CHARACTERIZATION OF CERAMIC BODIES THROUGH OPTICAL TECHNIQUES: STATE OF TENSION AND GREEN MECHANICAL PROPERTIES

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Abstract

The optical techniques shown in this work allow the characterization of ceramic bodies from different points of view. The measurement of thermo-mechanical properties is performed without any contact, so the sample is completely free from constraints. Optical Fleximeter measurements are particularly meaningful for glazed tiles, since this method permits the study of the state of tension established between the glaze and the ceramic body after the firing process. Due to recent interest for larger sized tiles with their reduced thickness and glazing, the mechanical properties of green tiles take on great technological importance. The method presented here tackles the problem of the breaking of single-fired tiles during the glazing process. This problem has always been present concerning the green flexural strength, the highest stress experienced within the tile at its moment of rupture. This work outlines the importance of studying the elastic and plastic components of deflection during the cyclic load application on green tiles, as a simulation of rotary tile glazing and decorating machines.

Keywords: Glazed tiles, state of tension, delayed crazing, green mechanical properties, deformations, glazing line, optical Fleximeter

Introduction

In glazed or double layer tiles, deformations may be generated from the different behaviours of the 2 overlapped layers, both during the heating and cooling phases. The coupling of materials with different thermal behaviours inevitably gives rise to a system of stresses due to the thermal incompatibility between the layers. This problem was tackled by Timoshenko in 1925, when he developed an equation that calculates the deformation of bimetallic strips as a function of the temperature. Unlike bimetallic strips, that bend only because of the differences between the thermal expansion coefficients of the 2 metals overlapped, in the case of a glazed ceramic material it is necessary to take into account the physical transformations occurring in the ceramic body and the glaze. The ceramic

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support shows the characteristics of an elastic solid, while glasses and glazes exhibit a strongly temperature-dependent mechanical behaviour. At room temperature, they behave as elastic solids, obeying Hooke's law; at temperatures higher than their glass transition temperature, they behave as plastic fluids and their viscosity decreases as the temperature rises, in accordance with Arrhenius' law. Another characteristic point of the glaze-body system is the coupling temperature (Tc), in correspondence of which the glaze softens during heating (absorbing tensions) and solidifies during cooling (building up tensions) (Paganelli and Sighinolfi, 2008, 2009; Venturelli and Sighinolfi, 2012). As a direct consequence of the different thermal behaviours of the glaze and the body, crazing, peeling, or planarity defects may appear after cooling in glazed porous products. Delayed crazing in glazed porous tiles is due to the volume increase of the body because of absorption of humidity after firing. The body, in fact, can show a slow but inexorable tendency to react with the water present as humidity in the air, which changes its properties permanently. This dimensional increase of ceramic bodies occurs in a period of time which can vary from some days to some years. The only type of body that can be considered stable during the time is the completely sintered body, characterized by a lack in porosity. Since all glazes, like glasses, are characterized by a very low resistance to traction stress, a little amount of traction may cause their rupture. If the body expands, even by a small percentage, the glaze may easily crack, unless it is in a state of compression with respect to the body. In this case, a little expansion of the body reduces the state of compression, without generating a dangerous traction. The old trick of increasing the state of compression of the glaze onto the body to avoid delayed crazing works well only for the old, thick, and small tiles.

The size of tiles is growing quickly: now the market is asking for wall tiles up to one meter in size and above. Thickness is down to a minimum, to save in cost and transportation. The value of the product lies in the richness of the surface and the thickness of the glazes and is rising. Geometrical perfection is a must: tiles are mechanically squared to give a marble-like look to the wall. A high level of compression on a large sized tile has a nasty side effect: bending. To reduce the bending there is only 1 solution: reduce to the minimum the amount of compression.

Coupling between the glaze and the ceramic body was extensively studied by Spanish authors from the last 1980s (Amoros *et al.*, 1989a, 1989b, 1990).

