GLAZE COUPLING IN PORCELAIN TILES: EFFECTS OF THE NATURE OF THE GLAZES ON THE TENSIONS DEVELOPED DURING FIRING

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ABSTRACT

The production of glazed porcelain tiles and the demand for products of larger sizes have increased considerably in the last decade. This trend makes it more difficult to produce tiles with the required planarity. The classical studies of glaze/body coupling, based on thermal expansion differences, commonly used to control the tensions and the planarity of the tiles, was developed a long time ago and in a different context. Since than different types of glazes have been developed and all the glazed commercial products have a layer of engobe between the glaze and the body. The peculiar characteristics of some glazes, such as the matt glazes, and the presence of the engobe layer are not considered in the classical theory. In this context, the objective of the present work was to study the effects of glazes that do not behave as predicted by the classical theory on the curvature of the fired ceramic tiles. To achieve this, samples (85 x 5 x 5 mm) of an industrial spray-dried powder, used to produce glazed porcelain tiles, were pressed at 380 kgf/cm^2. The layers of different engobes and glazes were industrially applied by pulverization on the surface of the pressed samples. After drying the samples were fired at 1185ºC in an optical fleximeter and the deformation during the firing cycle was monitored. Samples of engobes, glazes and grits for polishing were also characterized by dilatometric analysis and vitrification curves. The results showed the importance of the thermal expansion coefficients of the glazes during the cooling step. However, the analysis of the specimens containing layers of engobes indicated important changes in the curvatures of the samples around the maximum temperature of the firing cycles. The results are explained by the sintering behavior of the engobes, which contained a large volumetric fraction of crystalline phases. For this reason, the study concluded that the control of the thermal expansion coefficients of glazes and engobes is not enough to assure the required planarity of glazed porcelain tiles in the current conditions of production.

1. INTRODUCTION

The world production of porcelain tiles has increased at considerable rates in the last decade. In Brazil[1], between 2014 and 2018, porcelain tiles presented annual growth rates of approximately 10%. Furthermore, in the last few years, the demand for porcelain tiles of larger sizes (more than 60 cm x 60 cm) has increased notably. However, the production of porcelain tiles of large sizes brought some technical difficulties, which were present but not so relevant in tiles of smaller sizes. Particularly the curvatures and deformations displayed by larger tiles became much more critical. Tiles larger than 1.0 m long and wide shall present curvatures smaller than a few millimeters. Among the several aspects that affect the planarity of the tiles, three are the most relevant: pyroplastic deformation[2], tensions due to temperature gradients and phase transformations occurring during the firing cycle[3], and the coupling tension between the body and glaze layer. It is worth mentioning that these phenomena may all occur simultaneously. Therefore, to produce relatively large tiles with the required planarity is not an easy task.

The curvatures developed as a result of the tensions generated by the difference in the thermal expansion of the body and the glaze layer during cooling is the subject of interest of this study. There is abundant information in the technical literature, dating back over 50 years on this topic[4]. In short, the general theory states that, during firing, the glaze suffers several transformations and at relatively high temperatures softens (Tm) and gives rise to a continuous liquid layer. During cooling, glaze viscosity increases until it behaves as a rigid stratum and starts to shrink simultaneously with the body. Meanwhile, during heating, the body also suffers a series of transformations and reactions and shrinks. However, at temperatures higher than Tm, when the glaze behaves like a liquid, no tension is developed between the glaze and body layers. Therefore, there are no important tensions between the glaze layer and the body during heating and at the maximum temperature of the thermal cycle. During cooling the coupling between the glaze layer and the body takes place (at the coupling temperature Ta) and the tensions generated by the differences in shrinkage (ΔC), due to differences of the coefficient of thermal expansion, cannot be released anymore and give rise to tensions that produce curvatures.

