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Nanomechanical properties of cement paste

Propriedades nanomecânicas de pastas de cimento



F. PELISSER [a]
pelisser@hotmail.com

P. J. P. GLEIZE [b]
ecv1phg@ecv.ufsc.br

M. D. MICHEL [c]
mdmichel@bol.com.br

Abstract

Understanding the influence of each phase of concrete, among which cement paste deserves prominence, is important for the development of a more efficient concrete, with an improved hydration process and resistance to plastic shrinkage cracks. The elastic modulus of the concrete is one of the main project parameters of structures and it has extensive influence on the speed of the construction process and the durability of structures. The capacity for deformation of the concrete depends on the intrinsic characteristics of the cement hydration products, aggregates, transition zone and pores, besides variables inherent to the process, including the speed of hydration and climatic conditions. The aim of this research was to analyze the mechanical properties of the elastic modulus and hardness of a cement paste, through the nanoindentation technique, and compare these using the conventional method for concrete. The results obtained for the nanostructure of cement pastes presented mean elastic modulus values of 17.9 GPa and 0.90 GPa for hardness. Determination of the elastic modulus calculated by NBR 6118 [1] was 9.6 GPa. Nanoindentation proved to be a valid method for evaluating nanostructure modifications in cement pastes.

Keywords: nanoindentation, cement paste, elastic modulus.

Resumo

O entendimento da influência de cada fase do concreto, dentre as quais merece destaque a pasta de cimento, é importante para o desenvolvimento de um concreto mais eficiente, com maior velocidade de hidratação e resistência à propagação de fissuras. O módulo de elasticidade do concreto é um dos principais parâmetros de projeto de estruturas e têm grande influência na velocidade do processo de construção e na durabilidade das estruturas. A capacidade de deformação do concreto depende das características intrínsecas dos produtos de hidratação do cimento, agregados, zona de transição e poros, além de variáveis inerentes ao processo, como velocidade de hidratação e condições climáticas. O objetivo deste estudo foi avaliar as propriedades mecânicas de módulo de elasticidade e resistência superficial (dureza) para uma pasta de cimento, através da técnica da nanoindentação instrumentada e, complementarmente, comparar este valor do módulo de elasticidade, utilizando o método normatizado para concreto. Os resultados obtidos pela nanoindentação foram de 17,2 GPa para o módulo de elasticidade e de 0,90 GPa para a dureza. A determinação do módulo de elasticidade tangente inicial calculado pela NBR 6118 [1] foi de 9,6 GPa. A nanoindentação mostrou-se uma ferramenta válida para avaliar modificações nanoestruturais de pastas de cimento.

Palavras-chave: nanoindentação, pasta de cimento, módulo de elasticidade.

[a] *Programa de Pós-Graduação em Ciência e Engenharia de Materiais - PPGCEM. Universidade do Extremo Sul Catarinense. pelisser@hotmail.com. CEP: 88802225. Criciúma. Brasil;*
[b] *Programa de Pós-Graduação em Engenharia Civil. Universidade Federal de Santa Catarina. ecv1phg@ecv.ufsc.br. C.P. 476. Florianópolis. Brasil;*
[c] *Centro Interdisciplinar de Pesquisa e Pós-Graduação. Universidade Estadual de Ponta Grossa. mdmichel@bol.com.br. CEP: 84030900. Ponta Grossa. Brasil.*

