

*Hot-stage microscopy has been used successfully to characterize glaze-melting behavior.*

# CHARACTERIZING GLAZE-MELTING BEHAVIOR VIA **HSM**

**T**he melting behavior of glazes and glass coatings affects surface smoothness and homogeneity, bubble evolution, crystallization, dissolution of colorants and refractory oxides, reactions between the body and underglazes, and formation of the body-glaze interface. To improve industrial glazes, it is important to understand the melting behavior under industrial firing conditions.

Hot-stage microscopy techniques can be applied for direct characterization of glazes, glasses and ceramic bodies during firing.<sup>1-7</sup> Newer models of the hot-stage microscope (HSM) can simulate industrial firing curves up to 1600°C with heating rates as high as 80°C/min. The primary parameters of interest for HSM analysis are the side-view dimensions and shapes of samples.

Samples are typically formed in 3 mm high × 2 mm diameter cylinders, and dimensional changes as small as ±0.01% can be measured every 1°C during heating and cooling. The small sample size ensures that the surface tension forces during melting are large relative to the hydrostatic pressure, which allows for spherical and semispherical shapes to form. The sample dimensions can be then directly related to sintering, softening, flow, wetting of the substrate and surface tension.

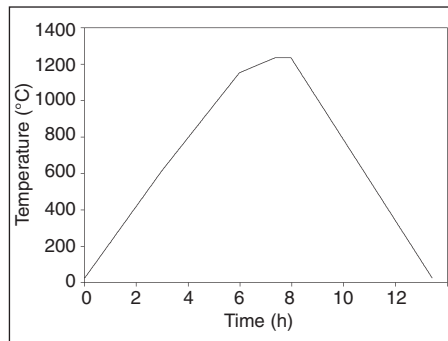
Melt viscosity vs. temperature curves also can be derived based on models that require inputs from HSM and dilatometric measurements. The HSM has been applied in assessing the thermal behavior of glasses, ceramic frits, glazes, clays, feldspars and other silicate materials.

The current study uses a HSM to characterize the melting behavior of three porcelain glazes with different SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratios. The HSM technique has been widely used in Europe to study the melting behavior of tile glazes. The purpose of the article is to introduce the technique and illustrate its application to the study of melting behavior of glazes for high-voltage porcelain and dinnerware.

## **Background**

Several characteristic points are important for studying the melting behavior of ceramic glazes and frit powders. Above the

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Typical industrial dinnerware firing cycle. Only the heating cycle is used for the HSM runs.

glass transition temperature ( $T_g$ ), particles sinter together, and viscosity decreases rapidly. Depending on the heating rate, glazes can develop a more orderly structure (crystallization) or pass to a viscous liquid state.

With an increase in temperature to and above the softening point ( $T_s$ ), there is a further decrease in viscosity, and the glaze behaves similar to a high-density liquid. At  $T_s$ , the effects of surface tension and viscosity become relevant. At the peak firing temperature, the glaze viscosity is ideally in the range of  $10^3$ – $10^4$  Pa·s to ensure proper coverage of the substrate and a smoothly fired surface.<sup>3</sup>

Glasses and ceramic glazes follow Arrhenian behavior at high temperatures and below  $T_g$ , and their viscosity dependence on temperature is given by

$$\eta = \eta_0 \exp(Q/RT) \quad (1)$$

where  $Q$  is the activation energy for viscous flow,  $\eta$  the melt viscosity, and  $\eta_0$  a temperature-independent coefficient. However, at intermediate temperatures above  $T_g$ , the actual viscosity is greater than Eq. (1) predicts, because the activation energy for viscous flow is not constant.

The Vogel–Fulcher–Tamman (VFT)<sup>8–10</sup> equation adds another variable,  $T_0$ , to the Arrhenian expression:

$$\log \eta = A + B/(T - T_0) \quad (2)$$

where  $A$ ,  $B$  and  $T_0$  are constants.

Glaze			
Temperature	A	B	C
1100°C			
1125°C			
1150°C			
1175°C			
1200°C			

HSM images of samples at 25°C intervals during the firing cycle. Improved leveling of the glaze occurs as the  $\text{SiO}_2\text{:Al}_2\text{O}_3$  ratio decreases from A to C.

The VFT equation provides a good fit to viscosity data over a wide temperature range and is commonly used to calculate the viscosity of industrial glasses and glazes.




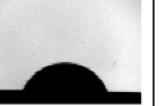
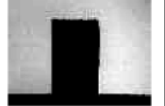







In Eq. (2), constant  $\eta_0$  is replaced by  $A$ ,  $Q$  is replaced by a less-defined variable  $B$ , and  $T$  and  $T_0$  are given in degrees celsius rather than kelvin.