Historically, based on the shrinkage difference (ΔC) between the glaze and body layers, the Timoshenko equation[5] has been used to predict the tension. The shrinkage difference (ΔC) is determined by the overlapping of the dilatometric curves making them coincide at Ta[6], as shown in Fig.1

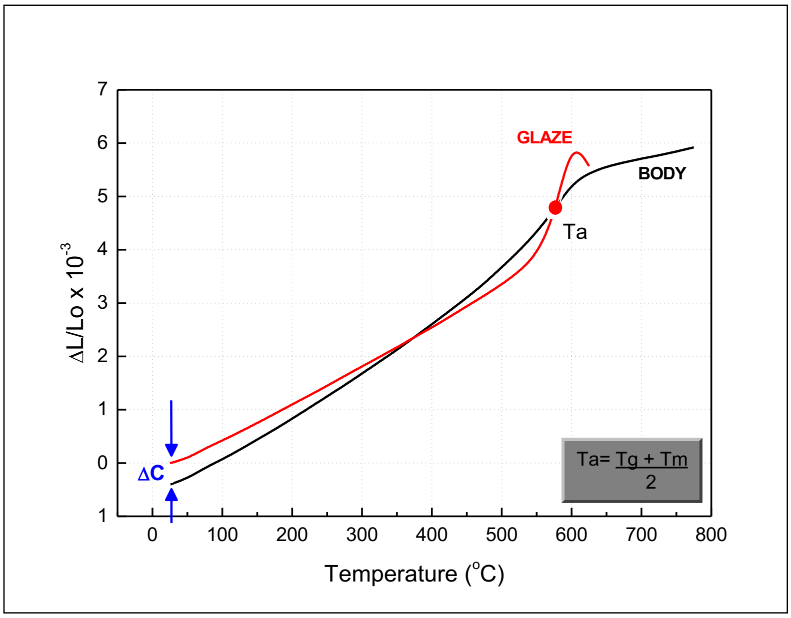

Figure 1: *Determination of the shrinkage difference (ΔC) between glaze and body.*

Since the development of this theory, several changes have taken place in the materials, the fabrication process and the final products. One of these changes, present in almost all industrial glazed tiles, is the presence of an engobe layer between the glaze and the body. In theory, the coefficient of thermal expansion of the engobes should be somewhere between those of the glaze and the body. Despite the fact that an engobe layer is present in almost every industrially produced glazed tile, there are just a few references[7] about its effect on the tensions developed between the layers during the firing cycle.

Another aspect that has not been taken into consideration by the classical theory is the effect of considerable volumes of crystals present in matt glazes and engobes, which will influence their behavior during firing and, consequently, the tension and curvatures of the products. As a matter of fact, in practice, in ceramic tile companies, engobes with coefficients of thermal expansion quite different from those of the glaze and body and with varying fusibility have been used to adjust the curvature of ceramic tiles[7]

Another questionable aspect of the classical theory is the procedure to determine the coupling temperature (Ta). The theory dictates that this temperature corresponds to the arithmetic mean of the transition temperature (Tg) and the melting temperature (Tm). Besides the questionability of using the arithmetic mean, this procedure is almost impossible when dealing with glazes containing large amounts of crystalline phases, such as the engobes and matt glazes, because it is not possible to identify Tg and Tm and, consequently, work out Ta.

The objective of the present work was to study the effects of glazes that, in accordance with the previous considerations, may not behave as predicted by the classical model, on the curvature of the fired specimens.

2. MATERIALS AND METHODS

The strategy used to achieve the objective presented above was to obtain dilatometric curves of the individual materials (body, engobes and glazes) and to predict the curvatures of the fired samples with combinations of these materials using the classical theory and an optical fleximeter to monitor the actual development of the curvatures during firing.

The samples used were produced in a factory using materials and production lines of a company that produces glazed porcelain tiles. The samples were produced in two different fabrication configurations:

- Line 1: pressed spray-dried body + Engobe L.1 + Matt glaze L.1;
- Line 2: pressed spray-dried body + Esmaltobe L.2 + Gritt L.2

The spray-dried body is a typical composition (white body) prepared by the wet route and used to produce glazed porcelain tiles. Engobe L.1 and Esmaltobe L.2 are the first layers applied on the surface of the bodies. Engobes have been used in ceramic tiles for a long time. The use of the term "esmaltobe" is more recent and refers to compositions of engobes with higher content of frits, intended to yield a product with intermediate characteristics between those of engobes and glazes. Matt glazes and grits are vitreous materials applied on the surface of the green body. Due to their very fine particle size, grits are used on the surface of polished products.

Samples of the body, 60 x 20 x 5 mm produced by pressing at 380 kgf/cm^2, were fired at different temperatures in a laboratory roller kiln. The values of water absorption and shrinkage, measured with a caliper, were used to plot the vitrification curves.

