



# Changes in the physico-mechanical characteristics of a ceramic paste during drying



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## ABSTRACT

This paper is a contribution to the determination of the variations of the physical and rheological properties of a ceramic paste during drying. The ceramic's density was determined as a function of moisture content using the Archimedes' Principle. The shrinkage was derived from the experimental density data and also determined by measuring the variation of the sample's dimensions during drying. Compression tests were performed at different deformation rates in order to identify the linear and non-linear viscoelastic domains of the material. Relaxation tests were carried out and the results of fitting showed that the generalized Maxwell model could be used to describe the viscoelastic behavior of the samples. Rupture tests were also made to measure the strength of the material for different moisture contents and to study the influence of temperature on the strength of the dried product.

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## 1. Introduction

Controlling the drying process of ceramic bodies is of great interest in order to limit the formation of defects that occurs in the products. There are a lot of properties that are usually examined for the prediction of the quality of the dried material and for process design calculation. The characterization of these properties may improve the understanding of drying mechanisms.

The particular structure of the material and the mechanical characteristics of its elements at equilibrium define the sample's volume and determine its size and shape. When water is removed from the material, a gradient of pressure is produced between the interior of the material and the external pressure, generating contracting stresses that lead to material shrinkage, changes in shape and occasionally cracking of the product.

Density is one of the main properties that should be identified because it intervenes in many equations (heat, mass, momentum) and calculations of characteristics. This property, as most properties of a hygroscopic material, varies with the moisture content in the product. Also, controlling shrinkage is an important criterion, especially in the case of manufactured building products (bricks, faience, and tiles), because excessive shrinkage causes the deformation of the items during firing [1]. Density and shrinkage were investigated in many papers. For food products, it has been shown that density peaked at low values of the moisture content, and then decreased with increasing moisture content. This behavior was observed for apple, potato, calamari, and garlic [2,3]. And in this case, drying is accompanied with an important shrinkage that decreased

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almost linearly when moisture content decreased. For clay materials, it has been shown that shrinkage does not continue till the end of drying. Thus, density increased at the beginning of drying under the effect of shrinkage and then, in a second stage, the volume of the sample does not change with further loss of water [4,5].

In the case of ceramics and wood industry, the knowledge of only shrinkage and density data occurring during dehydration is generally scanty. Mechanical properties are the main properties qualifying materials because the mechanical deterioration of dried materials is the most undesirable change. Mechanical resistance of some products to compression has been studied by many authors [1,6] in order to predict the strength variation.

Rheological modeling is also used to predict the physical response under various conditions of stress and strain and consequently enables one to decrease damage risks. Wet products can generally be considered as viscoelastic materials [7]. The stress relaxation test is often used to measure the viscoelastic properties. These properties are expressed as a function of time and there are no works reporting their dependency on moisture content [8,9].

Our objective in this study is to determine the variation of the shrinkage and of the density of porcelain with moisture content. Compressive tests will be investigated to determine the linear and nonlinear viscoelastic domains. Relaxation tests will be carried out in order to forecast the different rheological properties and their variation as a function of moisture content. Ultimate strength will be studied as function of moisture content and the influence of the drying temperature will also be examined.

## 2. Materials and methods

For all the experiments the ceramic samples are prepared by wetting a porcelain powder with water. The composition of the porcelain powder was: 50% kaolin, 25% quartz and 25% feldspar. The samples were dried in a convection oven operating at 40 °C.

### 2.1. Density

The Archimedes method was used to measure the samples' density [4]. Spherical samples with a radius of 5 mm were placed in the oven at 40 °C and were weighted every 15 min in order to obtain a large range of moisture content ranging from 0 to 0.4 kg/kg d.b. To ensure sealing of the surfaces, each sample was covered with a thin layer of parafilm. The apparent density  $\rho$  can be determined as follows

$$\rho = \frac{W_a[\rho_f - \rho_a]}{0.99983 G} + \rho_a \text{ (kg/m}^3\text{)} \quad (1)$$

where

$\rho_a$  is the density of the air under standard conditions;

$\rho_f$  is the density of the fluid;

$G = W_a - W_f$  is the buoyancy of the immersed solid;

$W_a$  and  $W_f$  are the weight of the solid in the air and in the fluid, respectively.