They used the Steger method to calculate the state of tension established between the glaze and the ceramic body. Since the Tc was not determinable with this method, they introduced a simplifying approximation (Amoros *et al.*, 1989b):

$$T_C = \frac{T_g + T_{soft}}{2}$$

where T_{soft} = the softening temperature of the glaze.

In a further publication, Amoros *et al.*, (1990) underlined that, during firing, diffusion and dissolution phenomena between the glaze and support layers occur and a glaze-body interphase develops. Thus, the glaze and the body do not behave as independent layers because of the presence of such an interphase which affects the properties of the final product, including planarity. For this reason, they state that the coupling between the glaze and support should be investigated experimentally in conditions which better reproduce the industrial ones.

The Steger tensionmeter analysis, however, is quite problematical. The tests are performed with a very long (30 cm) specimen which is not placed completely inside the kiln, with consequent lack in homogeneity in the sample temperature. Furthermore, the specimen to be tested has to be prepared on purpose in a laboratory and cannot be cut directly from an industrial tile (Venturelli and Paganelli, 2005).

The experimental method presented in this paper is a novel technique based on the

Steger method principle. It entirely consists of optical measurements, which allow the characterization of the material's behaviour during the firing and cooling without entering into contact with the specimen and, thus, with no interference caused by the measuring system, so obtaining a good comprehension of the material's real behaviour in an actual industrial firing cycle. This method allows the quantitative determination of the state of tension of the glaze in respect to the ceramic body, and it is based on the Tc determination. The Tc is not obtained with an approximation, but experimentally determined from the flexion curve of the glazed material.

Materials and Methods

The state of tension between the glaze and the body depends essentially on 2 factors: the relation between their thermal expansion curves and their Tc.

All the experimental part of this work was performed by using the optical instrument MISURA FLEX-ODLT produced by Expert System Solutions, Modena, Italy. With this instrument (which combines together the Optical Fleximeter and Optical Dilatometer), it is possible to perform both thermal expansion and flexion measurements with no contact with the samples tested: thus, their behaviour is never modified by the measuring system.

The first experimental phase consists of a flexion analysis performed on a fired glazed body. The specimen was cut directly from an industrial tile and placed inside the kiln. During the test, the small sample bar obtained (85×5×5 mm) is suspended between 2 holding rods spaced 70 mm apart, while a camera frames the centre of the sample, which moves downward or upward during the heat treatment as schematically shown in Figure 1(a).

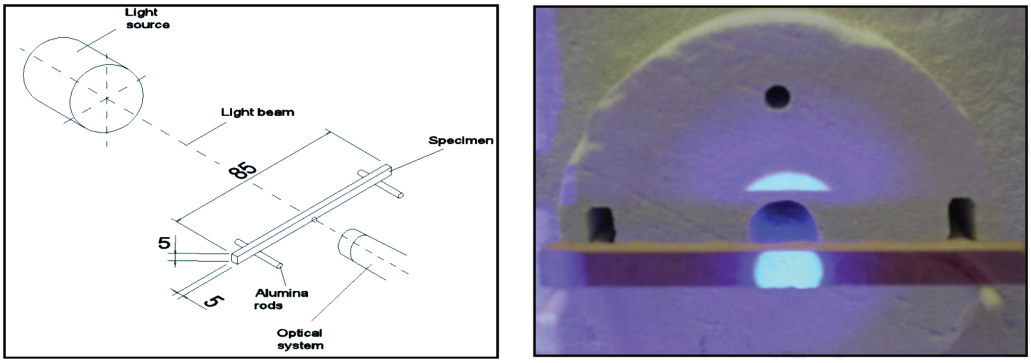
The beam of blue light which lights the centre of the specimen (Figure 1(b)) has a wavelength of 478 nanometres and is able to reach the optical resolution of 0, 5 micron per pixel of the digital camera.

The test is performed heating the sample up to a temperature high enough to cause the glaze to soften and then follows with cooling to below about 100°C.

The heating cycle consists of a heating rate of 20°C/min up to 1000°C and free cooling.

The curve obtained with this instrument allows the identification of the Tc between the glaze and the ceramic body.