Dilatometric analysis of the body, engobe, glaze and grit was performed in a horizontal dilatometer using a heating rate of 5°C/min and maximum temperature of 1000°C. The samples of 50 x 5 x 5 mm were obtained by pressing (380 kgf/cm^2) and previously fired at 1185°C in cycles of 45 minutes in a laboratory roller kiln. The firing temperature and thermal cycle required to achieve the same water absorption and shrinkage as the industrial product were defined in previous tests. These results were used in the classical theory.

The samples of the body (85 x 5 x 5 mm), made with the spray-dried powder, to be analyzed in the optical fleximeter were produced by pressing (380 kgf/cm^2), dried at 110°C and positioned over industrial tiles for the application of the glaze by pulverization in the production line of a ceramic industry. The setup used in the application of the engobe, esmaltobe, glaze and grit (thickness, viscosity and density) was the same as that used in the production lines.

The samples, body, engobe or esmaltobe and glaze or grit, were fired at 1195°C in an optical fleximeter - Optical Platform - ODP 868 - TA Instruments - with continuous monitoring of the deformation during heating and cooling. The samples were positioned as seen in Figure 2. The heating rate was 50°C/min between 25°C and 1100°C; and 20°C/min between 1100°C and the maximum temperature. The maximum temperature was previously adjusted in the equipment to achieve the same water absorption as the industrial tiles, which was not the same as that established in the roller-kiln due to constructive and operational differences.

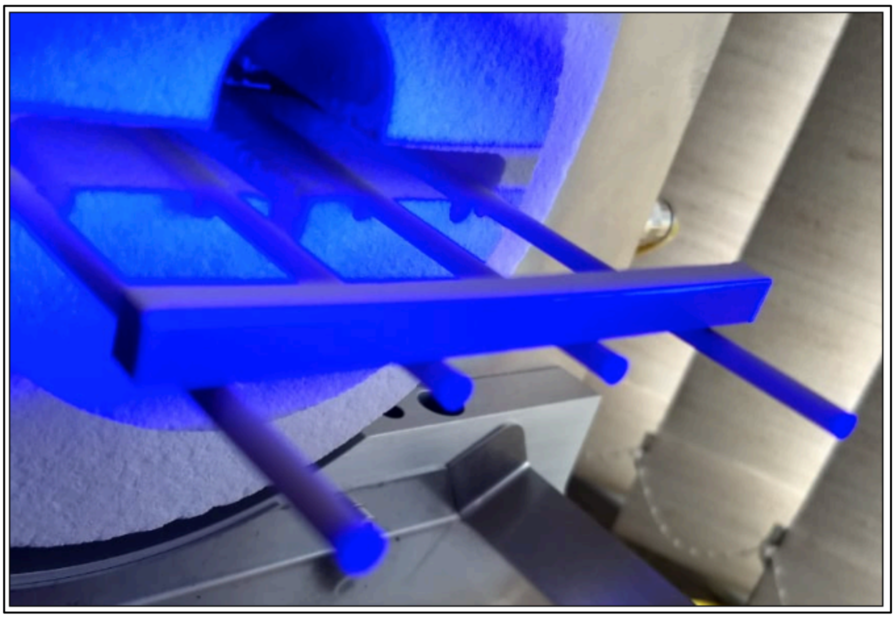

Figure 2: *Position of the samples in the Optical Fleximeter used to evaluate the curvatures.*

3. RESULTS AND DISCUSSION

3.1. DILATOMETRIC METHOD

The results of the dilatometric analysis of the samples (body, engobe, esmaltobe, glaze and grit) are presented in Figures 3 and 4 and Table I. They show important differences between the samples. Engobe L.1 has the highest thermal expansion of the group, while Esmaltobe L.2 presents a dilatometric curve very similar to the body. Glaze L.1 and Grit L.2 have thermal expansions lower than the body at low temperatures and high thermal expansions above Tg.

As can be seen in in Figure 3, it is not possible to identify Tg and Tm in the Engobe L.1 and Esmaltobe L.2 curves and, therefore, to calculate Ta for these layers and the body.

Although the values of Tg and Tm for Glaze L.1 and Grit L.2 may be questionable, these values are presented in Table I, that also contain the calculated differences of shrinkage (ΔC) between the samples and the body at the end of the cooling step. The procedure used to calculate ΔC was based on the literature[5].