Graphically, the VFT equation can be represented with a straight-line plot of  $\log \eta$  vs.  $1/(T - T_0)$ , where  $A$  is the y-intercept,  $B$  the slope of the line and  $T_0$  the measure of deviation of the curve from the ideal straight line of nonassociated liquids.

The activation energy for viscous flow and the corresponding slope of the tangent to the viscosity curve increase with decreasing temperature. Fulcher<sup>8</sup> introduced  $T_0$  as a purely empirical constant whose purpose was to linearize the hyperbolic viscosity curve. The  $T_0$  constant characterizes the degrees of association of molecules (with nonassociated liquids,  $T_0 = 0$ ) and, therefore, depends on the type of glass and the viscosity range being measured.

The elimination of the term  $B/(T - T_0)$  results in  $\log \eta = A$ . This occurs when either  $B = 0$  or  $T = \infty$ . Therefore, the constant  $A$  represents a theoretical viscosity of completely free particles requiring no activation energy for their induction into viscous flow or viscosity at an infinitely high temperature.<sup>11</sup>

The melt viscosity can be estimated from dilatometric and HSM measurements based on three known reference points: <sup>5–7,12–13</sup>  $\eta = 10^{12}$  Pa·sec at the dilatometric  $T_g$ ;  $\eta = 10^{9.25}$  Pa·sec at the dilatometric  $T_s$ ; and  $\eta = 10^{3.55}$  Pa·sec at the HSM  $T_{1/2}$ , where  $T_{1/2}$  is the temperature where a sample forms a half-sphere shape during HSM analysis. The half-sphere point is

Firing stage				
Glaze	Sintering	Rounding	Half-sphere	Third-sphere
A	 1071°C 95.39% 96°	 1134°C 84.62% 70°	 1158°C 52.20% 89°	 1206°C 36.82% 116°
B	 1064°C 94.6% 88°	 1136°C 80.00% 73°	 1165°C 49.5% 88°	 1207°C 36.82% 116°
C	 1055°C 94.51% 82°	 1127°C 90.61% 80°	 1170°C 50.55% 91°	 1194°C 39.02% 110°

Selected HSM images of the samples during firing. Listed below the images are the characteristic shape temperatures, percent of initial sample height and contact angles.

Compositions of Three Glossy Dinnerware Glazes Studied			
Molecular formula	Molar equivalents†		
	Glaze A	Glaze B	Glaze C
SiO <sub>2</sub> :Al <sub>2</sub> O <sub>3</sub>	9.22	8.40	5.99
Al <sub>2</sub> O <sub>3</sub>	0.38	0.40	0.65
Σ RO <sub>2</sub>	3.64	3.40	3.92
Σ R <sub>2</sub> O <sub>3</sub>	0.50	0.50	0.81
Σ R <sub>2</sub> O	0.19	0.19	0.26
Σ RO	0.81	0.81	0.74

†Calculated based on the Seger rules.

reached when the height of the sample is half the width of the base and the contact angle is 90°. The three reference points can be input into the VFT equation to solve for the three unknown constants A, B and T<sub>0</sub>:

$$T_0 = \frac{12T_g - 3.55 T_{1/2} + (9.25 T_s - 12T_g) \frac{T_{1/2} - T_g}{T_s - T_g}}{8.45 - 2.75 \frac{T_{1/2} - T_g}{T_s - T_g}} \quad (3)$$

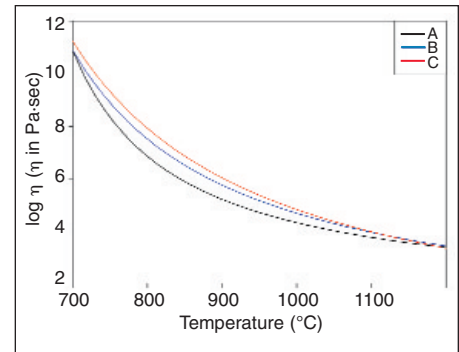
$$A = (9.25T_s - 12T_g + 2.75T_0)/(T_s - T_g) \quad (4)$$

$$B = (T_g - T_0)(12 - A) \quad (5)$$

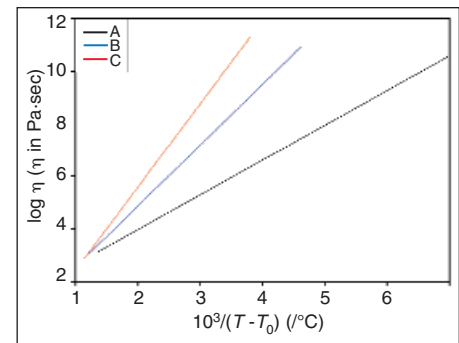
where all temperatures are in degrees celsius, and the coefficients and constants refer to viscosity values in Pa-sec.