The second testing phase consisted of 2 thermal expansion tests, performed on the fired glaze and body with the horizontal Optical Dilatometer. During this test, 2 beams of lights illuminate both ends of a specimen 50 mm long placed horizontally into the furnace and 2 digital cameras capture the



(a) (b)

Figure 1. (a) Scheme of the optical Fleximeter; (b) Sample inside the kiln

images of the last 200 microns of each tip. The specimen, completely free to expand or contract, is measured by the image that it projects on an image sensor. With a wavelength of 478 nanometres, a resolution of 0, 5 microns can be obtained.

The final part of this work presents 2 applications at room temperature of the Optical Fleximeter in the field of traditional ceramic materials (single-fired products).

The green mechanical properties investigated are parameters of technological importance. Two industrial phases were simulated thanks to the flexion tests: bending due to water application (during the glazing process) and bending due to cyclic loading (imposed by the decoration machines).

The materials tested are 2 industrial Thai tiles for double firing (state of tension) and 8 Turkish ceramic bodies for single-firing (green mechanical properties).

Results and Discussion

The results shown below are obtained for the 2 types of Thai tiles for double firing, here named the "white tile" and "blue tile".

White Tile

The flexion vs temperature curve obtained for the glazed tile is shown in Figure 2. The flexion is expressed as the percentage ratio between the absolute flexion and the distance between the 2 sample holder rods, which is 70 mm.

The downward flexion of the initial part of the curve is due to the differences between the coefficients of thermal expansion (CTE) of the glaze and the body; with the body having a higher CTE compared with the glaze, it is subjected to higher expansion, becoming longer than the glaze. The specimen appears concave. The curve shows a negative peak at 600°C, after the transition α quartz – β quartz occurring into the ceramic body: correspondening to this point, the difference between the thermal expansion curves of the glaze and the body is the maximum, also because the glaze is near the Tg.

After the Tg, the glaze thermal expansion curve undergoes a sharp change of expansivity, due to the fact that the molecular groups are acquiring all the degrees of freedom typical of a liquid material. Graphically the Tg is determined from the expansion curve as the point of intersection of the tangents below and above the slope change (elbow of the glaze thermal expansion curve) (Sighinolfi, 2010).

Considering again the flexion curve, at 627°C a rapid variation of inclination occurs: in correspondence with this point it is possible to identify the (Tc). This is the temperature at

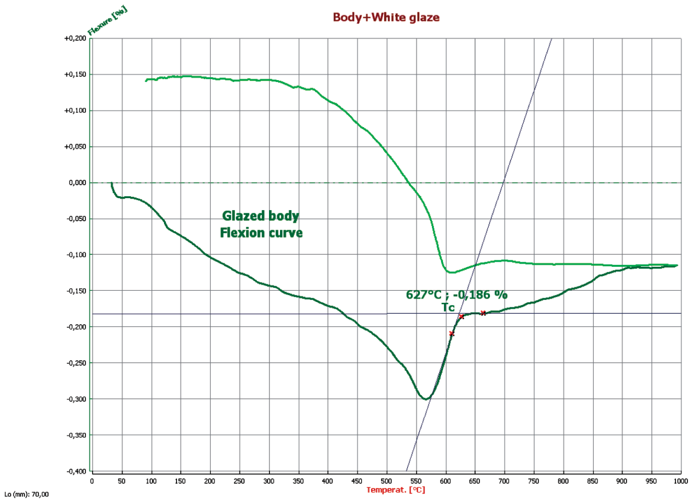


Figure 2. Flexion curve of the white glazed body and determination of the Tc

which the glaze releases all its tensions. The curve after this point becomes flat: the upward flexion trend is interrupted because of the stress release.

A quantitative study of the state of tension established between the glaze and the body after firing is fundamental in order to prevent some frequent problems occurring in glazed products, for example delayed crazing or serious planarity defects.

Once the Tc is identified, the second testing phase consists of 2 thermal expansion tests performed on the fired glaze and the body. The results obtained are shown in Figure 3, in which the dimensional variations of the specimens with respect to their initial length are expressed in a percentage as a function of the temperature.