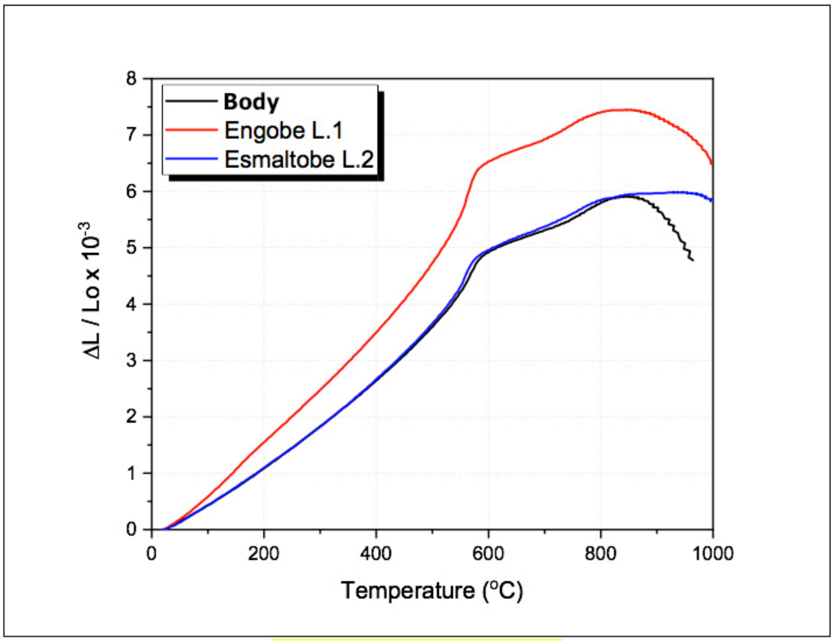

Figure 3: *Dilatometric curves of the body, engobe L.1 and "Esmaltobe" L.2.*

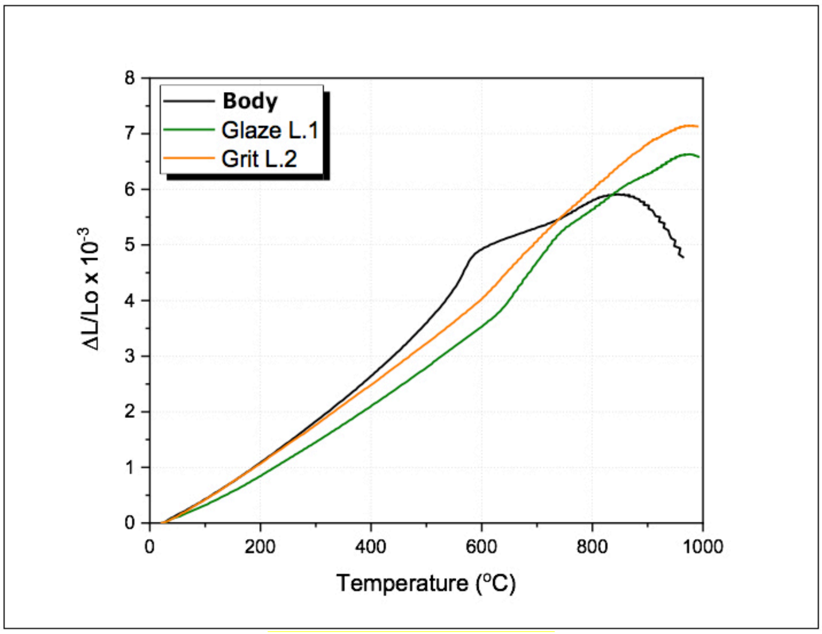

Figure 4: *Dilatometric curves of the body, Glaze L.1 and Grit L.2.*

Samples	α_{25-325}	α_{25-Ta}	Tg (°C)	Ta (°C)	Tm (°C)	ΔC (%)
Body	67.1 x 10^{-7}	n/d	n/d	n/d	n/d	n/d
Engobe L.1	88.9 x 10^{-7}	n/d	n/d	n/d	n/d	n/d
Esmaltobe L.2	66.0 x 10^{-7}	n/d	n/d	n/d	n/d	n/d
Glaze L.1	52.7 x 10^{-7}	72.7 x 10^{-7}	626	802	977	-0.016
Grit L.2	63.2 x 10^{-7}	77.4 x 10^{-7}	619	800	982	+0.019

Table I. *Thermal expansion coefficients (α), characteristic temperatures and differences in shrinkage (ΔC) between the samples and the body.*

As can be seen in Table I, in accordance with the classical model, the set body/Glaze L.1 shall present a positive ΔC while the set body/Grit L.2 shall present a negative ΔC.