Finally, the samples are dried at 105 °C for 24 h in order to determine the mass of the dry sample  $m_s$  (dry basis) and to consequently determine the moisture content  $w$  expressed as:

$$w = \frac{m - m_s}{m_s} \text{ (kg/kg d.b.)} \quad (2)$$

### 2.2. Plastic limit

The plastic limit PL is defined as the lowest moisture content at which a clay material can be rolled into threads one-eighth inch in diameter without breaking into pieces. This is also the moisture content at which the material changes from a plastic state to a semisolid state.

The plastic limit tests were performed by following the conventional ASTM D4318 [10]. It consists in forming a small ball of porcelain paste that is rolled on a flat non-porous surface.

The PL is reached when the thread breaks apart at a diameter of 3.2 mm.

### 2.3. Shrinkage

Shrinkage of the ceramic material was examined by using two methods.

#### 2.3.1. Direct measurement

Shrinkage was determined experimentally by monitoring the variation of a porcelain sample dimensions during drying. A cylindrical sample having an initial diameter  $d = 20$  mm and a height  $h = 24$  mm was used. Each 15 min, the sample

dimensions were measured in two positions with the use of a slide caliper (precision 0.01 mm) and weighted by the balance (type 770 KERN, precision  $10^{-4}$  g) and then placed in the dryer.

Assuming that the cylinders kept exactly their initial cylindrical shape, the volume and the surface of the samples at each instant of drying were respectively evaluated by the following expressions:

$$V = \pi \frac{d^2}{4} h \quad \text{and} \quad S = \pi d \left( \frac{d}{2} + h \right) \quad (3)$$

where  $V$ ,  $S$ ,  $h$  and  $d$  are respectively the sample volume, surface, length, and diameter.

### 2.3.2. Indirect measurement

The shrinkage coefficient noted  $R_v$  can be determined directly from the variation of volume using the following relation:

$$R_v = \frac{V - V_s}{V_s} \quad (4)$$

where  $V_s$  is the volume of the solid phase.

An indirect method to determine the shrinkage coefficient  $R_v$  based on the experimental results of the variation of apparent density can be used. In fact, there is a relation between density and shrinkage coefficient, and it is established below with the assumption that the porous medium is composed of solid and water only (saturated media).

$$\rho = \frac{m}{V} = \frac{m_s(1+w)}{V_s \left( \frac{V-V_s}{V_s} + 1 \right)} = \rho_s \frac{1+w}{1+R_v} \quad (5)$$

where  $\rho_s$  is the apparent density of the solid phase. So  $R_v$  can be determined from Fig. 1 using equation (6):

$$R_v = \frac{\rho_s(1+w) - \rho}{\rho} \quad (6)$$

## 2.4. Rheological behavior

The rheological laws express the relation between stress tensor and deformations and their derivatives. To analytically represent the behavior of a material, it is necessary to determine experimentally the mechanical characteristics of the material and its response to a given sollicitation using mechanical tests.

Uniaxial traction/compression is the most commonly used test for obtaining the mechanical characteristics for isotropic materials.

Assuming that porcelain is a homogeneous isotropic material, uniaxial compression tests were carried out on a cylindrical sample of 25 cm of length and 20 cm of diameter with an initial moisture content of 0.3 kg/kg d.b. at several deformation rates noted  $v_i$ .

The equipment used for the mechanical tests was an LRX plus 5000 stand (Lloyd Instruments), equipped with a load cell of 5000 N and connected to a microcomputer through an analogical–digital converter.

### 2.5. Linear viscoelastic properties

During drying, by losing moisture, the material evolves and its mechanical behavior also changes. Therefore, in order to understand the mechanical evolution of the material during drying, the rheological properties have to be determined at different values of moisture content.

One of the principal properties of a viscoelastic material is the relaxation modulus.

