ESTIMATION OF QUARTZ PARTICLE SIZE AND CONTENT FROM NON-DESTRUCTIVE MEASUREMENTS OF THE CERAMIC TILE MODULUS OF ELASTICITY

Marcelo Dal Bó[(1,2)], Vicente Cantavella Soler[(3)], Enrique Sanchéz[(3)], Dachamir Hotza[(1)], Anselmo Ortega Boschi[(4)].

[(1)] Graduate Program in Materials Science and Engineering (PGMAT), Federal University of Santa Catarina (UFSC), Florianópolis, Brazil

[(2)] Federal Institution of Education, Science and Technology of the Rio Grande do Sul (IFRS), Campus Feliz, Brazil

[(3)] Institute of Ceramic Technology (ITC), Jaume I University (UJI), Campus Riu Sec, Castellón, Spain

[(4)] Federal University of São Carlos (UFSCar), Brazil

ABSTRACT

In this study, an innovative method for evaluating quartz particle size and content in a glassy matrix from the hysteresis of the modulus of elasticity was developed. To perform the study, a dense glassy matrix was prepared from sodium feldspar to which variable quartz contents were added (between 18.5 and 37.6% by volume) of different particle size (D_{50} between 3.4 and 31 µm). The starting powders were moistened to 8% with a PVA solution and then used to form test pieces with a rectangular cross-section by uniaxial pressing. The dry test pieces were sintered in a laboratory kiln (~1200ºC).

To measure the modulus of elasticity, acoustic impulse excitation was used. This non-destructive technique measures the natural vibration frequency of the material when it is subjected to a mechanical pulse (tap). The maximum test temperature was 700ºC, with a heating rate of 400 ºC/h. The results show that the quartz considerably affected the behaviour of the modulus of elasticity. The effect of the quartz was analysed in two ways: (*i*) in the temperature range below 573ºC (allotropic transformation temperature of quartz) and (*ii*) in the temperature range above 573ºC (to 700ºC). At temperatures below 573ºC, the results show that the hysteresis area between the modulus of elasticity curves during heating and cooling was closely related to quartz particle size. On the other hand, in the range between 573 and 700ºC, the variation of the modulus of elasticity of the materials was related to the quartz content (volume fraction) in the test pieces.

At the same time, chemical and structural analysis of the test pieces showed that the results of the new methodology matched quartz particle size and content in the pieces. This study thus provides an innovative solution for the study of quartz particle size and content present in already sintered ceramic materials, enabling valuable information on the composition and microstructure of these materials to be obtained by a non-destructive method.

1. INTRODUCTION

Materials can be mechanically characterised by the relationship between the force applied to them and the resulting strain. As a result of the application of a force, the atoms move, which causes the material to deform. The strain can be reversible (the strain being recovered after the force has disappeared) or irreversible (the strain being maintained after the applied force has disappeared)[1, 2].

The linear elastic behaviour, found in ceramic materials, can be described by Hooke's equation. For uniaxial loads, Hooke's Law is described in accordance with Equation 1:

Equation 1 $$\sigma = E\varepsilon$$

where:

σ: stress (Pa)

ε: elastic strain

Hooke's Law shows that, for an elastic behaviour, stress and strain are related through a proportionality constant "E", which is the Modulus of Elasticity[3].

Knowledge of the modulus of elasticity is of enormous importance in the design, development, and quality control of ceramic materials. The modulus of elasticity can be characterised by destructive and non-destructive methods. The three-point bending method, which measures the strain produced in a material by a stress, is an example of a method that is usually destructive (unless the failure limit of the material is not reached)[4, 5]. In contrast, the impulse excitation technique[6-8] is a non-destructive test for measuring the modulus of elasticity.

In accordance with the international standard[6], the modulus of elasticity may be calculated according to Equation 2, for test pieces with L/t≥20:

Equation 2
$$E = 0.9465\left(\frac{mf^2}{b}\right)\left(\frac{L^3}{t^3}\right)\left[1 + 6.585\left(\frac{t}{L}\right)^2\right]$$

where:

E: modulus of elasticity (Pa)

m: test piece mass (g)

b: test piece width (mm)

L: test piece length (mm)

t: test piece thickness (mm)

f: natural vibration frequency (Hz)

The modulus of elasticity is a mechanical property that depends on many variables. In heterogeneous materials, composition and processing[9], microstructure[10-12], and temperature[13] affect the modulus of elasticity. Consequently, the presence of crystalline particles of different nature, porosity, and microstructural cracks affect the modulus of elasticity of such materials.