Thus, in accordance with the classical model, Glaze L.1 should be under compressive stress and present a convex surface, while Grit L.2 should be under tensile stress and present a concave surface. The prediction of the curvatures for sets Body/Engobe L.1 and Body/Esmaltobe L.2 could not be done because it was not possible to identify Tg and Tm in their dilatometric curves; therefore, the coupling temperature, Ta, could not be determined. However, the expected curvature of sample with Engobe L.1 should be more concave than the one with Esmaltobe L2, due to the higher coefficient of thermal expansion of the former.

3.2. OPTICAL FLEXIMETER

As can be seen in Figures 5 and 6, all the samples presented a convex curvature above 900oC, during the heating stage. The convexity increases considerably at higher temperatures and reaches its maximum values between 1100oC – 1150oC. Above this temperature range, the curvature became concave. The observed behavior was not mentioned in the literature because usually the studies of this subject are based on the classical theory and analyze only the cooling part of the dilatometric curves. It is possible that the pyroplastic deformation is responsible for part of these results, however it is unlikely that this phenomenon is responsible for the convexity near 900oC.

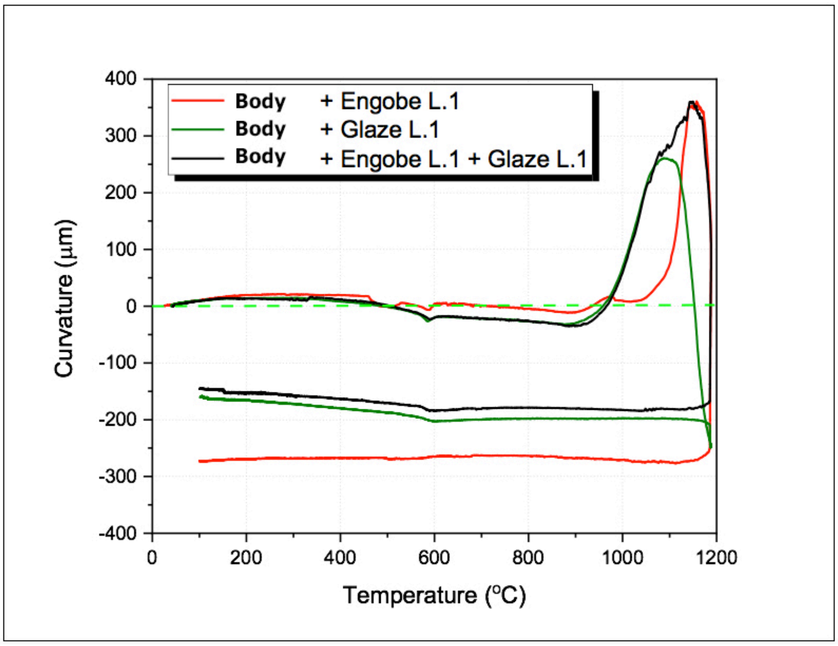

Figure 5: *Variation of the curvature of the green samples with temperature for the sets combining body, engobe and glaze in Line 1.*