The relaxation modulus  $E(t)$  is given by the material's response at a deformation echelon,  $\varepsilon_0 \cdot h(t)$ , where  $h$  is the Heaviside function:

$$E(t) = \sigma(t) / \varepsilon_0 \quad (7)$$

where  $\sigma$  is the uniaxial stress and  $\varepsilon_0$  is the imposed deformation.

The relaxation test is performed on cylindrical samples. The displacement velocity is fixed at 1 mm/min until a deformation of 0.01 to be in the linear viscoelastic domain.

The experiments were carried out on a long duration of 20 h. In order to limit water evaporation from the samples, the lateral surfaces of each of them were covered with a thin layer of parafilm, so that moisture content is maintained constant during the whole process.

In a relaxation test, the rheological behavior of viscoelastic products can be represented by a generalized Maxwell model. This model is constituted by the association in parallel of  $n$  branches of the Maxwell model. Each branch is characterized by an elasticity modulus  $E_i$  and a viscosity coefficient  $\eta_i$ . The response of this model to a deformation applied instantaneously can be written in the form of a Prony series [11]:

$$E(t) = E_{\infty} + \sum_{i=1}^n E_i e^{-\frac{t}{r_i}} \quad (8)$$

where  $E(t)$  is the relaxation modulus at time  $t$  defined as the evolution of stress when a deformation is imposed suddenly. The coefficient  $r_i = \eta_i/E_i$  is the relaxation time and is defined as the time required for the stress in the  $i$ th Maxwell branch to decrease to  $1/e$  (0.368) of its initial value [12].

## 2.6. Compressive strength

The main criterion for evaluating the quality and rigidity of a material is the failure strength and, as for all physical properties, it will certainly depend on moisture content. Therefore, the examination of the compressive strength and its response to process conditions is crucial for the analysis of the drying process. Thus it seems interesting to determine the variation of the strength as a function of moisture content. As for Young's modulus determination, cylindrical porcelain samples having different moisture content were subjected to compressive tests. Another experience was carried out in order to study the effect of the drying temperature on the compressive strength of the material at the end of drying.

## 3. Results and discussion

### 3.1. Density variation

Fig. 1 shows the variation of the density of porcelain samples as a function of moisture content. The density increases up to a maximal value of  $1700 \text{ kg/m}^3$  for a relatively high value of moisture content (0.3 kg/kg d.b.) and then decreases. This is explained by the fact that, at the beginning of drying, the migration of water induces simultaneously a loss of weight and a tightening of the solid matrix elements, but the effect of shrinkage prevails over the effect of water loss. Then for low values of moisture content, the displacement of the solid matrix elements becomes more difficult, and shrinkage stops, which causes a decrease in the weight without change in volume. Density varies between 1500 and  $1700 \text{ kg/m}^3$  for a moisture content varying from 0 to 0.4 kg/kg d.b. The value of the apparent density of the dried  $\rho_s$  porcelain is  $\rho_s = 1522 \text{ kg/m}^3$ . These results are very similar to those found for clay materials [4].

### 3.2. Plastic limit

For the determination of the plastic limit, the porcelain powder was mixed with water until it became sufficiently plastic to be molded into a ball. A part of the porcelain sample was formed into a thread as specified in Section 2.2. The procedure was repeated using three more parts of the sample and the percentage water content in all of the crumbled porcelain was determined as a whole. The realized tests allowed us to conclude that the plastic limit is 25%.

### 3.3. Shrinkage variation

Results of direct measurements are presented in Fig. 2, which shows the variation of porcelain volume as a function of moisture content. Two periods of volume changes could be distinguished. At the beginning of drying, the volume variation