Despite the extensive literature on the behaviour of the modulus of elasticity, no studies were found on the effect of crystalline quartz particle additions on the modulus of elasticity of heterogeneous materials. Nor were studies found on the effect of temperature on the behaviour of the modulus of elasticity of materials formed from a glassy phase with the addition of crystalline particles, though certain studies are available in the field of refractory materials.

This study examined the behaviour of the modulus of elasticity with the variation in temperature of glassy materials that contain crystalline quartz particles, using a non-destructive characterisation test.

2. MATERIALS AND METHODOLOGY

2.1 MATERIALS

The study was performed using sodium feldspar (Mario Pilato - Spain) and quartz (Sibelco - Spain). The chemical analysis of the materials is detailed in Table 1.

Oxides	Feldspar (% by weight)	Quartz (% by weight)
SiO_2	69.90	98.9
Al_2O_3	18.70	0.51
Fe_2O_3	0.06	0.05
TiO_2	0.12	---
CaO	0.50	0.03
MgO	0.10	---
Na_2O	10.00	0.01
K_2O	0.30	0.06
Others	0.02	0.17
L.O.I	0.30	0.27

Table 1: Chemical analysis of the materials used.

The quartzes referenced SE-500, SE-100, SE-12, and SE-8 according to the Sibelco nomenclature were used. The average sizes of the quartz particles (D_{50}) added to the sodium feldspar is given in Table 2.

Quartz	D_{50} (μm)
SE-500	3.4 ± 0.5
SE-100	13.4 ± 0.6
SE-12	20.4 ± 1.1
SE-8	31 ± 4

Table 2: Average sizes of the quartz particles.

The added quantity of quartz particles was also varied, three levels of percentage by weight being defined: 6.3% (corresponding to the matrix), 24.8% (M20Q), and 43.9% (M40Q).

2.2 PROCESSING AND CHARACTERISATION

The sodium feldspar was wet milled in a planetary grinding mill with alumina balls for 30 min. This yielded a material with a D_{50} of 6 µm. The resulting material was dried and then granulated with an 8% by weight aqueous solution at 5% PVA (polyvinyl alcohol, SIGMA-ALDRICH). The granulated powder was subjected to a uniaxial pressing pressure of 35 MPa, producing test pieces measuring 67x16.5x5.5 mm.

The quartz particles were added to the sodium feldspar by the wet method, homogenisation being performed in a planetary grinding mill for 10 min with a non-energetic charge.

The materials were sintered in an electric kiln (Pirometrol R-Series, Spain) at a heating rate of 210 ºC/min to 500ºC and 25 ºC/min to 1200ºC, holding the peak temperature for 6 min. Finally, conventional cooling was performed with the pieces inside the kiln.

The variation of the modulus of elasticity with temperature was determined by an acoustic method in which the natural vibration frequency of the material was measured using a J.W. Lemmens Grindosonic, model MK5I, instrument.

The crystalline phases were determined with a diffractometer (Bruker Theta-Theta, model D8 Advance). The measurement parameters depended on each respective sample, voltage varied between 30 and 40 kV, intensity between 40 and 45 mA, the time constant between 0.5 and 1.2 s, step size between 0.015 and 0.02º, and the angle from 2θ=5º to 2θ=90º.

Sample chemical analysis was performed using an X-ray fluorescence instrument (Axios, Panalytical).

Finally, a tile with a commercial porcelain stoneware composition (Spain) was selected to evaluate the method developed for the determination of quartz particle size and quantity.

3. RESULTS

3.1 EFFECT OF QUARTZ PARTICLE SIZE

To study the effect of quartz particle size on the modulus of elasticity, the quartz fraction was fixed at 24.8% by weight, keeping this value constant.

The behaviour of the modulus of elasticity of the materials with quartz is shown in Figure 1. The results show that the increase in quartz particle size reduced the modulus of elasticity at ambient temperature. This behaviour could be related to the damage caused by the quartz particles in the glassy matrix, generating cracks in the microstructure of the material. According to Budiansky et al., the increase in crack density in the microstructure reduces the modulus of elasticity, justifying the results[10].