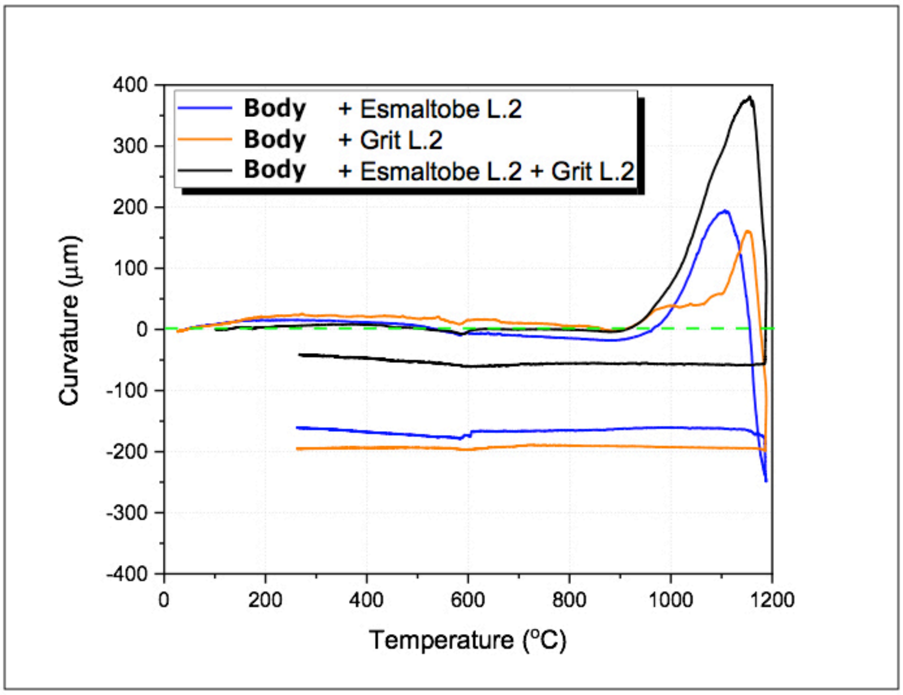

Figure 6: *Variation of the curvature of green samples with temperature for sets combining body, "esmaltobe" and grit in Line 2.*

As can be seen in Figure 7, during cooling, the sample body/Glaze L.1 presents a small concavity just below 800ºC, as predicted by the dilatometric method, and becomes progressively convex below 600ºC. Sample body/Grit L.2, Figure 8, presents a similar behavior, although in this case the intensity of the final curvature is smaller, probably because the thermal expansion coefficient of the Grit L.2 is considerably higher than Glaze L.1.

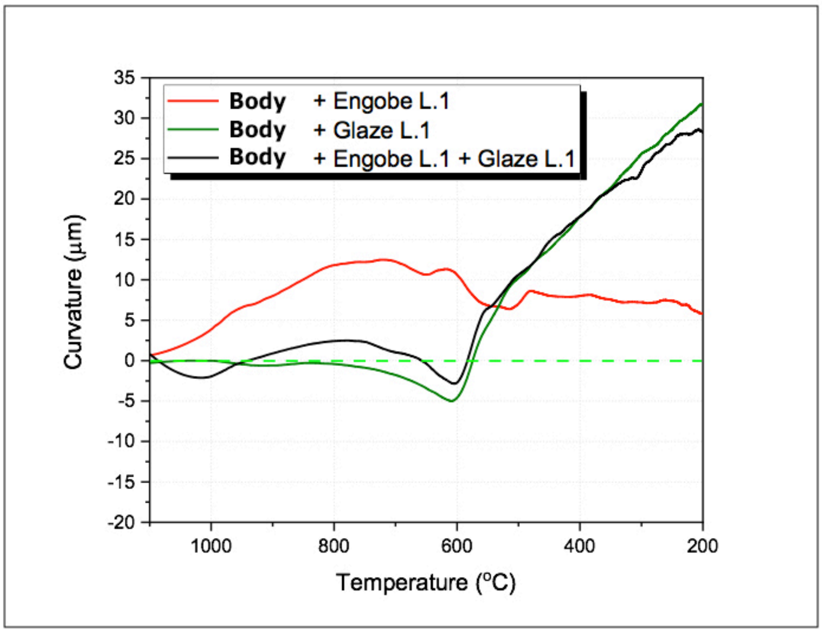

Figure 7: *Variation of curvature with temperature during cooling for the sets combining body, engobe and glaze in Line 1.*