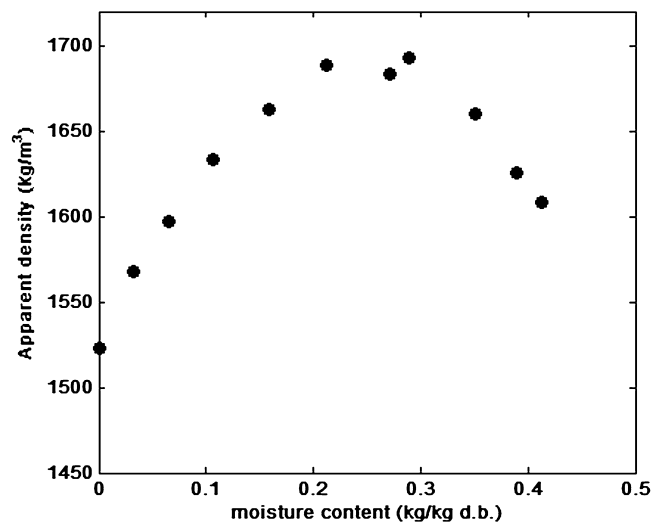


Fig. 1. Variation of the apparent density of porcelain as a function of moisture content.

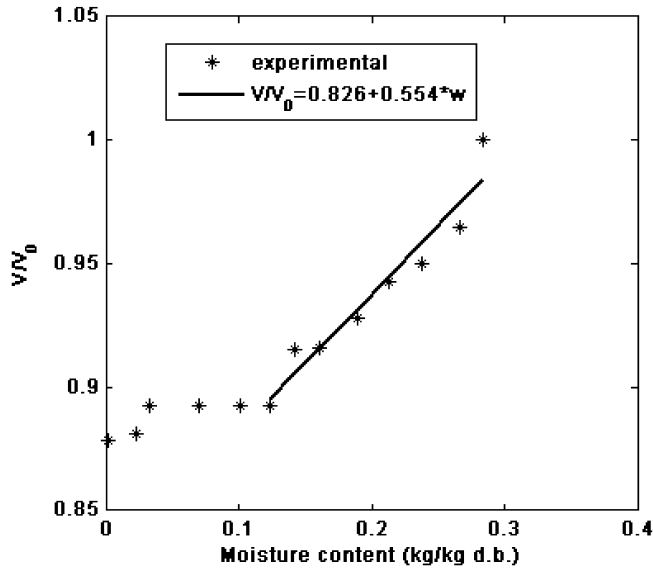


Fig. 2. Variation of porcelain volume shrinkage as a function of moisture content.

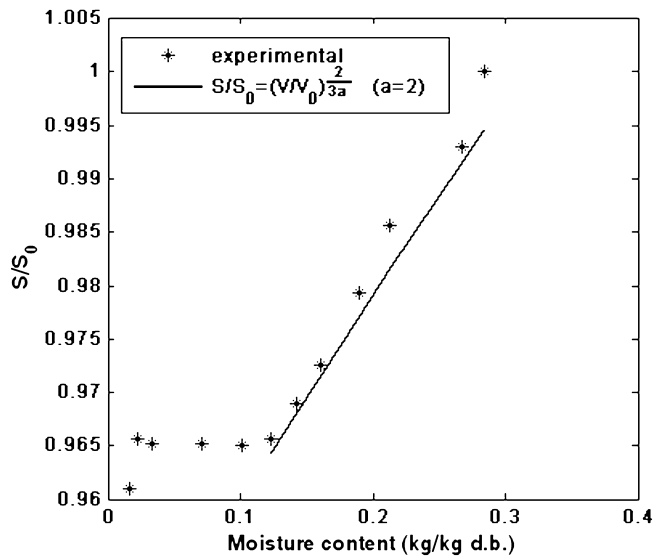


Fig. 3. Variation of porcelain area shrinkage as a function of moisture content.

is very important because a great moisture removal occurs and the dimensions of the sample change rapidly. Then for a certain value of moisture content called critical moisture content,  $w_c \approx 0.123$  kg/kg d.b., the volume remains constant because shrinkage stops.