To obtain the final result, a technique was developed (Paganelli and Sighinolfi, 2008, 2009; Venturelli and Sighinolfi, 2012) according to which it is necessary to translate the glaze thermal expansion curve so that it coincides with the body thermal expansion curve in correspondence with the Tc, as shown in Figure 4.

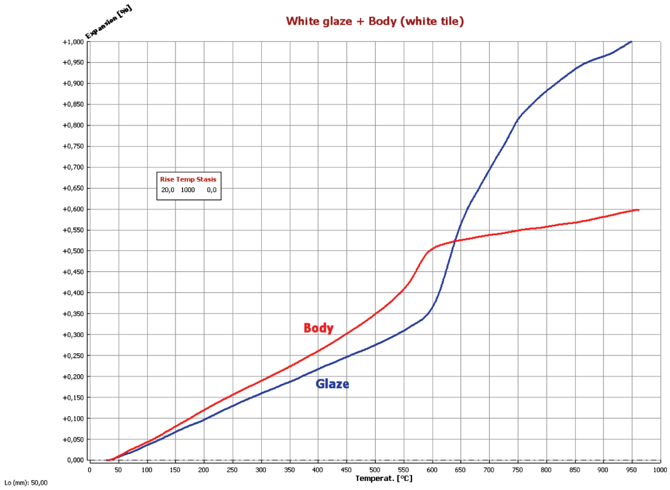


Figure 3. Thermal expansion curves of the body and white tile glaze

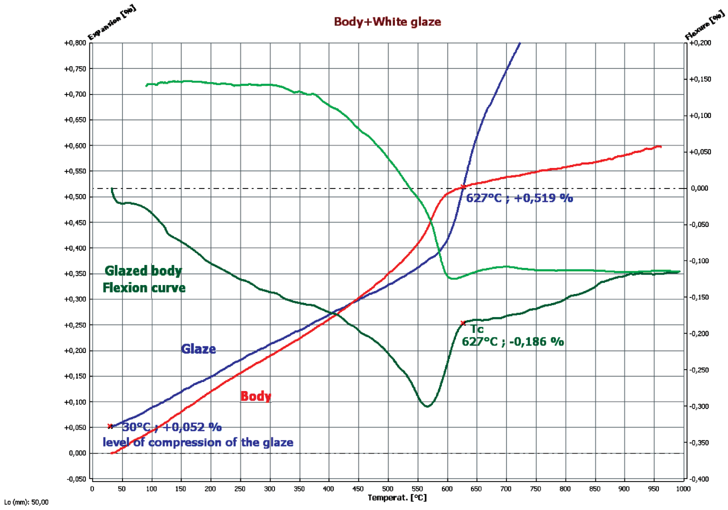


Figure 4. Level of compression established between the glaze and the body (white tile)

The 2 curves, after the translation, do not coincide anymore at the origin (room temperature), but they have 2 intersection points: beyond the Tc, they also coincide at another point between 400 and 450°C. In correspondence with this point, the glaze and the ceramic body are in a non-stress state, having the same dimensions.

The difference between the 2 translated curves at room temperature is indeed the traction or compression which has been established between the glaze and the body immediately after firing. From this moment, the body starts to react with the air humidity, increasing its volume. This phenomenon is favoured by the presence of humidity and high temperatures. This process of rehydration, in the case of tiles already placed on the floor, may require some years, but can be also artificially accelerated by increasing the water vapour pressure and the temperature. Performing an autoclave test at high temperature and pressure, the process can be completed in a few hours. The measurement of the percentage of expansion due to the adsorption of water should be compared with the measurement of the percentage of compression of the glaze layer with respect to the body. If the value of expansion after the autoclave test is lower than the level of compression established between the glaze and the body, then the product will not be at risk of delayed crazing.

A body formulation and a firing cycle intended to avoid delayed crazing do not exist. The problem, however, can be successfully tackled by studying the state of tension between the glaze and the body by means of thermal expansion and bending tests.