A reference value of 10<sup>12</sup> Pa-sec for the viscosity at T<sub>g</sub> is well accepted for all types of silicate glasses.<sup>1,2,4-7,12</sup> The value for viscosity at T<sub>1/2</sub> has been adopted from research by Scholze,<sup>7,13</sup> where the viscosity of pressed powder samples from nine various types of glasses has been shown to be ~10<sup>3.55</sup> Pa-sec at T<sub>1/2</sub>. The half-sphere shape has been chosen as a reference point, because it is easily recognized and provides for precise measurements.

In a recent development, Duran and others<sup>6</sup> verified the



log η vs. temperature based on the derived VFT constants. As expected, viscosity increases as SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio is decreased from glazes A to C.



Straight lines have slopes equal to the VFT constant B. Shown is an increase in the rate of change of viscosity with decreasing SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> ratio from samples A to C.

observations by Scholze using rotational viscometer measurements of five commercial glasses, where log η at T<sub>1/2</sub> was 3.6 ± 0.1 Pa-sec. Although Scholze selected the HSM rounding temperature as the third reference point, Margini et al.<sup>5</sup> initiated the use of the dilatometric T<sub>s</sub>. Published values for the viscosity at the dilatometric T<sub>s</sub> tend to vary between 10<sup>8</sup> and 10<sup>10</sup> Pa-sec for various compositions.<sup>5,12,14</sup> Margini et al.<sup>5</sup> determined a viscosity of 10<sup>9.25</sup> Pa-sec at T<sub>s</sub> for multi-oxide silicate-based glazes and glaze frits.

## Principal Investigation Device

The HSM consists of three principal units mounted on an optical bench 1.5 m long: a halogen lamp light source; an electric furnace (200 mm in length and 20 mm in diameter) with sample carriage; and an observation unit with a microscope and

recording facility (either a photographic or a video camera).

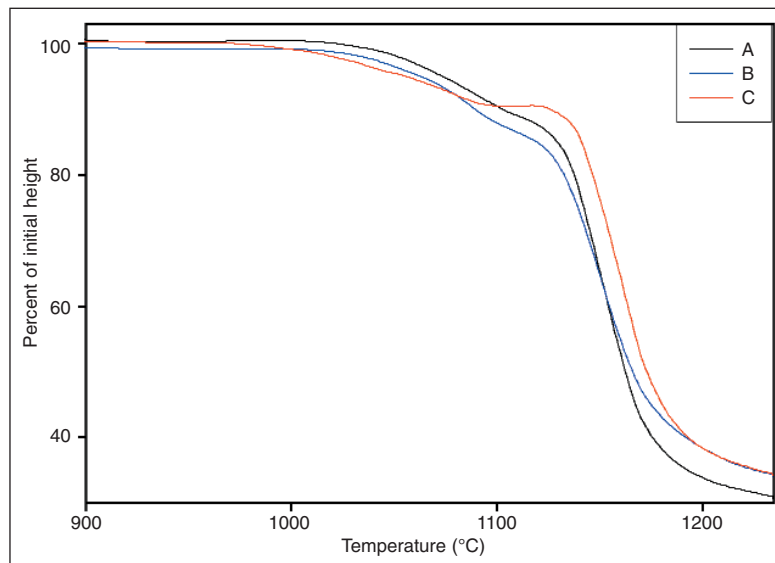
A sample is normally placed on a small alumina plate at the end of a thermocouple. An image analyzer accounts for the thermal expansion of the alumina substrate while measuring the height of the sample during firing, with the base as a reference. Various substrates can be used to investigate the effects of substrate–glaze interactions although viscosity calculations based on  $T_{1/2}$  yield erroneous results unless an alumina substrate is used.

The microscope projects the image of the sample situated in the furnace at  $\sim 5\times$  magnification through a quartz window and onto the recording camera. Temperature is controlled using an automatic furnace control unit, incorporating a program for variable heating rates and several dwell times. Sample images and shape changes are automatically recorded in-situ during heating.<sup>2</sup>

To use the HSM as an analytical technique, a simulated industrial firing cycle and a sample that is dimensionally equivalent to the glaze-layer on the ceramic ware must be used. The samples must be cylindrical in shape, because this is the only shape that enables the microscope to focus on a plane that does not change during the shape transformations induced by heating. The vertical cross section of the cylinder corresponds to the vertical cross section of the resulting sphere or hemisphere that appears during melting.

A further advantage of the samples having a cylindrical geometry is that axial and radial shrinkage can be recorded simultaneously, and anisotropy effects during sintering can be accurately assessed. The use of prismatic samples must be avoided, because they require a continuous change in the focus.

