.

Table 1. Isothermal workability and B values for various multicomponent glass melts (glass compositions see [3]). Numbers 6 to 1 indicate isothermal workability from "bad" to "good"

	borosilicate glass	optical glass	float glass	glass no. 1	glass no. 2	glass no. 3
isothermal workability (relative units)	6	2	3	1	4	5
B values (calculated [7 and 8])	6261	4450	4652	4158	4709	5261

2.2. Criteria for the isothermal workability and its contrast to the athermal workability

The examination of the criteria mentioned in section 2.1. may be done in connection with the extended investigations on glass melts with very different compositions and different types of melts [3 and 4]. It was found there that large values of B are typical for melts with high relaxation moduli and low ht-fracture strengths. This leads to a characteristic sequence which contradicts the athermal workability. For that reason the isothermal workability is defined because the contradicting results were obtained under isothermal conditions. This experimentally found situation is represented in table 1 by numbers 1 to 6, number 6 indicating the worst workability. The chemical compositions are given in [3]. Between 1 and 6 are differences in the ht-fracture strength and in stiffness up to 300 % [3, figures 6a and b and 11].

Because the authors' viscosity measurements were made only within a relatively narrow viscosity range (10^7 to 10^{12} Pa s) the calculated B values are connected with considerable deviations. This is a well-known effect for all constants of the VFT equation if the calculation is based on a small viscosity range. If this is based, however, on a wide viscosity range (10^1 to 10^{12} Pa s) the deviations become much less. Therefore, the B values given in the present paper are based on calculations from the specific factor data in [7 and 8] and on the chemical compositions of the applied glass melts. For these factors a viscosity range of $\eta_0 = 10^1$ to 10^{12} Pa s is quoted. The results are also given in table 1 from which a correlation may be seen between the calculated B values and the relative isothermal workability although some minor components of the optical glass could not be regarded for the calculation of the B value.

A very clear connection between the B values and the measured relaxation moduli and stiffnesses [3] is also obtained for non-silicate glass melts listed in table 2. The B values differ from each other by a factor of nearly two where the connection not only to the workability is obvious but also to the structure. While the structure of the NaPoLi glass melt is based on linear chains (lowest B value, best isothermal workability) and the CaBa glass melt on cross-linked chains (middle B value, middle isothermal workability), the silicate melts are based on a three-dimensionally interconnected network structure (highest B values, less isothermal workability). This tendency is seen from table 3 where those deformation rates $\dot{h}$ are given at which the relaxation modulus $E(t)_{max} = 5$ GPa at a comparable equilibrium viscosity of $\eta_0 = 10^{7.5}$ Pa s. It is obvious that the larger $\dot{h}$ is, in order to reach a certain value for the relaxation modulus at a certain viscosity, the better is the isothermal workability of a glass melt. This trend is valid even among the various investigated silicate glasses where differences in brittleness up to 300 % were observed [3]. It is expected that this trend is continued in the pure silica glass with its B value of 15.004 [9].

Table 2. Isothermal workability and B values of NaPoLi and CaBa glass melts (compositions in mol%. < 1 means a better isothermal workability than that of glass no. 1 in table 1)

	NaPoLi glass	CaBa glass
	Na_2O : 25 Li_2O : 25 P_2O_5 : 50	CaO : 25 BaO : 25 P_2O_5 : 50
measured B values	1100	2043
isothermal workability	<1	<1

Finally, as a further example, the lead ("crystal") silicate glass melts may be mentioned which usually are considered to have a very good non-isothermal workability [1]. The addition of PbO to these melts causes a decrease of B [8], thus, also an increasingly good isothermal workability may be expected as well

Table 3. Deformation rate, $\dot{h}$, in mm/s, at which the relaxation modulus of $E(t)_{max} = 5$ GPa is reached at a comparable equilibrium viscosity of $\eta_0 = 10^{7.5}$ Pa s

NaPoLi glass	CaBa glass	glass no. 1	optical glass	float glass	glass no. 2	glass no. 3	borosilicate glass
259	53	21	20	7	7.5	5.5	2.5

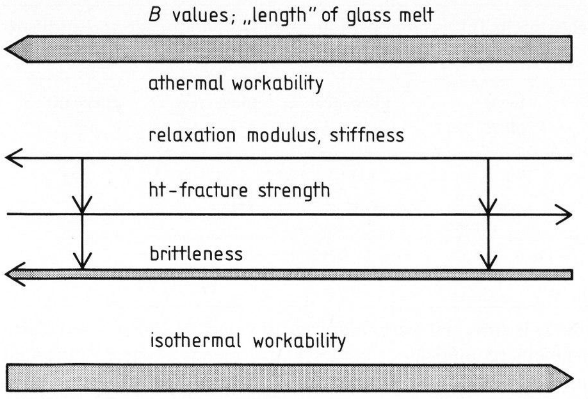

Figure 2. Connection between athermal and isothermal workability and various physical properties.

as a further classification within the lead silicate glass melts.

