CHARACTERISTIC POINTS OF CERAMIC GLAZES DETERMINED BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

DTA analysis was used to determine the lower annealing, transformation, Littleton, sintering and flow temperatures of different frits customarily used in the ceramic sector. These temperatures were used to plot the viscosity-temperature curve, which was superimposed on the curve obtained by dilatometry and hot stage microscopy. The DTA results match the foregoing findings quite well, when an appropriate particle size is consistently used in addition to a set heating rate.

1. INTRODUCTION

The use of the differential thermal analysis technique began towards the year 1916 with the study of the cooling of a glass sheet [1]. However, it was not until some years later that the work of Tool et al. led to the use of this technique in studies on phenomena directly related to glass properties in the transformation temperature domain [2], [3]. Based on these studies, the differential thermal analysis technique (DTA) was consolidated as a further measurement to be taken into account when studying a great part of the phenomena relating to glass.

The different aspects in which the DTA technique can be applied, while at the same time contributing a great deal of information, include:

- characterization of the vitrifiable mixtures, fusion, refining.
- structure and heat treatments.
- phase separation, crystallization, polymorphism.

These applications include the first ones conducted by Yamamoto [4], in which he proposed the determination of the characteristic glass points from the DTA curve, points that largely match those determined by three other independent techniques, namely dilatometry, hot stage microscopy and high temperature viscosimetry (specifically the Littleton point). In accordance with this work, if the DTA equipment is sufficiently sensitive, it is possible to determine the following points: shrinkage, transformation, annealing, deformation start, Littleton softening, sintering, flow and working point. These points or temperatures correspond to logarithm of viscosity values of 14.5, 13.3, 13.0, 11.0, 7.6, 6.0, 5.0 and 4.0, respectively. These values have an error below 5% with regard to the ones determined by other techniques, enabling construction of the viscosity-temperature curve of any glass just with the DTA technique.

However, as in addition to all these characteristic points it is possible to detect others relating to crystallization and phase separation processes, etc., as indicated previously, some of the points already mentioned may be masked by these processes.

In this work, we have applied the DTA technique to the study of several frits used in the ceramic floor and wall tile industry and have determined the most representative characteristic points in each.

2. EXPERIMENTAL PROCEDURE

In this study, we have used three frits of different composition employed in the glaze formulation used for porous single firing. For one of these frits, we studied the effect of particle size on the results obtained by the DTA technique, and after verifying that the best size was the finest, the other frits were milled in an agate mill. The equipment used for analysis was a Perkin-Elmer DTA-7 model instrument. The reference material used was high-temperature α-Al_2O_3. The set operating conditions were: peak temperature 1300 °C, heating rate 7 °C min^{-1}, cooling rate 10 °C min^{-1}, and air atmosphere. The characteristic points of the three

frits were determined beforehand by dilatometry and hot stage microscopy (HSM) measurements.

The samples used as well as their characteristic points are given in Table 1.

Characteristic Point (°C)	Nomenclature	Technique	Sample			
			A	B	C	D
Transformation	Tg	Dilatometry	657	588	681	675
Softening	Trd	Dilatometry	816	609	816	859
Sintering	Ts	HSM	900	679	877	917
Softening	Trc	HSM	1060	814	988	1139
Sphere	Te	HSM	1085	843	1078	-
Half sphere	Tme	HSM	1130	1135	1144	1172
Flow	Tf	HSM	1170	1160	1205	1189

Table 1. Characteristics of the frits used

3. RESULTS AND DISCUSSION

Figure 1 displays the different DTA curves obtained for sample A using different particle sizes. They show that when the particle size is below 50 micrometers, the transformation region appears where the Tg and Trd corresponding to the values measured by dilatometry, as well as the Littleton point (Tlt) and the sintering point (Ts), can be observed. After this last point (Ts), two minimums also appear which could resemble the softening (Trc) and sphere (Te) temperatures. The half sphere temperature (Tme) corresponds to the following maximum observed in the curve, and at the end of the curve there is a change in the slope attributable to the flow temperature (Tf). The temperatures (in °C) at which these characteristic points appear according to the DTA curve are detailed in Table 2, involving values that in several cases resemble the ones detected by the other techniques.