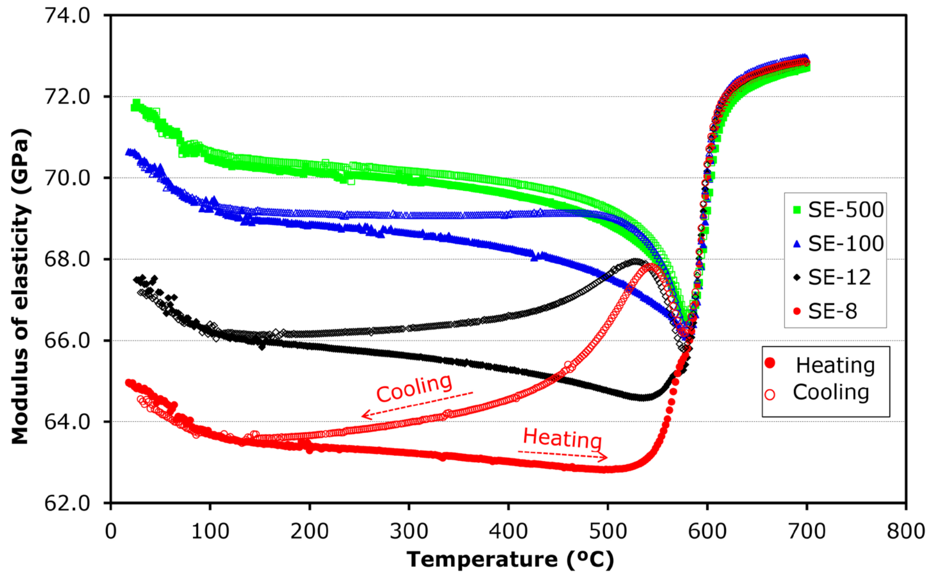

Figure 1: Behaviour of the modulus of elasticity for the materials with 24.8% quartz by weight.

With respect to the variation of the modulus of elasticity with temperature, it was observed that an increase in quartz size raised the hysteresis between heating and cooling at temperatures below 573ºC. On the other hand, the modulus of elasticity between 573 and 700ºC was the same for all materials with 24.8% quartz by weight.

Accordance to the literature surveyed, the modulus of elasticity depends on the composition[11], porosity[14], and crack density of the material[10,12]. As the modulus of elasticity was the same at temperatures above 573ºC (allotropic transition of quartz), it may be inferred that, under these conditions, all the cracks in the microstructure associated with quartz had closed.

The relationship between the hysteresis of the modulus of elasticity and quartz particle average diameter (D_{50}) is shown in Figure 2.

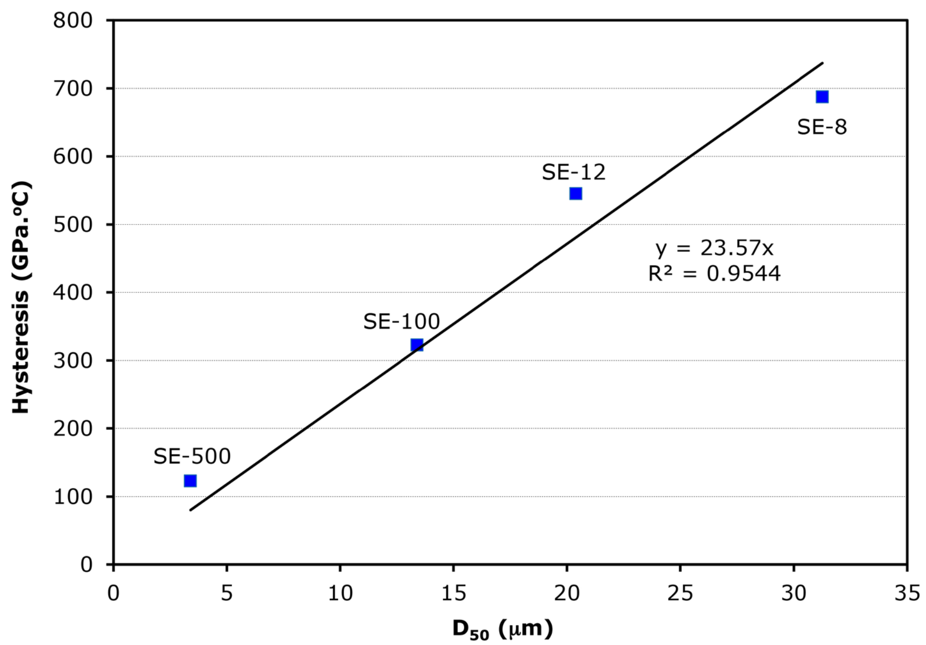

Figure 2: Relationship between the hysteresis and quartz particle average diameter.

The previous relationship was linear, and could be written in the form:

Equation 3 Hysteresis = $23.57 \cdot D_{50}$

With a view to extending the methodology to industrial products, the modulus of elasticity of a commercial porcelain tile was determined. In accordance with the hysteresis area of the porcelain tile obtained (~500 GPa·ºC), the D_{50} of the quartz contained in the porcelain tile would be ~21 mm, very close to the D_{50} of the SE-12 quartz. According to the literature, the average quartz particle size diameter is usually below 40 mm in materials of the porcelain tile type[15,16].