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1. Introduction

The principal phase of hardened Portland cement pastes is calcium silicate hydrate (C-S-H), which influences the physical and mechanical properties of construction materials. C-S-H is considered a lamellar, crystalline semi-continuum and inherently complex material, particularly in relation "bond" nature forces, consisting of order-disorder lamellae stacking of particles, where each lamellae is formed by stacking sheets (approximately 12 under the best synthesis conditions) and each sheet has a central Ca-O sheet that has silicate chains on both sides, which are kinked with a periodicity of three tetrahedra; these chains are called dreierketten. [2, 3].
In the science and engineering of materials, C-S-H is considered one of the more complicated systems. The cohesion of the C-S-H matrix depends on the bonding scheme forces of the intralamellae sheets, classified as nanostructures, together with the solid-solid bonds between lamellae stacks (interlamellae) and water adsorbed on the surface, classified as bonds in the mesostructure [4].
While several models coexist to describe the structure of C-S-H, to date no model relates the chemical composition and nano- and microstructure with its mechanical properties [5]. Using the nanoindentation technique, recent studies by Vandamme, Ulm and Fonollosa [6] showed that the water/cement (w/c) ratio influences the volume of C-S-H formed. While studying w/c ratios of 0.15, 0.20, 0.30, 0.35 and 0.40, they observed that the greatest difference did not occur in the total volume of C-S-H formed, rather in the increase of one type of C-S-H, LD (low density) C-S-H compared to HD (high density) C-S-H. In principle, the difference between LD and HD C-S-H is the packing density of C-S-H particles. Their observations also verified that the effect of temperature (hydration at 60°C) potentializes the formation of HD C-S-H, achieving similar levels irrespective of the w/c ratio (considering w/c ratios > 0.25). The authors concluded that dominating the morphology of C-S-H is important to improving its properties and highlighted that the w/c ratio is only one parameter that affects the control of the micro- and nanostructure through the packing of C-S-H particles.
The instrumented indentation technique **at micro-nanoscale** is more widely used to evaluate the mechanical properties of homogeneous materials, such as films. However, the technique can be extended to characterize rough materials, such as C-S-H, though, in certain cases, measurements should be corrected due to roughness at the site of indentation [5,7]. This technique has two important limitations: first, quantifying surface roughness is not a simple procedure and different procedures adopted for the test can result in different indices; and second, the proposed amendments are applicable to a very small surface layer compared to total indentation depth. Other authors have avoided the need for correction using a statistical approach [8] and greater indentation depths in order to minimize the effect of surface roughness.
Some authors [5, 7, 8] have used the indentation technique to characterize cement pastes, verifying a variation in the results of elastic modulus and hardness as a function of the different phases formed. The results were obtained in order from 26 to 39 GPa for regions of HD C-S-H, from 13 to 26 GPa for LD C-S-H, above 39 GPa anhydrous cement particles and from 0 to 13 GPa in regions of macroporosity [7].
One of the problems with the test frequently used in the indentation procedure are matrices with a high number of points, spaced between 10μm and 20μm, using a 2mn load in order to achieve a penetration depth of 100 to 400nm. However, this differentiation phase without visualization of the indented regions and without conducting further chemical analysis can complicate the interpretation of the results [9].
This research used the instrumented indentation technique at micro- and nanoscale to evaluate the mechanical properties of cement paste, comparing the results with literature values and with the initial tangent modulus, conventionally measured for concrete, using an electric extensometer.

2. Materials and methods

The nanomechanical properties of hardness and elastic modulus were evaluated using the instrumented indentation technique at a micro- and nanoscale, in accordance with the procedure described in the following item, and the initial tangent modulus, which was determined in accordance with NBR 8522 [1]. **The nanoindentation technique, or instrumented indentation at nanoscale, consists of applying a load to the material, controlling and recording, during both loading and unloading, the load and penetration depth, which is performed at the nanometric scale.**
A cement paste with a w/c ratio of 0.50 was used, elaborated with CP V-ARI RS cement. The test samples used for the indentation tests were approximately 1cm3. These were made in cylindrical molds and cut to produce 5-6mm thick test sections. Next, the sections were polished with sandpapers and cloths using diamond particles (up to 0.25μm) until a flat, smooth surface was achieved that was free from irregularities.
After polishing, the test samples were exposed to ultrasound to remove loose particles and potential contamination. To determine the initial tangent modulus **of elasticity**, test samples measuring 5x10cm (diameter x height) were used. Analyses were performed on day 7, at the end of the curing period, which was performed by immersion in saturated lime water at a controlled temperature.

2.1 Nanoindentation – Technique

The technique of nanoindentation consists of making a diamond tip penetrate the material, while controlling and recording the load and penetration depth. The maximal load is maintained constant for several seconds and then removed. The time, in seconds, is controlled in three stages: loading, maximal load and unloading. The data produced are structured in a load-displacement diagram (*P-h*), which describes a curve denominated load-unloading. The process of analysis of the measurements, i.e., the *P-h* curve, permits the characterization of the test samples and determination of the results of elastic modulus (*E*) and hardness (*H*).
Hardness *H* is defined as the mean pressure that supports the material under load and it is calculated in accordance with Oliver and Pharr [10], as follows:

$$H = \frac{P_{max}}{A(h_c)} \tag{1}$$

where P_{max} is the maximal load applied and $A(h_c)$ is the projection of the area of contact **between the indenter tip and the test sample**. The reduced elasticity modulus *E* of the indenter-sample set can be determined from the slope of the unloading curve, calculated in accordance with Oliver and Pharr [10], as follows:

$$E_r = \frac{\sqrt{\pi}}{2\beta}\frac{S_{max}}{\sqrt{A(h_c)}} \quad (2)$$

where $S_{max} = (dP/dh)$ is the stiffness obtained experimentally **from the top** of the unloading curve **(i.e., from the maximal load, the start of the unloading curve and up to 1/3 of the unloading curve)**, $A(h_c)$ is the projected contact area in the horizontal plane and β is a constant factor of correction for the indenter geometry. The reduced elasticity modulus considers the effects of non-rigid indenters and is related to the modulus of the material and the indenter. Thus, the elasticity modulus *E* of the material is determined by:

$$E = \frac{1-\nu^2}{\left(\frac{1}{E_r} - \frac{1-\nu_i^2}{E_i}\right)} \quad (3)$$

where E_r is given by equation (2), E_i and ν_i are the elasticity modulus and Poisson ratio of the indenter and E and ν are the elasticity modulus and Poisson ratio of the material. The mechanical properties of hardness and elastic modulus in the regions of micro and nano analysis were obtained according to ISO/DIS 14577 recommendations [11].

2.2 Nanoindentation – Proceedings

The indentations were performed using a XP Nanoindenter of the MTS System. To determine the hardness and elastic modulus, a Berkovich-type triangular base pyramidal tip was used.
Two matrices were indented in cement paste: an smaller matrix (matrix 1) of 2 by 3 points, totaling six indentations, with a spacing of 200µm; and a larger matrix (matrix 2) of 4 by 4 points, totaling 16 indentations, with a spacing of 200µm.
After contact, 10 cycles of loading were applied using loads of 1, 2, 4, 8, 16, 32, 64, 128, 256 and 512mN; load 2 mN was used as a reference for estimates and comparisons, as recommended in the literature [5,7,8]. During the indentation, a linear load for was applied 10s, until a maximal peak was achieved, this load was maintained for 5s, after which constant unloading occurred over 10s. The penetration depths were between 100 and 5000nm. The loading cycles with higher loads were conducted to minimize the effect of surface roughness and mark the sample for subsequent visualization under a scanning electron microscope (SEM).

3. Results and discussion

The results of the estimation of elastic modulus obtained in the indentations performed using two measurement matrices, the first with four valid points and second with nine valid points, are presented in Table 1. As observed in the table, under a 2 mN load, the mean modulus for matrix 1 was 17.2±2.9 MPa, with a variation coefficient of 17%. In matrix 2, also under a 2mN load, an esti-

Table 1 – Individual results of elastic modulus estimates in the indented

Matrices		Load (mN) 1 E-(GPa)	2 E-GPa	4 E-GPa	8 E-GPa	16 E-GPa	32 E-GPa	64 E-GPa	128 E-GPa	256 E-GPa	512 E-GPa
1	2	17.9	17.8	14.8	9.1	7.0	15.5	12.0	14.0	14.8	14.4
1	3	17.1	14.0	12.1	12.6	8.4	8.2	9.1	10.2	9.8	10.3
1	4	23.5	15.9	8.3	5.3	4.1	7.3	8.4	9.6	9.1	10.3
1	6	11.7	20.9	22.1	21.7	19.1	14.9	23.8	22.1	22.0	16.8
Mean		17,6	17.2	14.3	12.2	9.7	11.5	13.3	14.0	13.9	13.0
Sd.		4,8	2.9	5.8	7.0	6.5	4.3	7.2	5.8	6.0	3.2
COV.		27,5	17.2	40.7	57.6	67.9	37.7	53.7	41.2	42.7	24.8
2	1	22.3	18.4	14.6	18.9	16.8	13.4	14.4	11.2	8.9	9.7
2	2	10.4	11.7	9.6	7.2	5.3	5.4	6.3	7.5	8.2	9.0
2	3	13.2	12.4	5.1	5.1	8.9	10.4	12.0	11.9	10.3	9.3
2	6	13.9	5.7	7.8	8.7	9.4	7.7	7.5	8.9	9.1	8.8
2	8	5.7	7.8	12.0	15.7	17.1	16.5	14.2	9.3	7.3	8.5
2	9	12.7	10.6	11.0	11.4	12.3	11.6	11.1	9.5	10.0	9.5
2	12	6.6	6.5	5.7	9.1	10.6	9.3	5.3	6.5	5.7	5.3
2	14	15.2	8.6	7.7	6.4	6.4	4.1	5.9	6.0	5.7	5.9
2	16	18.9	15.1	16.2	15.1	10.7	8.5	10.6	9.4	6.3	5.9
Mean		13.2	10.8	10.0	10.8	10.8	9.7	9.7	8.9	7.9	8.0
Sd.		5.3	4.2	3.8	4.8	4.1	3.9	3.5	2.0	1.8	1.8
COV.		40.4	38.6	38.4	43.8	37.7	40.0	36.6	22.2	22.4	22.1