During the first period, the volume varies linearly with the moisture content. The experimental data can be fitted with a linear function with a standard deviation of  $S = 0.00937$  and a correlation coefficient of  $R^2 = 0.966$  and the expression of the fitting is:

$$V = V_0(0.826 + 0.554w) \quad \text{for } w > w_c \tag{9}$$

From the measurement of the sample’s dimensions, the shrinkage could be deduced as shown in Fig. 3. A theoretical relation (eq. (10)) between the area and the volume variation was established since the area  $S$  is a square dimension and volume  $V$  is a cube dimension [13]:

$$\frac{S}{S_0} = \left[ \frac{V}{V_0} \right]^{\frac{2}{3a}} \tag{10}$$

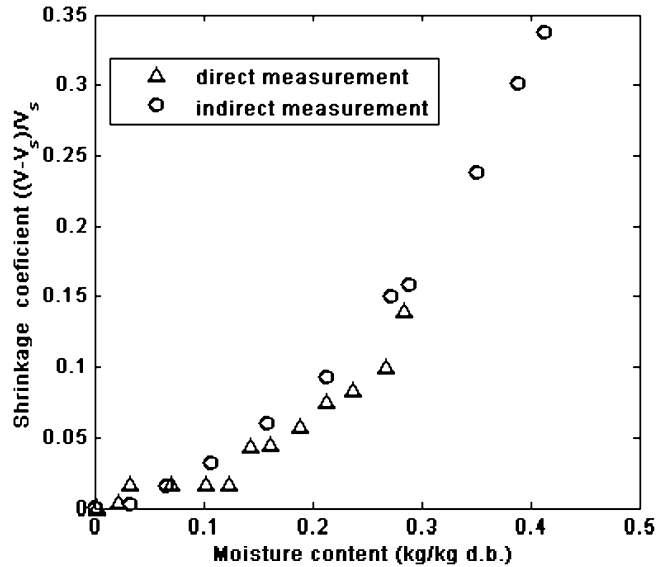


Fig. 4. Comparison of the variation of the shrinkage coefficient versus the moisture content of porcelain: data obtained by using direct and indirect measurement methods.

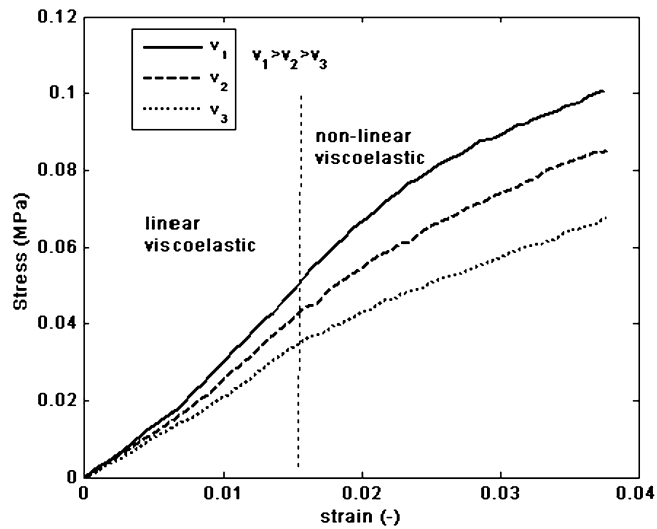


Fig. 5. Stress/strain porcelain behavior for several deformation rates.

The parameter  $a$  is a correction factor introduced to take into account the transition from the spherical to the cylindrical shape. The experimental results are well fitted with the previous equation with a standard deviation  $S = 0.0034$  and a correlation coefficient  $R^2 = 0.9706$  for  $a = 2$ .

Fig. 4 shows the shrinkage coefficient calculated from equations (4) (direct measurement) and (6) (deduced from the apparent density). Both curves have approximately the same trend. But the mismatch is due to the fact that in the second method (indirect measurement), the gaseous phase was not taken into account (hypothesis of saturated media). In reality, the volume shrinkage is not equal to the volume of water evaporated because vapor appears in the pores of the body.

### 3.4. Rheological behavior

The experimental results for three deformation rates ( $v_1 = 0.5$  mm/min,  $v_2 = 1$  mm/min, and  $v_3 = 1.5$  mm/min) are presented in Fig. 5. A displacement of the curves was noted when increasing the deformation rate, which justifies the inelastic behavior of porcelain. This is explained by the viscosity of the material, due to the presence of a liquid phase. Besides, for a deformation under 0.015, we notice that stress depends linearly on strain. So, the behavior of the material is linearly viscoelastic. Then beyond this value the material behavior becomes non-linear.