For those characteristic points where the values determined by DTA vary significantly compared with those of the other techniques, this variation is attributable to phenomena caused by the complex chemical compositions typically used in formulating frits for glazes. For certain compositions it is normal for phase-separation phenomena (of one or more phases) to occur, as well as crystallization (start and growth of crystals), etc., which are detectable by the DTA technique but not by the other techniques mentioned, which however originate thermal changes and therefore peaks or valleys in the DTA curve. Thus, for example, the Trd temperature of 695 °C obtained by DTA is considerably lower than the 816 °C provided by the dilatometric technique. If we take into account that a variation in the heating rate can originate changes of +/- 20 °C in these points, the difference found of 122 °C can only be due to possible phase separations which occur in the glassy structure of the frit [5], [6]. Therefore the Trd temperature (695 °C) found must correspond to the lower softening temperature phase. In this sense the DTA curve shows a flexion in the curve between the Trd and Tlt points at 810 °C, a value that coincides quite well with the dilatometric softening.

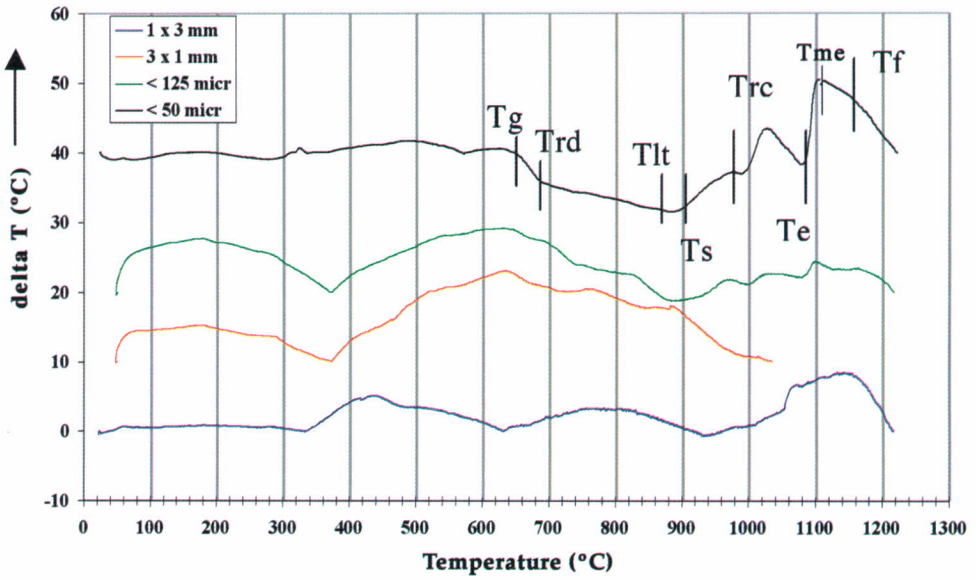

Figure 1. DTA curves of frit A for different particle sizes.

Figure 2 depicts the DTA curves corresponding to the other three frits referenced B, C and D of Table 1. The particle size was below 50 micrometers in every case. These three frits have been chosen because they have different transformation temperatures, which are temperatures that can be characterized quite well by DTA. The values of the temperatures corresponding to the characteristic points are given in Table 2, and are marked in Figure 2.

Figures 1 and 2 show that the four frits display quite differing thermal behaviour to each other due to their different chemical composition. Thus, for example, the DTA curve of frit D (Figure 2) displays a clear exothermic peak characteristic of strong crystallization, which will alter the mentioned characteristic points.