Figure 1 – View larger matrix showing the points of indentation

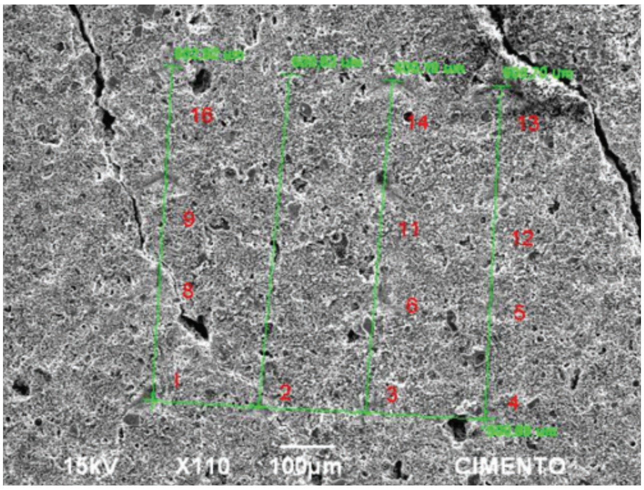
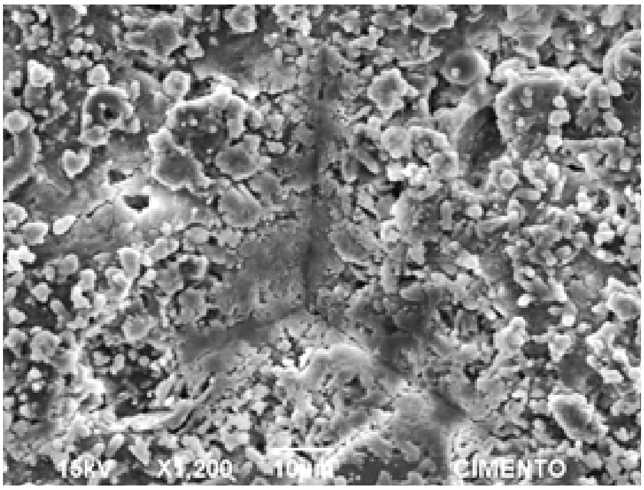


Figure 3 – Point image of the indentation 12



mated value for elastic modulus of 10.8±4.2 MPa was obtained, with a variation coefficient of 39%. The mean values of hardness were approximately 0.9 GPa and 0.2 GPa for the matrices 1 and 2, respectively.

The region and indentation points of matrix 2 can be seen in Figure 1. **For matrix 1, it was not possible to locate the indentation points under SEM.**

Estimates of elastic modulus for matrix 1 were similar to those obtained by Constantinides et al. [5] while evaluating a cement paste with a w/c ratio of 0.5, for which an elastic modulus M_{LD} of 21.7±2.2 GPa was determined. In another experiment, Constantinides and Ulm [7] evaluated the nanomechanical properties of C-S-H (w/c = 0.50) and observed the following for the two principal phases: LD C-S-H, elastic modulus of 18.2 GPa and hardness of 0.45 GPa; and HD C-S-H, elastic modulus of 29.1 GPa and hardness of 0.83 MPa.

Considering the classification range of the C-S-H phases [5], which define the values between 0 and 13 GPa as corresponding to regions of high porosity or macroporosity, and applying this range to matrix 2, a corrected mean value **(excluding values below 13 GPa)** of the elastic modulus of 16.8±2.3 GPa was determined.