3.2 EFFECT OF QUARTZ CONTENT

When the quartz content was varied, the modulus of elasticity E at temperatures above 573ºC exhibited a very important variation, as shown in Figure 3.

This behaviour may be considered related to the change in the modulus of elasticity of the quartz crystals with temperature, because quartz displays a much greater increase in E than the albite crystals and than the albite glass also present in the microstructure[17,18].

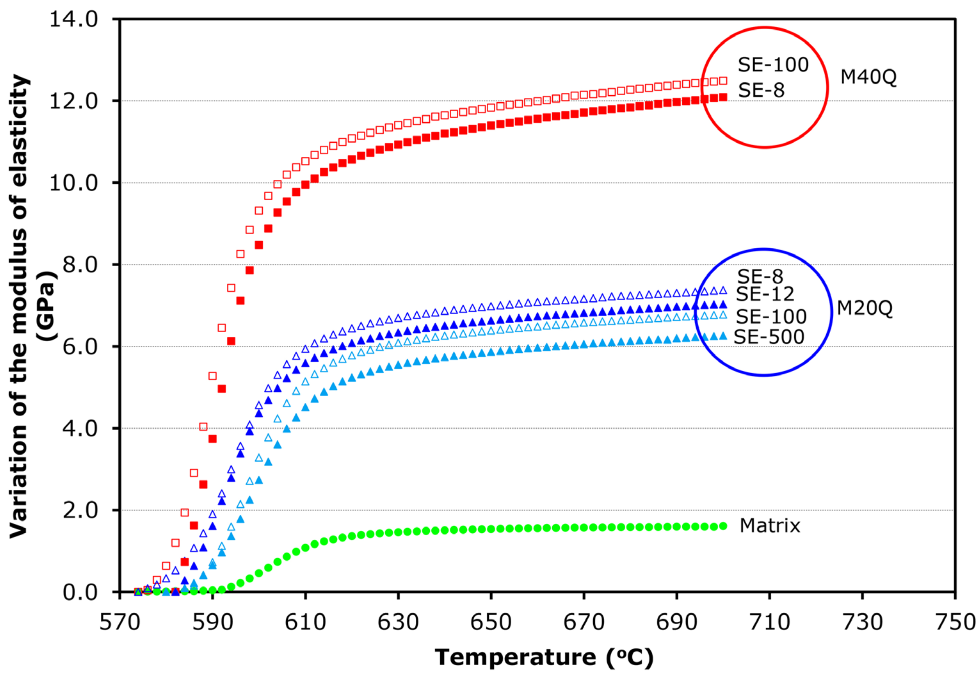

Figure 3: Variation of the modulus of elasticity of the materials between 573 and 700ºC.

The behaviour of the modulus of elasticity for the different samples suggested that there was a relationship between the variation of the modulus of elasticity ($\Delta E_{573\text{-}700}$ºC) and the quartz content in the materials. This relationship is described in Figure 4, in a range that covers the percentage customarily found in industrial products (commercial porcelain tile usually has a quartz fraction between 5 and 35%[19]).