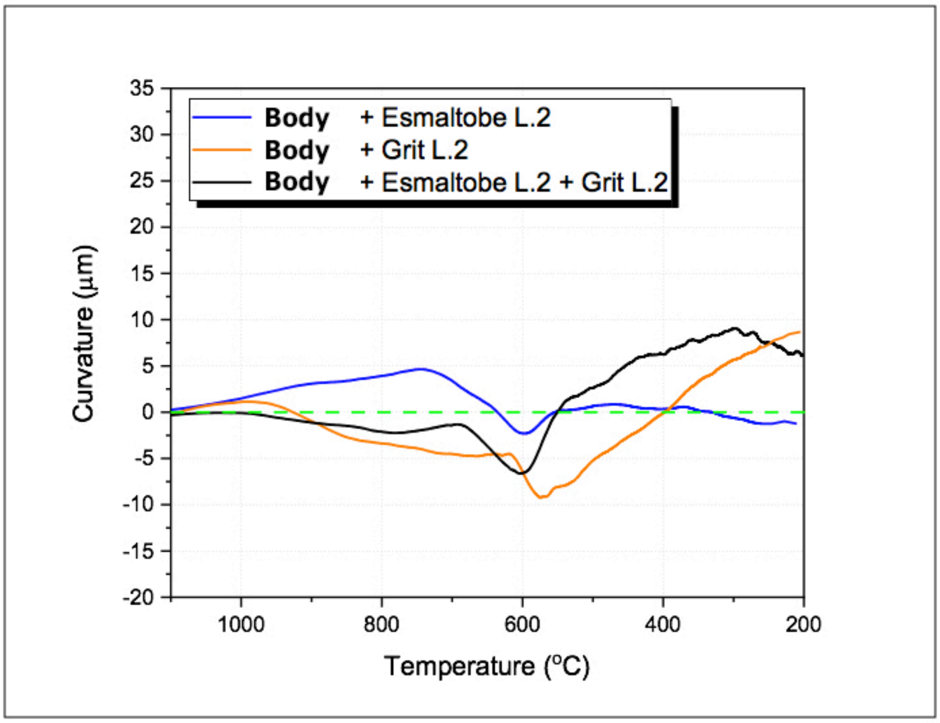

Figure 8: *Variation of curvature with temperature during cooling for the sets combining body, "esmaltobe" and grit in Line 2.*

Figures 7 and 8 show that samples body/Engobe L.1 and body/Esmaltobe L.2 presented curves that are considerably different from the others. Particularly interesting is the fact that below 600ºC these curves do not present the convexity observed in the curves of the other samples, resulting in flatter curves. Another interesting aspect is the fact that the sample body/Esmaltobe L.2 shows an evolution of the curvatures slightly more similar to the samples body/Glaze L.1 and body/Grit L.2, which can be explained by the higher content of frits in the Esmaltobe than in the Engobes. It is important to observe that, even though the thermal expansion of Engobe L.1 is the highest in the group, the sample body/Engobe L.1 did not develop a negative curvature during cooling.

The two final products, body/Engobe L.1/Glaze L.1 and body/Esmaltobe L.2/Grit L.2, during cooling developed curvature changes more similar to Glaze L.1 and Grit L.2 than to Engobe L.1 and Esmaltobe L.2.

3.3. VITRIFICATION CURVES AND VISUAL ASPECT

Figures 9 and 10 are useful to explain the observed curvatures developed during heating. The most likely cause of the convex curvatures of the samples above 900oC is the shrinkage difference between the body and the applied layers. Although the differences are not so pronounced, it is possible to verify that below 1100oC the shrinkage of the body is higher than that of the applied layer. For higher temperatures, up to the maximum densification of the body, the shrinkage of the applied layers, engobe, esmaltobe, glaze and grit, is higher than that of the body, so the situation is reversed, resulting in less convex curvatures. These shrinkage differences can be responsible for the reduction of the convexity observed in the tests carried out in the optical fleximeter.

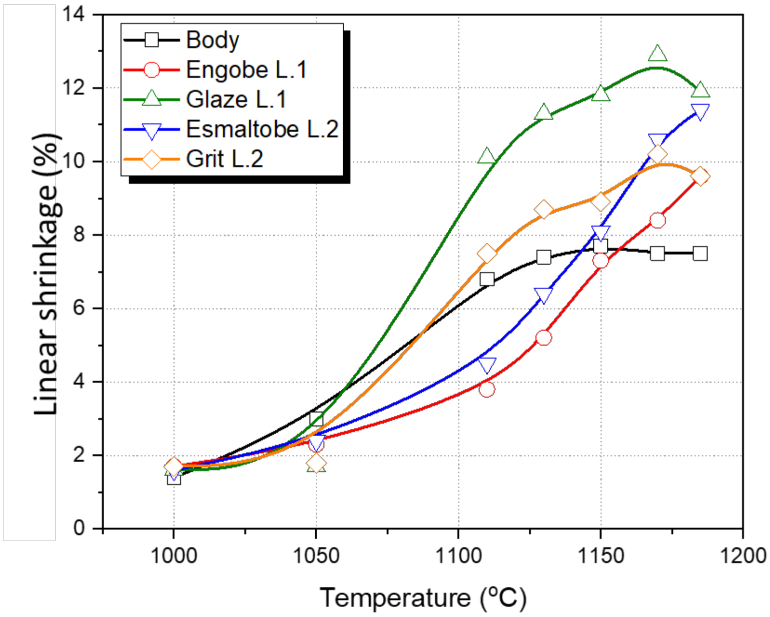

Figure 9: *Variation of linear shrinkage with temperature.*

According to the literature[4], in the firing zone, glazes behave as liquids and are not under any tension. Therefore, it is reasonable to suggest that the concave curvatures presented by all samples at the maximum temperature in the tests performed at the optical fleximeter do not necessarily occur in industrial tiles. The low tensions generated by shrinking layers of engobes and glazes may be strong enough to change the curvatures of small laboratory samples. However, they probably cannot modify the curvature of larger and heavier industrial tiles.

