STUDY OF THE BEHAVIOUR OF FRIT AND GLAZE MELTS BY HOT-STAGE MICROSCOPY AND DILATOMETRIC ANALYSIS

Amorós, J.L.; Belda, A.; Orts, M.J.; Villarroya, C.

Instituto de Tecnología Cerámica
Asociación de Investigación de las Industrias Cerámicas. Universidad Jaume I. Castellón. Spain.

1 INTRODUCTION

The variation interval of the viscosity of a molten glaze with temperature is very wide, with limits ranging from 10^3 to 10^{13} dPa.s. Its determination therefore requires using more than one experimental technique. In this study, hot-stage microscopy and dilatometric analysis have been used for the full determination of the viscosity-temperature curve of a molten glaze. These techniques do not directly measure the viscosity of the glaze melt, but allow determining certain characteristic glaze behaviour temperatures during fusion, to which specific effective viscosity values are assigned.

2 EXPERIMENTAL

In order to verify whether the effective viscosity values assigned to the characteristic temperatures were correct, NIST SRM-717 and SRM-710a standard glasses were used, whose viscosity-temperature curve was known.

Dilatometric analysis was run on the standard glasses and the glazes. The resulting thermal expansion curves allowed determining the transformation temperature (T_g) and softening temperature (T_R), to which viscosities were respectively assigned of $10^{13.3}$ and $10^{11.3}$ dPa.s.

The lowest effective viscosity values were determined by following the evolution that the geometry of a 3 mm high cylindrical test specimen, with a diameter of 3 mm, exhibited when it was heated in a hot-stage microscope. This procedure is based on obtaining the temperature values at which the test specimen acquires a certain degree of deformation or a certain geometrical shape, to which specific fixed effective viscosity values are assigned
(η_E).

The standard glasses were used to study how heating rate (a) and mean particle size ($\overline{D}$) affected the characteristic temperatures determined with a hot-stage microscope. It was also verified whether the proper viscosities had been assigned to these temperatures.

3 RESULTS AND DISCUSSION

The characteristic temperatures obtained by hot-stage microscopy and the effective viscosity values found were: shrinkage starting temperature (T_{ic}, viscosity = 10^{10} dPa.s), softening temperature or edge-rounding temperature (T_a, viscosity = $10^{6.2}$ dPa.s) and semi-sphere temperature (T_s, viscosity = $10^{3.7}$ dPa.s). These temperatures are not fixed viscosity points, but it was experimentally shown that these temperatures may be assigned to homogeneous glasses or glazes in which no phase separation or crystallization arises.

Table 1 details the characteristic temperatures of the standard glasses, obtained under different operating conditions.

Table 1. *Characteristic temperatures of standard glasses SRM-717 and SRM-710a*

Glass	$\overline{D}$ (μm)	a (°C/min)	T_g±3 (°C)	T_R±3 (°C)	T_{ic}±10 (°C)	T_a±10 (°C)	T_s±5 (°C)
717	10	10	510	588	610	810	1135
717	10	5	510	588	610	790	1125
717	25	10	510	588	630	810	1055
710a	10	10	566	622	630	825	1050
710a	10	5	566	622	630	800	1040
710a	32	10	566	622	660	800	1040

The operating conditions modified the characteristic glass temperatures obtained in a hot-stage microscope. On lowering the heating rate (a), the softening and semi-sphere temperatures decreased, while starting shrinkage temperature remained constant. On raising particle size, this last temperature rose, semi-sphere temperature dropped, and the softening temperature remained constant for glass SRM-717, whereas it fell for glass 710a.

The values have been compared in Table 2 of the temperatures at which the molten glass reached characteristic effective viscosities, obtained from the standard η-T curves (T^*) and the experimentally determined temperatures in the hot-stage microscope.

Table 2 *Viscosities of standard glasses SRM-717 and SRM-710a at the characteristic temperatures obtained in the hot-stage microscope.*

Glass	$\overline{D}$ (μm)	a (°C/m)	T_{ic}			T_a			T_s		
			T^* (°C)	T (°C)	ε_r (%)	T^* (°C)	T (°C)	ε_r (%)	T^* (°C)	T (°C)	ε_r (%)
717	10	10	612	610	-0.3	815	810	-0.6	1109	1135	+2.3
717	10	5	612	610	-0.3	815	790	-3.1	1109	1125	+1.4
717	25	10	612	630	+2.9	815	810	-0.6	1109	1055	-4.9
710a	10	10	630	630	0	816	825	+1.1	1065	1050	-1.4
710a	10	5	630	630	0	816	800	-2.0	1065	1040	-2.3
710a	32	10	630	660	+4.7	816	800	-2.0	1065	1040	-2.3

It can be observed that the relatively smallest errors arose when the following operating conditions were used: fine particles (milling till obtaining $\overline{D}$ of 10 μm) and a heating rate of 10 °C/min (except for the semi-sphere temperature of glass SRM-717). Moreover, the absolute values of these errors were small, which indicates that the selected viscosity values for the characteristic temperatures were correct.

With regard to the semi-sphere temperature ($T_{s)}$, the relative errors that arose exceeded those corresponding to the other characteristic temperatures, probably because the determination of this temperature was influenced by the surface tension of the melt and glass density.

4 REFERENCES

[1] FERNÁNDEZ, J.M. *El vidrio*, Madrid: CSIC, 1991.

[2] MAGRINI, F. *et al.* En: *3rd CERP Proceedings*, Faenza: Faenza Editrice, 1979, 94-102.

[3] CHESA, Técnica Cerámica, 213, 304-312, 1993.2