INFLUENCE OF GLAZE PARTICLE SIZE DISTRIBUTION ON SURFACE TENSION AND GLOSS

Felisbino(1), S.B.; Milanez(2), K.W.; Riella(2), H.G.; Bernardin(1), A.M.

(1) Departamento de Tecnologia em Cerâmica; Departamento de Engenharia de Materiais
Universidade do Extremo Sul Catarinense – UNESC
Avenida Universitária 1105; 88806-000; Criciúma, SC, Brazil
adriano@unesc.rct-sc.br

(2) Departamento de Engenharia Química
Universidade Federal de Santa Catarina – UFSC
Campus Universitário; 88040-900; Florianópolis, SC, Brazil
riella@enq.ufsc.br

ABSTRACT

This work shows a simple method to determine the influence of particle size distribution on the surface appearance of glazed tiles. Matte glaze was milled in a jar mill for eight different times (15min to 50min). The glazes obtained were then applied onto ceramic bodies with a prior engobe coating; the samples were fired in an industrial cycle, and the appearance of the final surfaces was analyzed using a glossmeter.

The same glazes were pressed uniaxially forming samples in cylindrical shapes. The specimens were applied onto the same engobe surfaces and fired at four different temperatures (1000°C, 1050°C, 1075°C and 1100°C) in a laboratory kiln. Finally, the contact angles between the molten specimens and the ceramic surfaces were measured to determine their surface tension. The results showed the correlation between glaze particle size distribution and the surface appearance of the final product.

KEY WORDS: Surface Tension; Glazes; Particle Size Distribution.

1. INTRODUCTION

Glasses are generally formed by solidification of a liquid. If the liquid crystallizes during the cooling, a discontinuity occurs in the volumetric contraction in the melting point region (Tm). However, if crystallization does not occur, the liquid maintains the same contraction observed in the liquid above the fusing point (Tm), until it reaches the discontinuity at a temperature known as the glass transition temperature (Tg). Below this temperature, the glass structure is not modified, independently of the cooling rate used. In this case the expansion coefficient of the glass state is approximately equal to that of the solid state for crystals of similar composition to the previous glass.

If smaller cooling rates are used, allowing relaxation of the structure, the supercooled state persists until lower temperatures, thus producing the densest glasses. In a similar way, during the heating of a glass material until its tempering temperature, at which a gradual relaxation occurs, the glass structure reaches a density corresponding to a supercooled liquid at this temperature. Therefore, a very important concept in glass properties is the glass transition temperature (Tg), which corresponds to the intersection temperature between the glass phase and a supercooled liquid. Different cooling rates correspond to different relaxation times, allowing different glass state configurations, corresponding to different Tg points along the supercooled liquid curve.

Amongst the rheological properties of glasses, viscosity is the most important. Viscosity is very sensitive to small differences in composition, allowing theoretical studies in glass structure or evaluation of important glass properties such as bubble retention, flow over ceramic bodies, quality control, glaze preparation or manufacturing. Viscosity controls several processes at different temperatures in tile manufacturing. Its magnitude during firing determines how the glaze flows over the ceramic body, forming a uniform layer without draining out of the surfaces. Viscosity also determines the ease of gas bubble elimination during glaze formation. Thus, the glaze firing interval is related to the magnitude of viscosity variation with temperature. This variation directly influences the workability, elaboration and relaxation of glasses.

Surface tension refers to the properties of an interface formed between two phases of a substance, and its magnitude depends on the state and nature of these two contiguous phases. Except when mentioned, the surface tension of a material usually involves air or vapour as second phase. In a multicomponent system (as a glass) there is a component concentration at its surface that reduces the surface tension. Reactions among liquid and solid glasses or refractories and metals involve three independent surface tensions, corresponding to three existing interfaces (liquid-vapour, solid-vapour and solid-liquid).

Simply put, surface tension can be defined as a force per unit area per length, which can be expressed by dynes per centimetre (dyn/cm). The surface energy per unit area has basically the same dimensions and can be expressed by the same units (dyn/cm^2). The glaze flow during firing is influenced considerably by its surface tension. There are few studies on this subject and the knowledge is comparative and empirical. Glass manufacturers have analyzed the influence of surface tension on reactions among glass components and on the disappearance of heterogeneities in glass fluids.