Figure 2 – Point image of the indentation 1

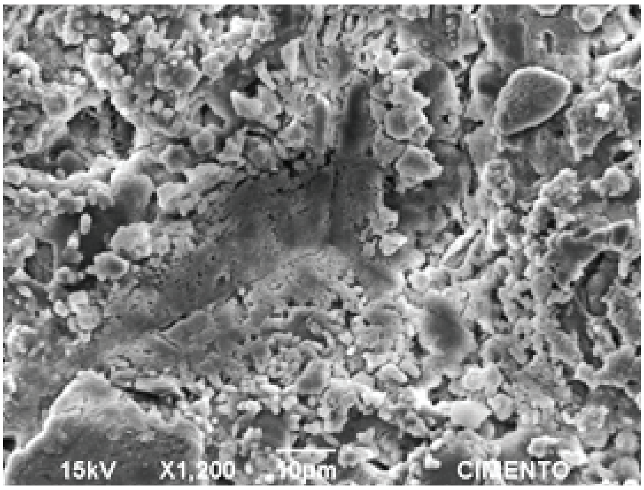


Figure 4 – Load-displacement curves for the indentations 1 and 12 (matrix 2)

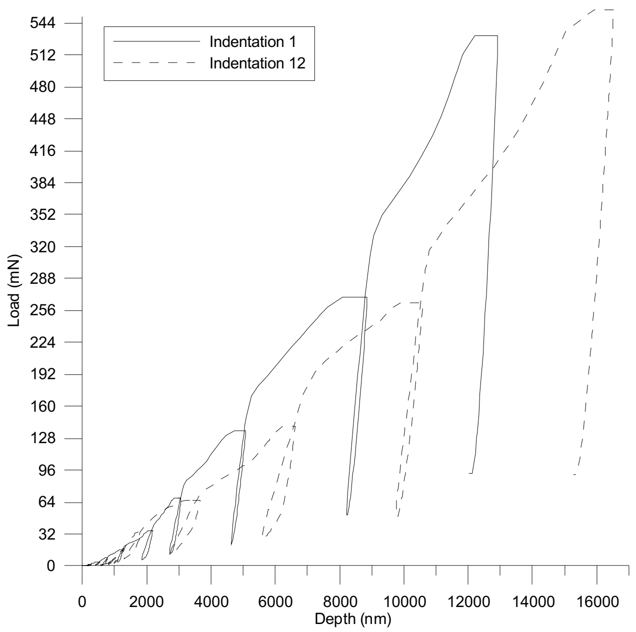
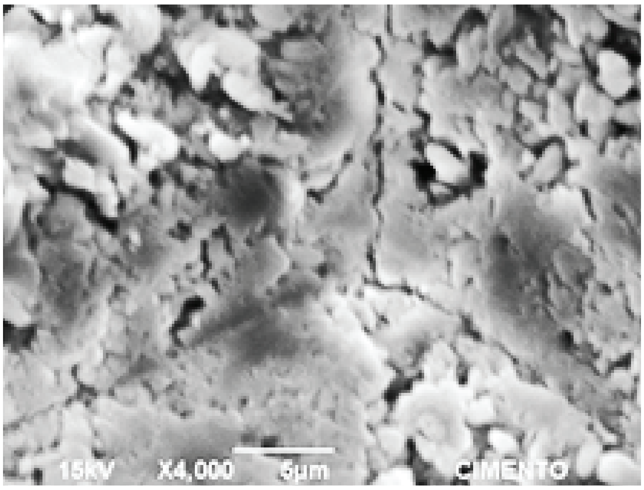


Figure 5 – Indentation point 13, site at which the chemical analysis by EDS was performed



Thus, the two tests presented similar behavior, with minimal variation between them. The greater variation of values initially verified in matrix 2 **could be the result of a natural increase in variability when testing a larger zone**.

Analysis of the results confirm that the formation of a low density C-S-H occurs **when using cement-type CPV ARI RS**, as indicated in the literature [7,12-15].

Examination of the images of the indentation points revealed the existence of a high surface roughness, which in theory, could have influenced the readings. However, comparison of the surface images of indentation points where the highest and lowest elastic

Table 2 – Results of chemical analysis at indentation point 13

Element	Weigth (%) – error
Ca	36.6 ± 0.22
Si	6.07 ± 0.07
Al	1.75 ± 0.07
Fe	1.02 ± 0.10
O	36.5 ± 0.29
Na	0.15 ± 0.04
C	15.9 ± 0.27
Mg	0.32 ± 0.05
K	1.66 ± 0.09

modulus values were obtained verified that the visual difference in porosity and roughness was minimal, as shown in Figures 2 (indentation 1, *E* = 22.4 GPa) and 3 (indentation 12, *E* = 6.6 GPa). These results indicate that the variation in the elastic modulus value is not only influenced by the presence of pores and surface roughness, but also by the internal porosity and packing of C-S-H particles during hydration.