Blue Tile

The following example (Figure 5) shows the thermal expansion and flexion curves of a product which is strongly at risk of crazing.

In this case the Tc is found to correspond at 663°C. The 2 thermal expansion curves already coincide at this temperature, without any need to be translated. This means that the second intersection point correspondent to the situation of non-stress between the glaze and the body is just the room temperature. In the case of the blue tile, at room temperature the glazed body shows no residual tension: if the body undergoes even a small increase of volume, the glaze will be in a state of traction.

A simple comparison between the CTE is misleading: the glaze CTE at 400°C is $6.13 \cdot 10^{-6}$°C^{-1}, while the body CTE at the same temperature is $7.26 \cdot 10^{-6}$ °C^{-1}.

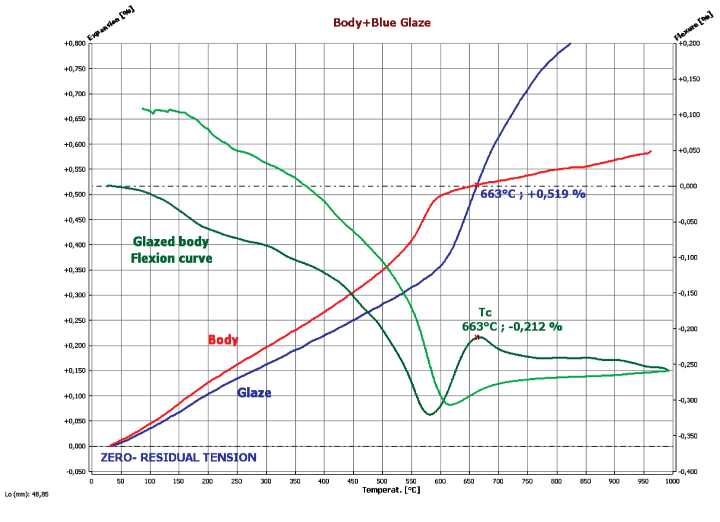


Figure 5. Flexion curve of the blue glazed tile and curves of thermal expansion of the glaze and the body

The fact that the glaze CTE at 400°C is lower than the body CTE at 400°C does not guarantee that the glaze will be in a state of compression after firing.

The experimental method based on the optical Fleximeter results proved to be a valid help for the study of the state of tension in both the double-firing and single-firing of glazed ceramic materials.

Green Mechanical properties Investigation

The optical Fleximeter also allows the investigation of some green mechanical properties which are fundamental when considering tiles for single-firing.

In the case of single-firing products, an extreme bending of the tiles during the glazing process due to the numerous applications of glazing liquids is a frequent problem on the glazing line. The deformation imposed by the decoration machines to green, thin, and bent tiles is sometimes so high as to give rise to breaks.

This problem has always been faced by considering the green flexural strength or modulus of rupture (MOR), the stress required to provoke the specimen to rupture during a bending test.

But tiles do not break just when their capacity to tolerate applied loads (tile weight, glazing line vibrations, collisions within tiles) is exceeded, but also in the case of high deformations.

Green bodies undergo deformations during glaze applications: it is due to the volume increase of the upper tile layer when wet owing to the aqueous solution of glazes (clayey networks expand).

Once bent, tiles have to withstand high deformations without coming to failure.

The method presented here tackles this problem from a different point of view: instead of the classical measurement of the MOR, the “imposed deformations” are investigated, thanks to simulations of the bending of the green tiles due to water and cyclic load applications.

The parameters measured are the maximum value of bending and the flexural modulus of elasticity (E_f).

In the elasticity field, the relation between the applied load and the deformation of the material is expressed by Hooke’s law, which states that the deformation is directly proportional to the deforming load:

$$\sigma = E\varepsilon$$

The constant of proportionality is the elasticity modulus (Young’s modulus), E.

With a constant applied stress, the higher the modulus E is, the higher is the material stiffness and therefore the lower is the allowed deformation.