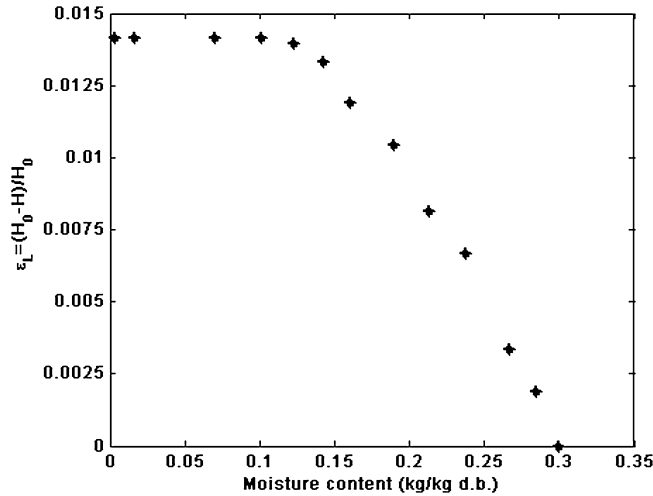


Fig. 6. Longitudinal strain as a function of the moisture content of a porcelain paste with an initial height of  $H_0 = 24$  mm.

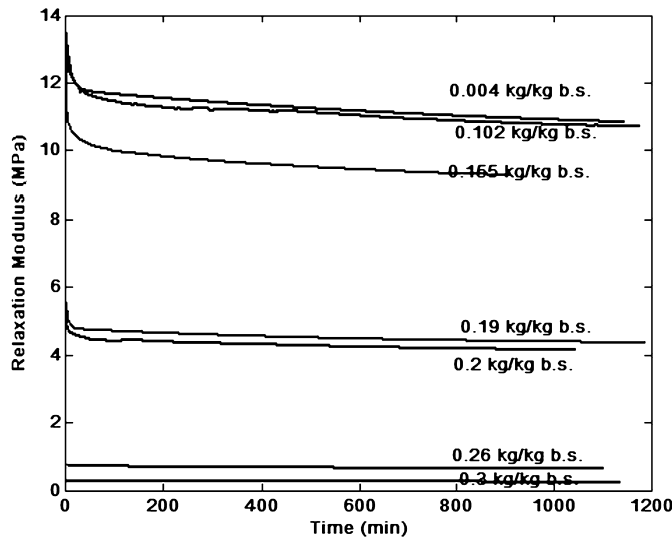


Fig. 7. Experimental relaxation modulus of porcelain versus time for different moisture contents.

To know the domain behavior of porcelain when it is exposed to drying and at free mechanical loads, it is possible to calculate the maximum deformation that can be reached during drying.

Fig. 6 shows the deformation of porcelain during drying, which was deduced from measurements of the longitudinal shrinkage. For an initial moisture content of 0.3 kg/kg d.b., the maximum deformation is 0.0141, which is less than 0.015. Thus, it could be concluded that during drying, the porcelain paste is always in the domain of linear viscoelasticity.

### 3.5. Viscoelastic properties

The results of relaxation tests for eight samples are presented in Fig. 7. Linear viscoelastic parameters (two Maxwell branches) with elastic constants ( $E_\infty$ ,  $E_1$ ,  $E_2$ ) and relaxation times ( $r_1$ ,  $r_2$ ) were determined by fitting equation (8) to the corresponding experimental data using a non-linear least squares procedure implemented in the MATLAB 9.0 programming environment.