Figure 4 shows load-displacement curves for indentations 1 and 12, showing the greater depths of penetration for test sample 12 and the indentation fracture in both test samples due to lack of linearity in the loading curve.

In Figure 5, a point of indentation is shown in which chemical microanalysis was performed by EDS. The values are presented in Table 2 and show a high concentration of calcium, indicating a high Ca/Si ratio (CaO/SiO_2) characteristic of hardened cement pastes.

In relation to the cement pastes, C-S-H synthesis presents lower

Figure 6 – Images of indentations in C-S-H synthesis (a) for a load of 32mN (b) for a load of 512mN

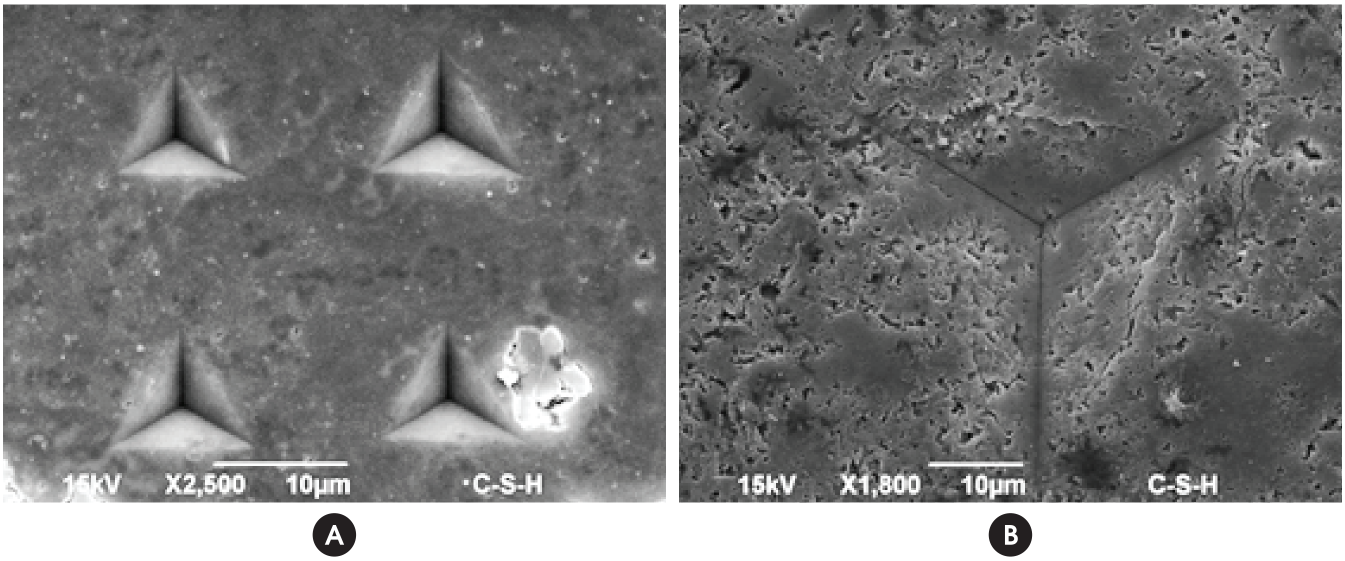


Figure 7 – Mean elastic modulus as a function of applied load

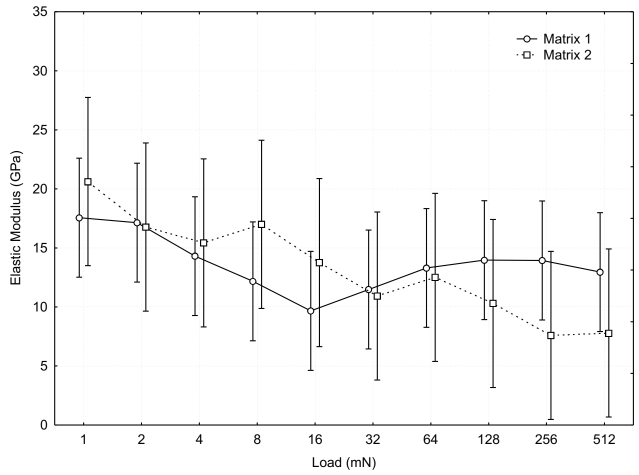
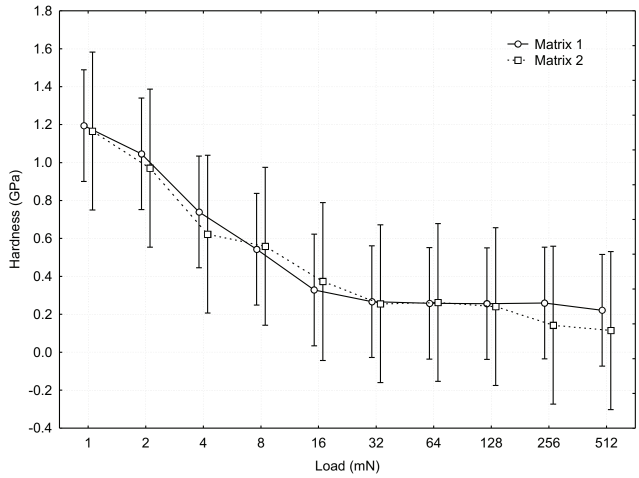


Figure 8 – Mean hardness as a function of applied load



surface roughness, as shown in Figures 6 (a) and 6 (b), and thus lower variation coefficients. The values of elastic modulus and hardness of the C-S-H synthesis, with high and low Ca/Si molar ratios, were determined and values of E = 19.3±1.2 GPa for elastic modulus and H = 0.19±0.05 GPa for hardness were verified for a high Ca/Si ratio (» 2.1) [16]. Considering that C-S-H synthesis was performed with a high solid/liquid ratio (1:20), mechanical results similar to the pastes indicate that the formation of the nanostructure of C-S-H is independent of the w/c ratio and is more directly related to nanoporosity, which is influenced by the particle structuring and packing and by the Ca/Si ratio [3,5,6].
One way to minimize the effect of surface roughness and verify the homogeneity of the material is to apply loading cycles with higher load points. When performing this procedure, a reduction in the elastic modulus and hardness occurred, as shown in Figures 7 and 8, respectively. Furthermore, when applying higher loads in sites with low elastic modulus, no significant increased was observed, indicating the influence of structural features of C-S-H and not surface roughness alone. In some cases, the application of cycles of greater loading resulted in a reduction in elastic modulus due to fractures at the indentation points.