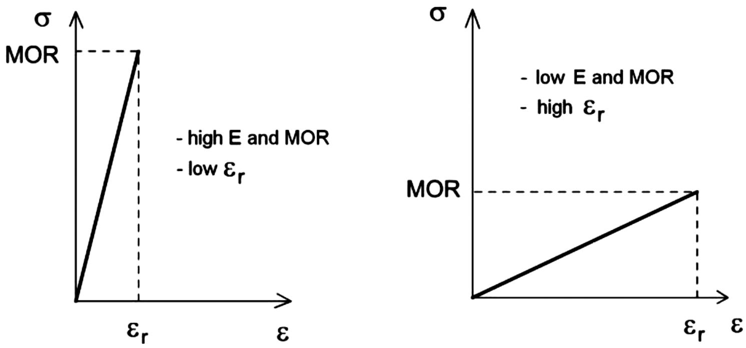


Figure 6. Mechanical behaviour of green tiles

In Figure 6, 2 possible mechanical behaviours are represented. The material on the right shows low E and MOR: this means it is able to tolerate higher deformation without breaking with respect to the material on the left, which has high E and MOR but bears low deformation before its rupture.

The preferable behaviour in a glazing line is the one represented on the right, even if this means a low MOR. This does not represent a problem unless the MOR falls under the limit of about 1 MPa = 10 kg/cm^2, which is the minimum value which allows the tile to tolerate its own weight and the glazing line vibrations.

The solution to the problem of "imposed deformations" is to design bodies with low bending due to glazing and with a low modulus of elasticity.

The optical Fleximeter allows the simulation of the glazing process, investigating the bending of the green tiles and the deformation imposed by the decoration machines.

Bending Due to Water Application

A simulation of the glazing process has been carried out on 8 different Turkish ceramic bodies for single-firing by using the optical Fleximeter.

A small bar of a ceramic body, placed on 270 mm spaced alumina rods, was subjected to 4 successive water applications at room temperature (Figure 7).

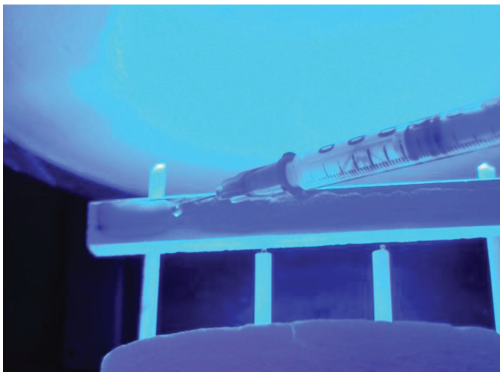


Figure 7. Water application on the upper surface of a green sample inside the optical Fleximeter

On the upper surface of the test piece, 0, 2 cm^3 of water is applied every 2m30s, while the optical system records the sample bending.

The water application of 0,8 cm^3 on a sample of 100×10 mm inside corresponds to a glaze application of about 800 g/m^2.

The results of these tests are shown in Figure 8. When the water wets the upper tile surface, clayey networks expand and the upper layer increases in volume. Samples become convex causing problems during the decoration.

This bending behaviour depends on the mineralogical nature of the clayey matrix: the differences among the samples tested are due to the presence of different clays in the ceramic body formulations. At the end of water applications, tiles have a concave appearance: the dry lower tile surface resists the upper layer contraction which undergoes a plastic deformation able to eliminate the initial compression.

Bending Due to Cyclic Loading

With the optical Fleximeter, it is also possible to simulate the bending due to cyclic loading.

This test is carried out applying a dynamic load (400 g) in the central portion of the sample (Figure 9).

The optical camera frames the centre of the sample, which moves upward and downward during the sample bending, providing a typical fatigue test (load and unload with steps of a few seconds) without the sample breaking.

Figure 10 shows the results of this test on the same 8 samples tested previously. The absolute bending is reported as a function of the time. The fatigue cycle consists of 30 loads and unloads.

If the deformation width remains constant, the sample is deforming fully elastically. High widths correspond to a low E_f. This is the best performance, which allows the sample to tolerate high deformations without breaking.