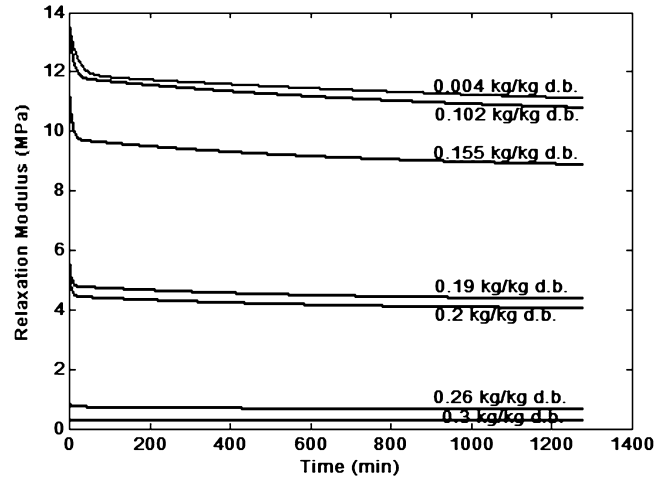
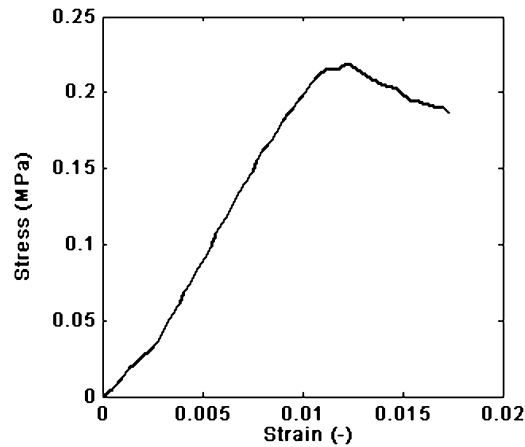
The fitting constants for a compression–relaxation experiment, however, approximate very well the experimental data: the average  $R^2$  value was very close to 1 ( $R^2 = 0.98$ ). The average values and standard deviations of these parameters, determined by model fits, are given in Table 1. The fitted curves of the relaxation modulus are presented in Fig. 8.

We notice that the elastic modulus  $E_i$  varies considerably with moisture content. For low moisture contents, the variation of the elastic modulus is negligible, since the solid skeleton imposes the behavior of the product. But for high moisture contents, the variation is very important due to the considerable quantity of water inside the porous media, which makes it very deformable. The relaxation times  $r_1$  and  $r_2$  tend to decrease with increasing moisture content. Thus, a lower value

**Table 1**

Variation of the Maxwell model parameters of porcelain with moisture content.

$W$ (kg/kg d.b.)	$E_{\infty}$ (MPa)	$E_1$ (MPa)	$E_2$ (MPa)	$r_1$ (s)	$r_2$ (s)	$S$ (-)	$R^2$ (-)
0.004	10.4540	1.6338	1.4277	1150.2224	95871.3673	0.0401	0.9856
0.102	10.3933	1.6303	1.4037	579.1678	59872.1356	0.0673	0.9810
0.155	8.6742	1.4522	0.0488	390.9203	45717.6415	0.04836	0.9834
0.19	4.2888	0.7634	0.4893	289.5497	37207.5216	0.02063	0.9765
0.2	3.9822	0.7071	0.4560	283.4075	36664.1176	0.0249	0.9824
0.26	0.6342	0.0910	0.0908	179.3741	26787.4757	3.9e-005	0.9669
0.3	0.2338	0.0291	0.0387	138.6814	22452.1392	0.0012	0.9926

**Fig. 8.** Relaxation modulus of porcelain versus time for different moisture contents obtained by the fitting model.**Fig. 9.** Stress–strain curve of a compression test applied on a porcelain sample ( $w = 0.06$  kg/kg d.b.).

of elastic modulus and relaxation time at higher moisture contents was mostly due to the plasticizing effect, which reduced the value of the relaxation force. In fact, as the moisture content in the ceramic increases, the product becomes more viscous. Consequently, less force was required to maintain a certain deformation level. Previous researchers have reported similar results for other products [14].

### 3.6. Strength variation

An example of a compression test until material's rupture is presented in Fig. 9. When the sample breaks, stress diminishes and strength intensity is defined as the peak of the stress–strain curve.