The HSM sample size has been developed considering the balance between gravitational, viscous and surface tension forces acting on the glaze during the melting process. The viscosity alters the rate of mass transfer, which is essential for



From  $\sim 1100$  to  $1125^\circ\text{C}$ , the high- $\text{Al}_2\text{O}_3$  glaze ceases to flow, possibly because of  $\text{Al}_2\text{O}_3$  dissolution.

Measured Values of Reference Temperatures and Calculated VFT Constants						
Glaze	Reference temperature ( $^\circ\text{C}$ ) <sup>†</sup>				VFT constant <sup>†</sup>	
	$T_g$	$T_s$	$T_{1/2}$	$T_0$	A	B
A	686	729	1158	562.2	1.3	1320.2
B	679	738	1165	484.0	0.2	2309.6
C	685	753	1170	437.4	-0.8	3160.8

<sup>†</sup> $T_g$  is glass transition temperature;  $T_s$  is dilatometric softening temperature;  $T_{1/2}$  is HSM half-sphere temperature;  $T_0$ , A, and B are calculated VFT constants.

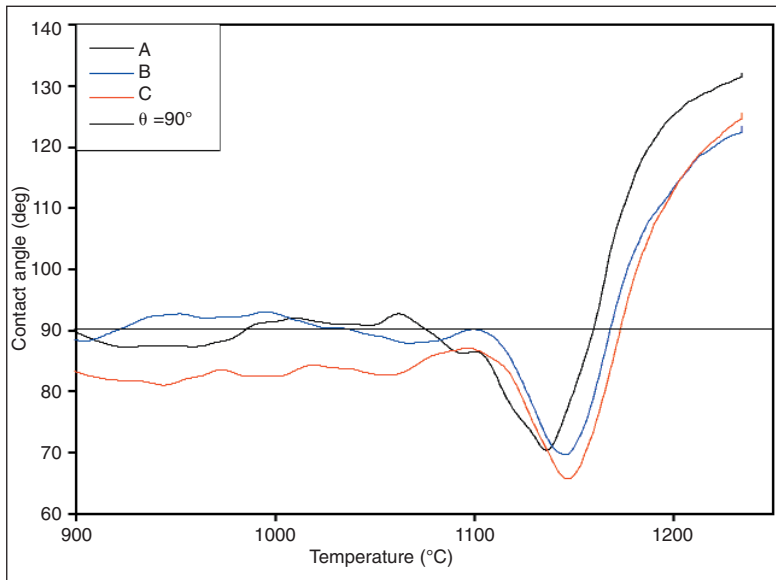
producing a shape change.

Paganelli<sup>1</sup> analyzed two industrial glaze compositions using an automatic HSM to determine the optimum sample size. After samples of three different dimensions were analyzed, it was concluded that a medium size of 3 mm in height and 2 mm in diameter gave the optimum results. This was an optimal compromise between the difficulties of sample preparation and consistency of results.

## Test Procedure

The three industrial dinnerware glazes investigated differed mainly in the  $\text{SiO}_2\text{:Al}_2\text{O}_3$  ratio. The particle-size distributions of the glazes were almost identical, with mean diameters of  $\sim 9\ \mu\text{m}$ . Glaze powder samples were pressed into 3 mm high  $\times$  2 mm diameter cylinders for analysis using an automatic HSM (Misura 3, Expert Systems Srl, Modena, Italy). A typical industrial dinnerware firing curve was used for the heating profile.

Other data collected using the HSM are the percent of initial sample height and the contact angle curves. The percent of initial height plots indicate the balance between gravitational, viscous and surface tension forces acting on the glaze during the melting process. The contact angle plots relate to the interfacial tension between the melting glaze and the body substrate. A



Contact angles are determined by drawing tangents to outer surfaces of the HSM images. Although the surface tensions of these samples were not high enough to form spherical shapes, glaze C reached the lowest contact angle and, thus, appeared to have the highest surface tension.

lower minimum on a plot corresponds to a higher interfacial tension, where the contact angle is  $\sim 45^\circ$  when the sample forms a sphere shape.

Glass and glaze viscosity values derived from the method described in this article are being compared with rotating-spindle viscometer measurements and values predicted by the Sci-Glass program. Other work also is being performed to derive surface tension values directly from HSM images.

The dilatometric data, VFT constants, HSM images and derived viscosity-temperature plots show the expected transition in melting behavior with changes in the  $\text{SiO}_2:\text{Al}_2\text{O}_3$  ratio. The expected increase in viscosity of the glazes with increasing  $\text{Al}_2\text{O}_3$  content also has been illustrated. Although the data derived is approximate, the relative changes induced in glazes by varying the composition can be effectively characterized using the technique. ■

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### References

The list of references to this article is available on the Internet, [www.ceramicbulletin.org](http://www.ceramicbulletin.org); by Email, [references@acers.org](mailto:references@acers.org) or by fax at 614-794-5822. Request Data Depository File No. 365.