A low surface tension favours the elimination of gaseous bubbles during glass melting and prevents inhomogeneities, while a high surface tension favours the reabsorption of these bubbles during glass cooling. In a cast glaze with low surface tension, its surface will be smoother, bubbles and craters will be eliminated easily and the solid surface will be brighter; on the other hand, a very high surface tension favours the reabsorption of bubbles during cooling, causing glaze roughness (like "wrinkles").

When a glaze at a high temperature is in contact with the ceramic body, simultaneously to the surface tension σ (between the glaze and the air), interfacial stresses τ (between the ceramic body and the air) and λ (between the glaze and the ceramic body) act. The intensity and orientation of these three surface forces determine the so-called contact angle, related to the known Young equation: $\tau-\lambda = \sigma.\cos\theta$.

The contact angle plays an important role in high temperature glaze processing control, because it is the measure of the glaze capacity to wet the ceramic body (wetting force). If θ is greater than 90°, the glaze does not wet the ceramic body, but if it is smaller than 90° the glaze wets the ceramic body; the lesser the angle, the bigger will be the glaze "ability" to wet the surface. When $\theta=90°$, then $\cos\theta=0$, therefore $\tau=\lambda$. σ and τ vary very little with temperature, however λ (the surface tension between the glaze and the ceramic body) varies highly, because some important physico-chemical changes occur in the interface between the glaze and the ceramic body during firing.

The reduction in contact angle with increasing temperature is followed by a gradual reduction of the glaze/air tension, because the lesser the tension between the glaze and the air, the greater will be the affinity between the glaze and the ceramic body, causing greater wetting of the ceramic body; with the reduction of the glaze/air tension, there will be a parallel increase in glaze/ceramic body tension. When two glazes with different surface tensions overlap, the glaze with lesser glaze/air tension will tend to spread more over the other surface, penetrating it and breaking it, obtaining decorative effects. Surface tension is an additional function in relation to glass composition, and can be calculated from its chemical composition.

There are some methods to calculate surface tension. The drop weight method consists of dropping a cast glass through a calibrated orifice of a platinum pipe. The drops formed in the exit of the orifice leave the pipe at the moment where the weight force equals the surface tension, i.e., $mg=2\pi r\sigma$, where m is the mass of the drop, g the gravity acceleration, r the platinum pipe radius and σ the surface tension. In general it is necessary to introduce a correction factor to the previous equation due to experimental errors.

The bubble formation method is another procedure to measure the surface tension of a cast liquid. It is based on the formation of an air bubble when a platinum pipe is introduced a little depth into the centre of a cast glass, through which air is injected under pressure. The formed air bubble increases its volume; when the internal pressure increases, the bubble exits the pipe when its radius equals the radius of the platinum pipe. At this moment the air pressure p compensates the sum of the pressure ps, due to the surface tension, plus the hydrostatic pressure p_h of the cast: $p=p_s+p_h$. With p is calculated using the previous formula, it is possible to calculate the value of the surface tension:

$P=(2\sigma/r)+Tgh$, where r is the radius of the platinum pipe, T the cast glass temperature, and h the penetration depth of the pipe in the glass.

Any cause that modifies the cast glass chemical bond energy is reflected in a variation of its surface tension. Therefore, its magnitude generally diminishes when the temperature increases; however, the reduction is small, around 1% to 2% for each 100°C of temperature increase. Some glasses, especially those containing large amounts of PbO and B_2O_3, show anomalous behaviour and a positive surface tension coefficient. This fact can be explained as a consequence of lead and boron ion orientations at low temperatures, when both adopt a parallel orientation related to the cast surface, due the high electronegativity of lead ions and triangular planar configuration of boron ions (BO_3^-). A temperature increase creates a disturbance in this molecular order, giving rise to increases in surface tension in both cases.