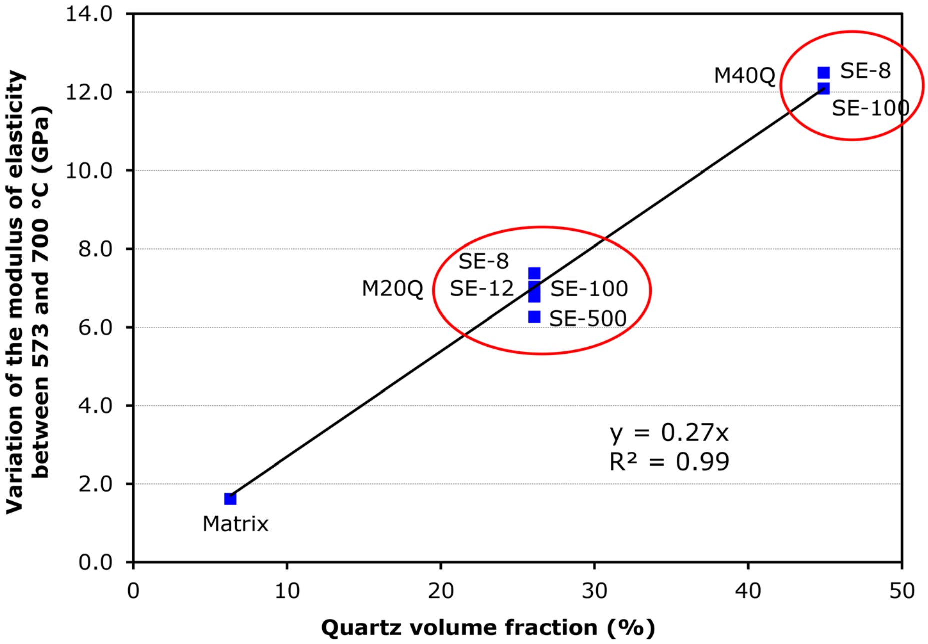

Figure 4: Relationship between the variation of the modulus of elasticity and quartz volume fraction of the samples.

In accordance with the results, an equation can be written that relates the variation of the modulus of elasticity between 573 and 700ºC to quartz volume fraction.

Equation 4 $\Delta E_{573\text{-}700} = 0{,}27V_{quartz}$ $\Delta E_{573\text{-}700} = 0{,}27V_{quartz}$

In order to validate the described calculation methodology, the modulus of elasticity of the commercial porcelain tile used in section 3.1 was determined. The ΔE found was 4.8 GPa with which the quartz quantity present could be determined from Equation 4.

At the same time, the crystalline quartz content in the porcelain tile was quantified using the Rietveld method. The results are detailed in Table 3, and in Figure 5 a comparison is shown with those of the other studied materials.

Crystalline phase	Quantity (% by volume)
Quartz	15.0
Mulite	12.0
Anorthite	2.5
Albite	1.5

Table 3: Quantitative chemical analysis of the crystalline phases present in the studied commercial porcelain tile.

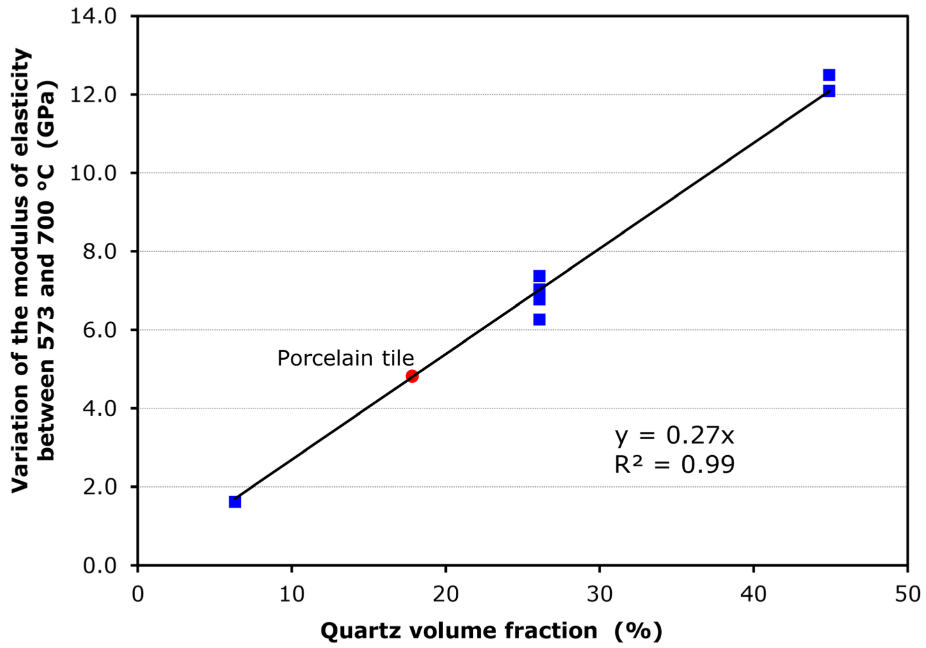

Figure 5: Quartz volume fraction in the commercial porcelain tile according to Equation 4.

The good agreement obtained between Equation 4 (quartz volume fraction: 17.7%) and the X-ray diffraction analysis with the Rietveld method (15%) indicates that, in principle, the developed methodology is appropriate for quantifying the quartz content in ceramic materials of the porcelain tile type. However, this result needs to be confirmed by analysing a greater number of industrial porcelain tiles.

4. CONCLUSIONS

- An innovative methodology has been developed for estimating the average size of the quartz particles, and for quantifying these, in already sintered ceramic materials.

- A linear relationship has been verified between quartz particle size and the hysteresis of the modulus of elasticity below the allotropic transition temperature of quartz (573ºC).

- A linear relationship has also been verified between quartz content and the variation of the modulus of elasticity above the allotropic transition temperature of quartz (573ºC).

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