The mechanical properties measured by the nanoindentation technique were compared with the mean initial tangent modulus (NBR 6118) measured in cylindrical speciments, the mean value for the cement paste was 9.6 ± 0.3 GPa, with a mean compressive strength of 23.4 MPa. Compared to the value determined using the nanoindentation technique, this lower value is associated with the fact that the traditional test is influenced by macroporosity, **which is eliminated in nanomechanical testing, thus the properties of C-S-H and its porosity packing (nanoporosity) are more precisely assessed**.

4. Conclusions

The nanoindentation technique proved to be a useful tool in assessing the nanomechanical properties of cement pastes. Observation verified that measurements of the depth of the indentations are influenced by surface roughness, by nanoporosities in the structure of C-S-H and by the load intensity used.
Characterization of the cement paste resulted in mean values of 17.2±2.9 GPa for a four-point matrix analysis and mean values of 16.8±2.3 GPa for a nine-point matrix analysis, indicating the formation of low density C-S-H. Comparing the results obtained in the cement paste (w/c = 0.5) with those obtained for the synthesized C-S-H (w/c = 20) [16], it can be concluded that improvements in the structuring and packing of the particles in the meso- and nanostructure of C-S-H, together with a reduction in porosity, would further improve the mechanical behavior of cement-based materials.
Considering that the nanomechanical properties of C-S-H are not yet fully understood, the results clarify the importance of visualizing the indentation points and performing **chemical microanalysis** to achieve the correct interpretation of the results.
In conclusion, nanoindentation is a valuable tool for assessing nanostructural changes in cement pastes and can be used in the study of the Macro-Defect-Free (MDF) cements and for monitoring the result of changes arising from the use of mineral admixtures, polymers, nano-fibers and other materials. Moreover, it can be useful in studying the degradation process and durability of cement-based materials.

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