Regarding the influence of chemical composition on surface tension, if the glass former groups degree of symmetry is large, the chemical composition influence is also large. Therefore, silicate glasses that present tetrahedral coordinations possess a bigger surface tension than borate glasses. The surface tension of glass former ions increases when the relation r/Z, between the radius and the charge of a cation, also increases, showing that modifier oxides diminish surface tension. Other factors that affect surface tension are glaze particle size distribution and cast glaze temperature.

Another important property related to surface glazes is brightness, the property of a surface to directly reflect the light. Brightness depends basically on surface roughness and absorbance. If brightness is high, it is easy to identify surface defects (flaws); for a low surface brightness the defects can be disguised and not identified. The surface degree of brightness can be measured observing the light reflection behaviour in surfaces using instruments called glossmeters. The numerical value obtained from these instruments corresponds to the surface reflection when a light with a definite angle of incidence strikes this surface. To obtain good measuring results the surface must be flat, free of flaws and uniform.

2. MATERIALS AND METHODS

The raw materials used to form the glaze composition were: a calcium matte frit, quartz (#325 mesh), kaolin, zirconium oxide, feldspar (#325 mesh), barium carbonate, bentonite, alumina (#325 mesh) and additives. The samples were prepared in an eccentric jar mill; the raw materials were milled in water according to eight predefined times, from 15min to 50min with 5min intervals between millings, forming eight homogeneous glaze compositions. The glaze particle size distributions were analysed using a LASER diffractometer (Sympatec Helos, 0.5μm resolution). The glaze suspensions were applied over an engobe coat with 0.4mm thickness (glaze coat). The samples (ceramic body with engobe and glaze coats) were thermally treated at four temperatures, 1000°C, 1050°C, 1075°C and 1100°C. Finally, the specular reflection index of each sample was measured using a glossmeter (Gloss Checker IG330).

In addition, the eight milled glazes (glaze powders) were uniaxially pressed (50bar specific pressure) in cylindrical shapes after drying, forming compact specimens with a constant weight; the specimens were dried at 110°C for 24h and fired at the same temperatures and conditions mentioned above. The purpose of this step was to compare the glaze melting interval when glaze particle size distribution were changed, measuring the wetting (contact) angle variation. After fast cooling (quenching), photographs were taken using a digital camera (2M pixel resolution) for a better comprehension of the milling influence (particle size distribution) on the measured internal contact angle θ.

3. RESULTS AND DISCUSSION

Observing the particle size distribution curves (figure 1), except for 15min milling, all the curves present a particle size distribution between 0.9μm and 10.5μm, with a mean size at 5μm (average diameter); as all the curves present the same form and particle size distributions, it can be concluded that the equipment resolution (0.5μm) is lower than the minimum required, i.e., the measurements overlap. Probably the real glaze size distributions are of smaller particle size than that measured by the equipment, and all results show curves with practically the same form, because the equipment cannot distinguish particle size distributions below 0.5μm (figure 1).

Particle size clearly influences the cast glass viscosity and modifies its surface tension. Excessively milled glazes present an intense contraction and breach when applied on a ceramic body; on the other hand, when a glaze is not sufficiently milled its particles will be very large, tending to deposit and to provoke segregation, causing defects after firing (surface roughness due to quartz presence, for example).

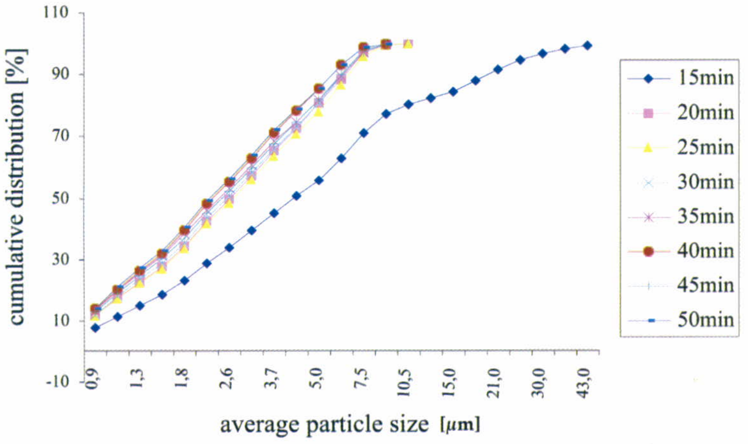

Figure 1. Graph of glaze particle size cumulative distribution curves.