FRIT	TEMPERATURES OF THE CHARACTERISTIC POINTS (°C)							
	Tg	Trd	Tlt	Ts	Trc	Te	Tme	Tf
A	657	695	880	908	997	1084	1113	1155
B	553	600	670	707	776	872	922	1000
C	683	720	800	870	975	1077	1112	1192
D	682	725	785	1020	1157	1195	1236	1244

Table 2. Experimental results obtained by DTA

In accordance with the results of Table 2, it can be concluded that the DTA technique enables accurately determining the characteristic points of the frits provided they display no phase transformation or crystallization phenomena, etc. Phase separation mainly affects the dilatometric softening points, whereas crystallization affects sintering, sphere, half sphere and flow points. The effect of these phenomena is that different values are found for the characteristic temperatures of each frit. However, if this DTA technique is applied independently as a characterization of each frit, the results are reproducible and could replace the dilatometry, viscosimetry and hot stage microscopy techniques.

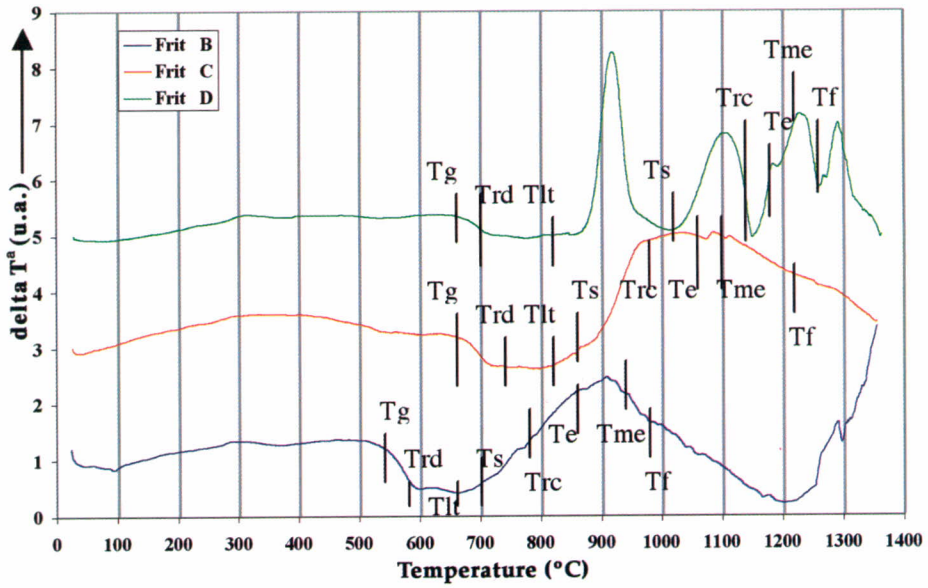

Figure 2. DTA curves for three frits with different characteristics.

4. CONCLUSIONS

In this study, it has been attempted to correlate the characteristic points of the frits used for ceramic glazes, determined by different techniques, with those determined by DTA. The results indicate that while the transformation temperature is practically the same as that obtained by the different techniques used, the rest of the temperatures can vary, depending on the chemical composition of the frit and particularly of the presence of phase separation and crystallization.

REFERENCES

[1] K. Quasebart. Die Entsickelung und der gegenwärtige Stand in der Feurungstechnik in der Glasindustrie. Sprechsaal, 49 (1916) 3-5

[2] A. Q. Tool, C. G. Eichlin. Absorption of heat in glass. J. Opt. Soc. Amer. 4 (1920) 419-450;

[3] A. Q. Tool, C. G. Eichlin. Certain effects produce by chilling glass. J. Opt. Soc. Amer. 8 (1921) 419-450

[4] A. Yamamoto. Detection of characteristic points of commercial glasses by differential thermal analysis. Proc. 1st. Int. Conf. Therm. Anal. (1965). Pp. 273-274

[5] A. Q. Tool. Effect of heat-treatment on the density and constitution of high silica glasses of the borosilicate type. J. Am. Ceram. Soc. 31 (1948) 177-186;

[6] R. L. Thakur, K. Takizawa, T. Sakaino, T. Moriya. Cent. Glass Ceram. Res. Inst. Bull. 11 (1964) 1-22