If the deformation width remains constant but the total downward deformation increases with further load applications, the sample has visco-elastic behaviour (it is able to adsorb partially internal stresses by means of a viscous flowing).

With this test, it is also possible to determine numerically the Ef through the formula:

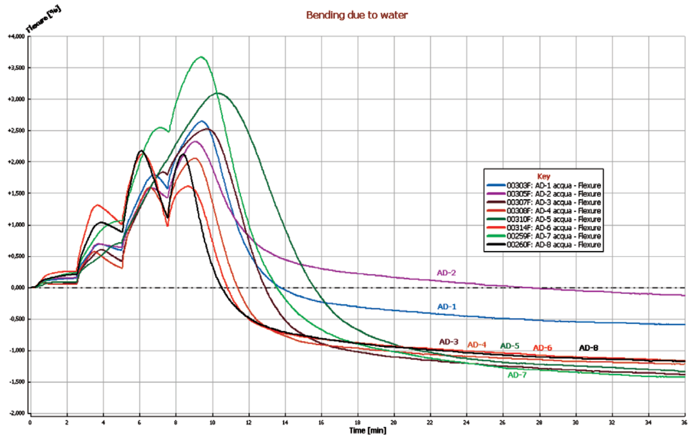


Figure 8. Example of bending curves of 8 different specimens while subjected to successive water applications (0, 2 cc X 4)

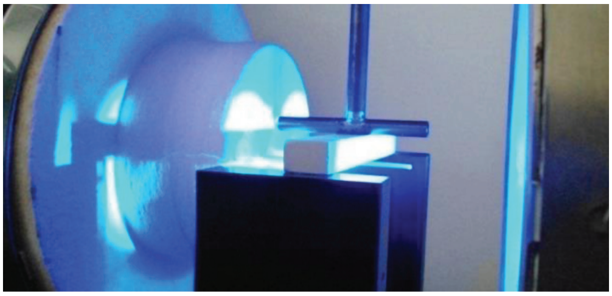


Figure 9. Deformation test with the optical Fleximeter

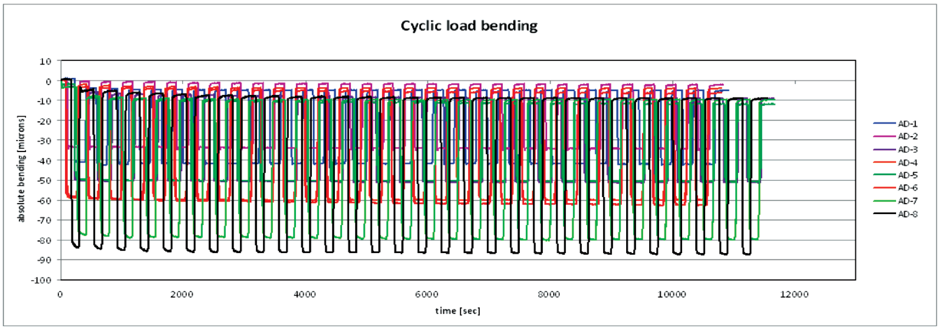


Figure 10. Deformation test results

$$E_f = \frac{L^3 F}{4\, f h^3\, d}$$

where:

L = support span, (mm)
b = width of test beam, (mm)
d = depth of tested beam, (mm)
E_f = flexural modulus of elasticity, (GPa)
F = deflection of the beam

Sample AD-8, represented by the black curves in Figures 8 and 10, has a low bending due to water application and a low E_f (it is able to tolerate high deformations without breaking): it shows the best mechanical behaviour during the glazing process,

Conclusions

The optical techniques shown in this work allow the characterization of the ceramic bodies from different points of view. The state of tension established between the glaze and the ceramic body after cooling can be studied in the case of double fired and single fired tiles. This is fundamental in order to prevent the typical defects occurring in glazed products: delayed crazing or serious planarity defects.

In the case of single-fired products, the study of the actual deformations of the green tiles during the glazing process has been carried out with the optical Fleximeter.

Thanks to simulation of the bending due to water and cyclic loading, it is possible to tackle the problem of tiles breaking in the glazing line.

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