Regarding the contact angle, photographs were shot using a digital camera (2M pixel minimum resolution) to measure the internal angle of the drop at 1100°C (figure 2). The internal angle of the drop diminishes with increasing glaze milling time until 35min milling. Further milling times (40min, 45min and 50min) resulted in an increase in internal drop angle. As discussed above, the extreme reduction of the glaze particle size involves an increase of surface tension between the liquid glaze and the air, because the cast glaze has a bigger interaction with air; this is the reason of the internal angle increase with higher milling times.

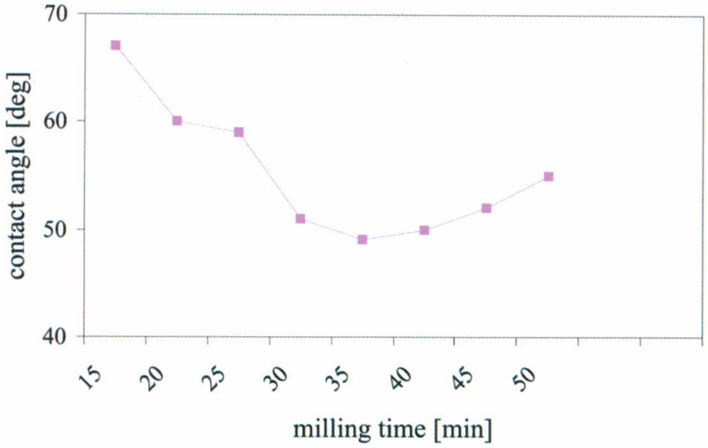

Figure 2. Graph of the relation between milling time and internal angle of the drop.

If such a glaze was applied on a ceramic body, it would form a coat with thousands of drops in contact each other; with the increase of surface tension between cast glaze and air, due to the extreme particle size reduction, there would be a strong interaction between the glaze and the air, resulting in an encapsulation of the air by the cast glaze. The glaze coat would be full of air bubbles.

This therefore shows the close relation between milling time and glaze wetting angle; the milling time directly affects glaze surface tension. The particle size reduction causes a decrease in the internal angle, figure 3. Probably the glaze viscosity reduction with temperature also takes part in this event, increasing glaze stretching over the ceramic body.

However, the internal angle (contact angle) tends to increase at greater milling times. As discussed above, the surface tension between glaze and air increases with the reduction of particle size. There is a greater interaction between the air and the molten glaze, resulting in air bubble absorption into the glaze bulk, what could be proven by a glaze microscopy analysis (not conducted). When applied on the ceramic body the glaze was completely stretched, because viscosity always diminishes with the reduction of the average particle size (increasing milling time). By microscopic analysis it could be proven that for bigger milling times the amount of bubbles would increase.

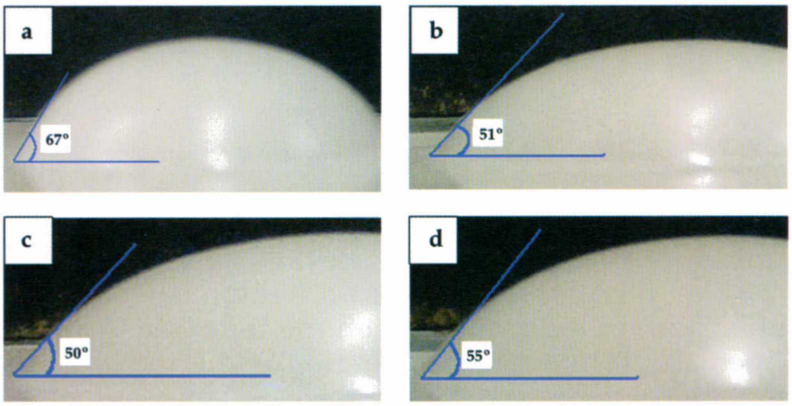

Figure 3. Contact angles measured for the studied glaze fired at 1100°C: (a) 15min, (b) 30min, (c) 40min and (d) 50min milling.