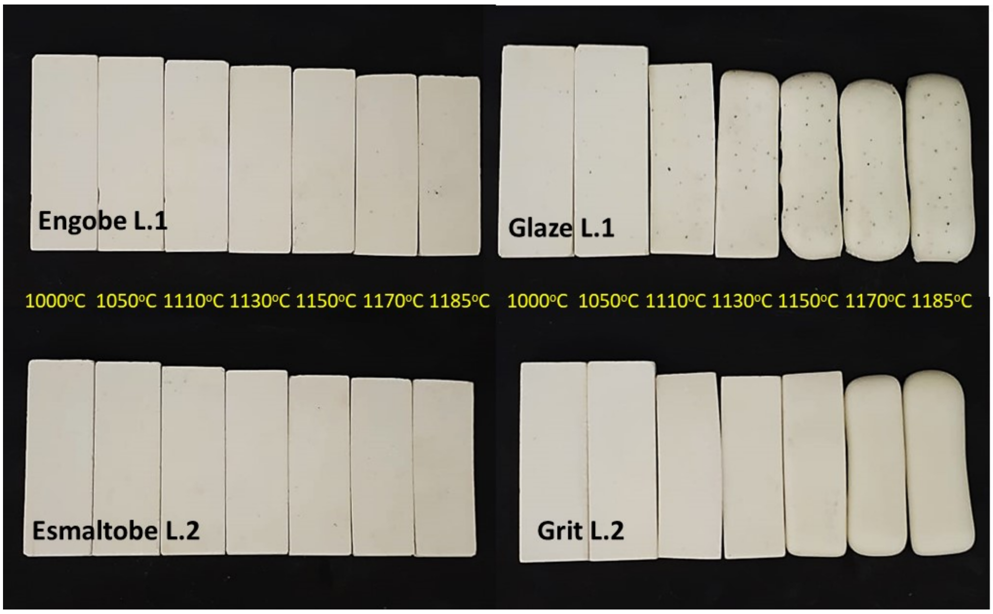

Figure 10: *Pressed samples after firing at various temperatures.*

Figure 10 shows that the samples prepared with Glaze L.1 and Grit L.2 lost their regular shape near the maximum firing temperature, suggesting that these and similar materials, at this stage of the firing cycle, should be treated as liquids. However, the specimens prepared with Engobe L.1 and Esmaltobe L.2 preserved the original regular shape even at the highest temperature of the firing cycle, suggesting that these and similar materials should be treated as solids at this stage of the firing cycle and, therefore, could develop tensions and curvatures due to shrinkage differences during heating.

4. CONCLUSIONS

The results obtained allow the following conclusions to be drawn:

- The coupling temperature (Ta) of engobes and esmaltobes cannot be predicted from dilatometric curves, because it is not possible to identify the vitreous transition (Tg) and the melting (Tm) temperatures in these curves.
- The determination of the coupling temperature from dilatometric curves is not so precise for matt glazes and grits, used in porcelain tiles, because of their high crystalline phase contents.
- The tests conducted in optical fleximeter can be useful to evaluate with more accuracy the evolution of the tensions and curvatures developed during the firing process.
- The tested esmaltobe presented behavior more similar to that of the engobe than to that of the glazes, although is possible to identify the effects of its higher frit content in the composition.
- The curvatures developed by the final products, Body/Engobe L.1/Glaze L.1 and Body/ Esmaltobe L.2/Grit L.2, were strongly affected by the thermal expansion of the glazes, Glaze L.1 and Grit L.1, during the cooling step of the firing process.
- The curvatures generated by the Engobe L.1 and Esmaltobe L.2 during heating and at the maximum temperature cannot be disregarded. The differences in shrinkage of these layers in relation to the body is decisive in this part of the firing cycle.

5. AKNOWLEDGEMENTS

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