3. Conclusions

The statements given in the introduction could be well confirmed. Concluding from the results one can say that a good isothermal workability is characterized by a low relaxation modulus, low stiffness and a large ht-fracture strength and that this is connected to a low B value of the VFT equation (figure 2). This gives the possibility to estimate the isothermal workability of a glass melt from the quantity B of the VFT equation or from the specific factors for calculating the B value from the chemical components if available. In both cases, however, the determination of the constants in the VFT equation has to be done with exact measurements over an extended viscosity range ($\eta_0 = 10^1$ to 10^{12} Pa s) for which the three-points method [10] is only suitable for a rough comparison but usually not sufficient for exact comparisons and fine distinctions.

The given statements become problematic if the melts show phase separation because decomposition, nucleation and crystallization change the mechanical properties of a melt drastically [11].

The main result of this paper is that a distinction has been made between "athermal workability" and "isothermal workability" (figure 2) which are acting in a contrary course. This may be the reason why the conception "workability" was so difficult to define and why it has led to controversial conclusions. A good athermal workability is connected to a high B value which characterizes a "long glass". Usually a "long glass" can be handled much better in practice when a glass body is formed relatively slow because the viscosity does not change so much within a given temperature interval. A good isothermal workability in contrast is connected to a low B value which characterizes a "short glass".

Now, the question arises about the relative importance of the isothermal workability concerning the assessment of the forming process of glass melts. It can be stated that its importance increases with increasing deformation rate which is equivalent with increasing production rate. This leads to relatively small viscosity and temperature intervals for which the "length of a glass" is of decreasing importance and the preconditions for isothermal workability are dominating.

Three typical examples may be given:

First, the fiber drawing process is a very strong forming process in which a low viscous melt with a low velocity and with a small surface is formed to a rigid body with high velocity and with a very large surface. During this process extremely high deformation rates up to 10^5/s and cooling rates up to 10^7 K/s can be obtained [12]. Thus, stresses are built up within the viscoelastic range during a very short time interval which may overcome even the strength at a certain distance from the nozzle but within the gob. Exactly at this local point of ht fracture not the athermal workability – which should be good among other criteria for good fiber spinnability – is of importance, but exclusively the isothermal workability with its characteristic properties of the glass melt (stiffness and brittleness, determined by relaxation modulus, ht-tensile strength and flow behaviour depending on distinct values for deformation rate, deformation stress and temperature). These properties at the moment and location of fracture have nothing to do anymore with the slope of the viscosity-temperature curve and nothing with the B value and therefore nothing with athermal workability directly. The empirical findings of tables 1 and 2 only say that athermal workability and B values are usually contrary to isothermal workability.

Second, the situation of the fiber drawing process seems at first to be an exotic situation of failure. This is not the case because it characterizes the situation of failure for a viscoelastic material at a relatively high temperature, low viscosity, high deformation rate and high degree of deformation compared with the situation of the glass container pressing or blowing process, for instance. The field for the isothermal workability with its various properties responsible for a possible failure is only shifted to lower temperatures, higher viscosities, lower deformations and deformation rates; thus, the situation with respect to isothermal workability is readily transferable to any local point within a glass melt body which is under deformation where the stresses overcome the tensile strength of the glass melt. This is even valid in the neighbourhood of T_g (above and partly below) when additionally thermal stresses are built up in the surrounding of the critical point of failure.

Third, a well-known process is the cutting-off process of the glass melt gob from the feeder/plunger device, where high deformations and deformation rates during the short moment of cutting are shifting the various properties of workability from those which determine the athermal towards those which determine the isothermal workability. Failures at this point depend on the special conditions, particularly on the cutting speed, viscosity and thickness of the gob.

In all these cases other properties than the viscosity-temperature curve are dominating and these are the relaxation modulus which characterizes the stiffness of a glass melt and the ht-fracture strength, both properties characterizing the brittleness of a glass melt. The result is that isothermal workability becomes increasingly better with decreasing brittleness, that means, with increasing ht-fracture strength and decreasing relaxation modulus (figure 2). But also in cases of similar glass melts which differ in small variations of minor components as "water" content, arsenic, redox condition or additions of cullets in the batch, the influence of properties on the isothermal workability becomes more and more significant and can influence the production very sensibly [13]. At any rate the two kinds of workability show contrary behaviour as indicated in figure 2. Thus, when one property from this diagram is determined the trend of the other properties can be obtained. This is, however, only valid for glass melts without any crystalline or liquid-liquid (amorphous) phase separation [11].

What does "good workability" mean in practice? It has to be found an optimum between athermal and isothermal workability which is directed to the special forming process at its most critical point. The isothermal workability is determined by the field of mechanical properties and parameters of a glass melt, which is directed to the brittleness, degree of deformation, deformation rate, mechanical stress and viscosity, but the athermal workability is determined by the field of thermal properties and parameters which is directed to the slope of the viscosity-temperature curve, cooling rate, temperature gradient, heat radiation, specific heat, thermal conduction, thermal expansion and thermal stress. Because of the fact, which is the main point of this paper, that the two conceptions do not act in the same direction they have to be distinguished and considered separately. In special cases a distinction has to be made also between isothermal and isochomal workability as was emphasized already in section 1. and in [3 and 13].

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