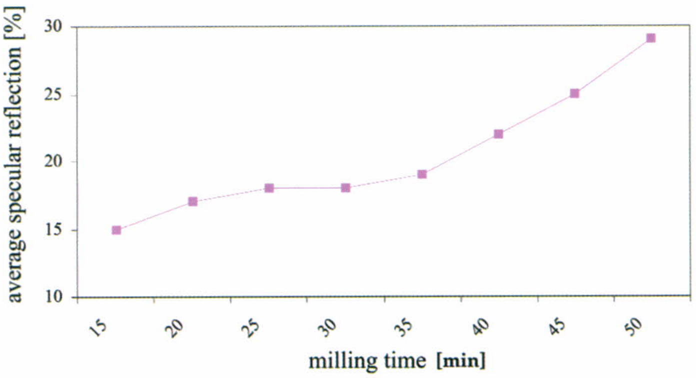

Figure 4. Graph showing the relation between milling time and specular reflection.

Finally, each sample was analysed regarding its brightness. The surface reflection was measured using a glossmeter (Gloss Checker IG330); ten readings were taken for each sample and the average used to qualify the surfaces (figure 4). Analysing the results, the specular reflection is directly proportional to the milling time; therefore, with the increase in glaze milling time, the magnitude of specular reflection also increases.

As the glaze in question is a glossy matte, the magnitude of the specular reflection is low; as the particle size diminishes with an increasing milling time, its surface area increases, also increasing the contact area between the particles. Glaze reactivity increases and its viscosity diminishes when molten; when it is applied over a ceramic body, its surface becomes smoother and without roughness (stretched). Regardless of the measurement angle used, if particle size diminishes, the glaze surface gradually stretches, increasing glaze reflection (figure 4).

4. CONCLUSIONS

Except for the 15min milling curve, all the curves present the same form and particle size distributions because equipment resolution (0.5μm) is lower than the minimum required, i.e., the measurements overlap. Therefore, the influence of particle size on surface tension cannot be directly inferred from its measurement, but qualitative conclusions have been drawn based in the results obtained from the experiments.

Drop angle (contact angle) is reduced with increasing milling time until 35min milling, where the glaze studied is apparently not affected by the presence of atmospheric air; the surface tension between the molten glass and the solid body (ceramic body) changes with particle size. Increasing milling time produces significant changes in the wetting angle, due the increasing affinity between the molten glaze and the air, tending to increase the contact angle between the drop (molten glaze) and the ceramic body.

As a result, the glaze coat formed from the smallest particle size can absorb the atmospheric air, easily forming bubbles inside the glaze, due the increase in tension between the melt and the air. This effect could be proven by means of microscopic analysis. The increase of specular reflection as glaze particle size diminishes results from the reduction of glaze viscosity with temperature, making the glass layer more stretched and uniform, without roughness.

REFERENCES

[1] FERNANDEZ NAVARRO, J.M. El Vidrio: constitución, fabricación, propiedades. Madrid: Consejo Sup. de Investigaciones Cient., 1985, 667p.

[2] DURÁN, A. (Editor). Introducción a los esmaltes cerámicos. Italia: Faenza Ed., 2002, 224p.

[3] ESCRIBANO LÓPEZ, P.; CASTELLÓ, J.B.C.; CORDONCILLO, E. Esmaltes y pigmentos cerámicos. Castellón: Faenza Editrice, 2001, 299p.

[4] PEREZ, E.A. Apuntes de esmaltes y colores cerámicos. Valencia: Generalitat Valenciana, 1991, 107p.

[5] NAVARRO, J.E.E. Controles de fabricación de pavimentos y revestimientos cerámicos. Valencia: AICE, 1986, 235p.

[6] OLIVEIRA, H.J.; LABRINCHA, J.A. Esmaltes e engobes para monoporosa. Cerâmica Industrial. São Paulo: ABC, v.7, n.02, p.25-29, 2002.

[7] NUEVOS productos y tecnologías de esmaltes y pigmentos cerámicos. Madrid: Sociedad Española de Cerámica y Vidrio, 1992, 201p.

[8] STEFANOV, S. Smalti ceramici. Itália: Faenza Editrice, 1991, 280p.