Fig. 10 shows that compressive strength values of porcelain depend on different moisture contents. The largest strength was observed for moisture contents of about 0.15 kg/kg d.b., and that the lowest values correspond to moisture contents



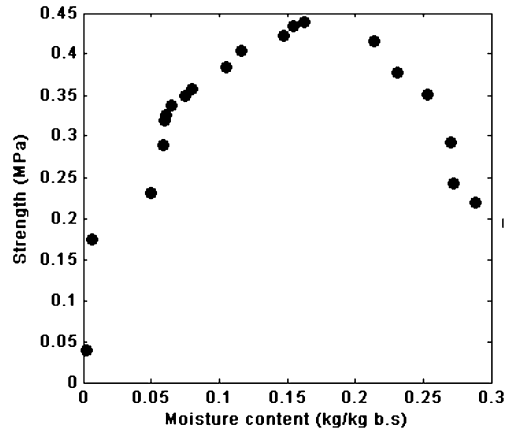


Fig. 10. Compressive strength of porcelain as a function of moisture content.

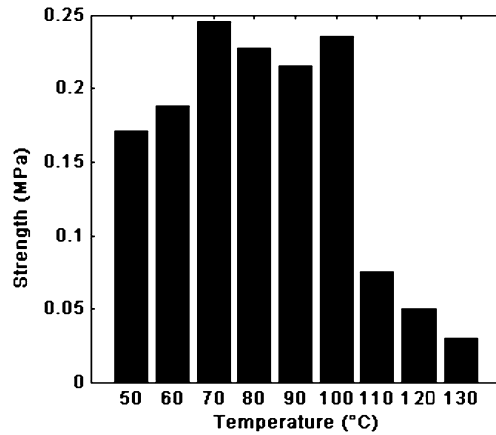


Fig. 11. The average strength of the porcelain samples dried convectively.

above 0.25 kg/kg d.b. and under 0.05 kg/kg d.b. So porcelain loses strength when it is fluid-like as well as when it is very brittle. This result is very similar to those of other works dealing with clay strength [15,16].

### 3.7. Influence of drying conditions on the compressive strength of dried porcelain

One of the parameters qualifying materials is the strength of the dried material, which is an important feature in many industrial branches.

As it is well-known, drying under severe conditions can deteriorate the quality of the product and especially mechanical strength. The influence of the drying temperature on the mechanical strength of dried material was thus examined.

In order to evaluate the strength of the final product, porcelain samples were firstly dried in a convective dryer at different temperatures between 50 and 130 °C. Drying tests are stopped when the mass samples are stabilized. Then each sample undergoes a compression test until rupture.

The stress intensity as a function of temperature is shown in Fig. 11. We notice that between 50 and 100 °C, strength changes slightly. Then, between 110 and 130 °C, strength decreases quickly with the increase of temperature. In fact, for temperatures less than 100 °C, water evaporation is produced at the surface of the sample, but beyond 100 °C evaporation can be produced inside the porous medium, and the appearance of a gaseous phase can provoke a gas pressure increase that expands the pores and renders the skeleton fragile. So, porcelain drying should not be performed above a temperature of 100 °C.

## 4. Conclusion

The physicomaterial characteristics of a ceramic paste (porcelain) were examined and their variations with moisture content were established (from 0 to 0.4 kg/kg d.b.). The apparent density varied between 1500 and 1700 kg/m<sup>3</sup>, depending on moisture content. Volume shrinkage variation was deduced from density and was in agreement with the results of direct measurements of sample dimensions during drying. Mechanical tests were carried out to delimitate the linear

and non-linear viscoelastic domains. From the results of stress–strain curves, it has been shown that, during drying, the porcelain's behavior is linearly viscoelastic. Relaxation test were carried out in order to determine the mechanical properties of porcelain as a function of time and moisture content. The fitting of the experimental relaxation tests showed that the studied material can be modeled by a Maxwell model with two branches. The variation of strength with moisture content was determined. The influence of the air-drying temperature on the sample's strength was studied and results showed that there is a temperature above which the process should not be performed (over 110 °C) because of strength decreases.

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