Mapping the Mechanical Properties of Cement-based Materials By Using CSM and Ultra-fast Nanoindentation

Application Note

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Introduction

Cement-based composites still represent the most used materials in the construction industry, due to their low production and processing costs.

Nonetheless, the fundamental mechanisms underlying the microstructure build-up and the in-service mechanical behaviour are still mostly unknown, due to the extreme complexity of such materials [1].

Cement-based composites have been already identified as nano-granular multi-scaled materials, with a strong heterogeneity that manifests itself at multiple scales, in form of multiple pore spaces and multiple minerals that build-up the solid phase.

Such complexity is further increased by the recent growing use of nano-additives in cements [2], which often involves the formation of nano-phases that are not fully characterised, yet.

The primary hydration product of cement pastes and concrete is the calcium–silicate–hydrate (CSH), which act as the main binding phase and mostly influences the mechanical and creep properties of the system [1].

Recent studies [3–5] have also confirmed the presence of different solid phases in a cement-based composite: (a) mortar-concrete (>10^{-3}m), (b) cement paste (<10^{-4}m), (c) C-S-H matrix (<10^{-6}m) and (d) CSH solid phase (10^{-9}-10^{-10}m).

The elementary C-S-H particle is a nanoparticle of the average dimension of the order of 5nm, which includes an average nanoporosity of 18%. The presence of "structural water" at the nano-scale gives relevant time-dependent mechanical properties to these materials. Depending on the level of packing of the elementary building block, high-density (HD) and low-density CSH phases have been recently proposed as possible hydrated mechanical phases in cement. Tailoring of such phases is the key-issue for a proper control of the in-service behaviour of such materials.

In this study, we propose to investigate the nano-mechanical properties of a commercial cement paste by the use of an improved statistical nanoindentation method.

This technique, which was originally proposed in 2004 [3], is based on the realization of grids of hundreds of nanoindentation tests, coupled with

a statistical analysis (deconvolution) for the identification of the different mechanical phases and their distribution over the sampled area.

The principle of statistical nanoindentation is described in Figure 1a-b. If we assume that the distribution of the elastic modulus (E) is well approximated by a Gaussian distribution, then the average property of each phase can by analytically obtained, for a multi-phase material, by fitting the experimental frequency distribution of the mechanical property with the theoretical probability density function (PDF), as schematically shown in the Figure 1b. it is clear from Figure 1b that only those phases whose peak intensity is much higher than the background noise will be detected in a statistically consistent way. Starting from the original idea, the method has been further implemented and optimised in the last ten years by a number of research groups [4–23].

LD and HD CSH phases in cement pastes have been recently identified by the use of this method and the analysis of the elastic modulus maps [6–8]. Recent papers also showed that fitting of the cumulative distribution functions (CDF) is statistically more reliable, in comparison with the PDF, because CDF analysis does not require the choice of a bin-size to build the frequency histogram.

However, strong limitations are still present, due to the relatively low number of tests that can be realized using a conventional nanoindentation approach in a reasonable amount of time. This is absolutely not sufficient to make quantitative and reliable analysis of secondary phases (e.g. the HD-CSH and the unhydrated clinker phases), whose peak intensity is usually of the same order of the typical noise associated to the experiments.

To solve this issue, we propose the use of the Agilent's Express Test option in order to dramatically improve the statistical reliability and spatial resolution of mechanical properties mapping by nanoindentation. This target is achieved by the realization of more than 30000 valid tests in less than 10 hours on a commercial cement paste.

The maps obtained by using both the Express Test and the conventional Continuous Stiffness Measurement (CSM) approaches are compared with SEM-EDS microstructural observations of the same areas of the tests.

The final purpose of this work was to assess the correlation between hydration mechanisms and mechanical properties of the basic constituents of cement, by using a nanoindentation based approach, coupled with SEM-EDS mapping.

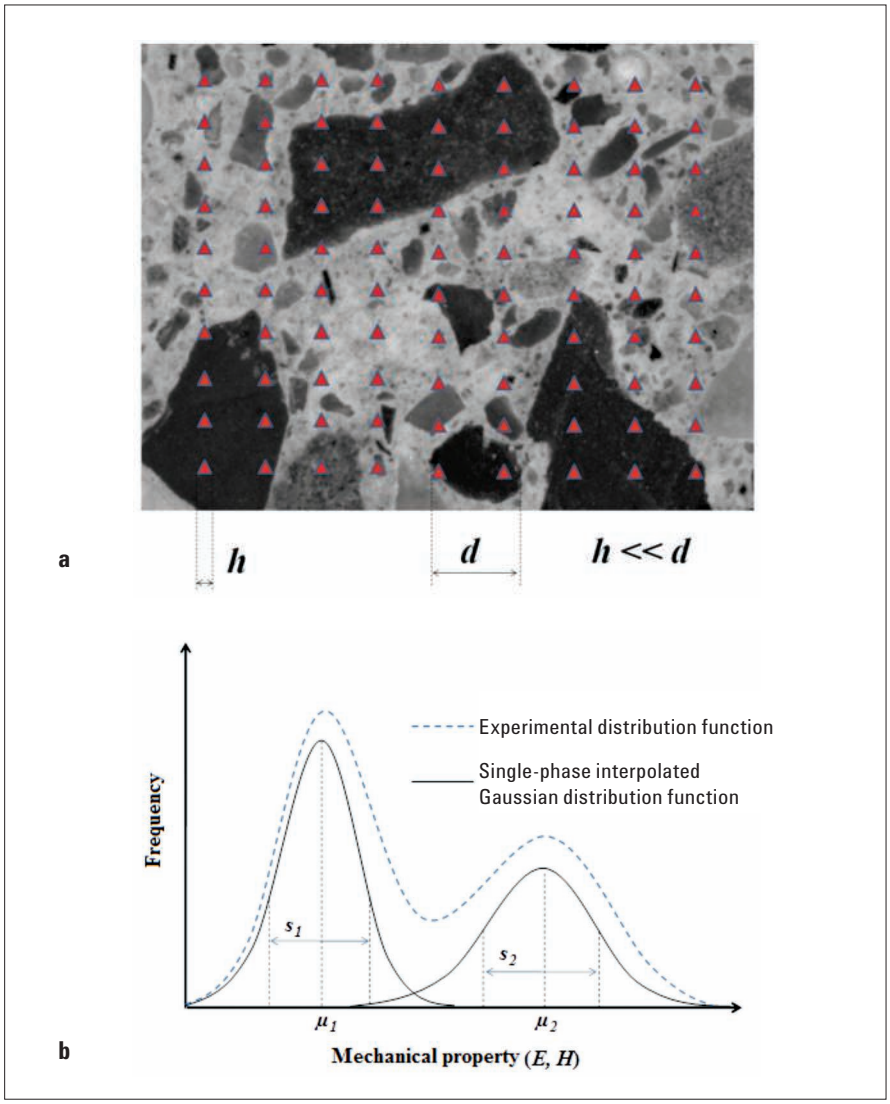


Figure 1. Concept of statistical nanoindentation to map the mechanical properties of multi-phase materials. (a) a grid of tests is performed and (b) the frequency distribution plot of obtained properties (Elastic modulus and/or hardness) are analyzed through deconvolution processes, in order to identify mechanical phases.

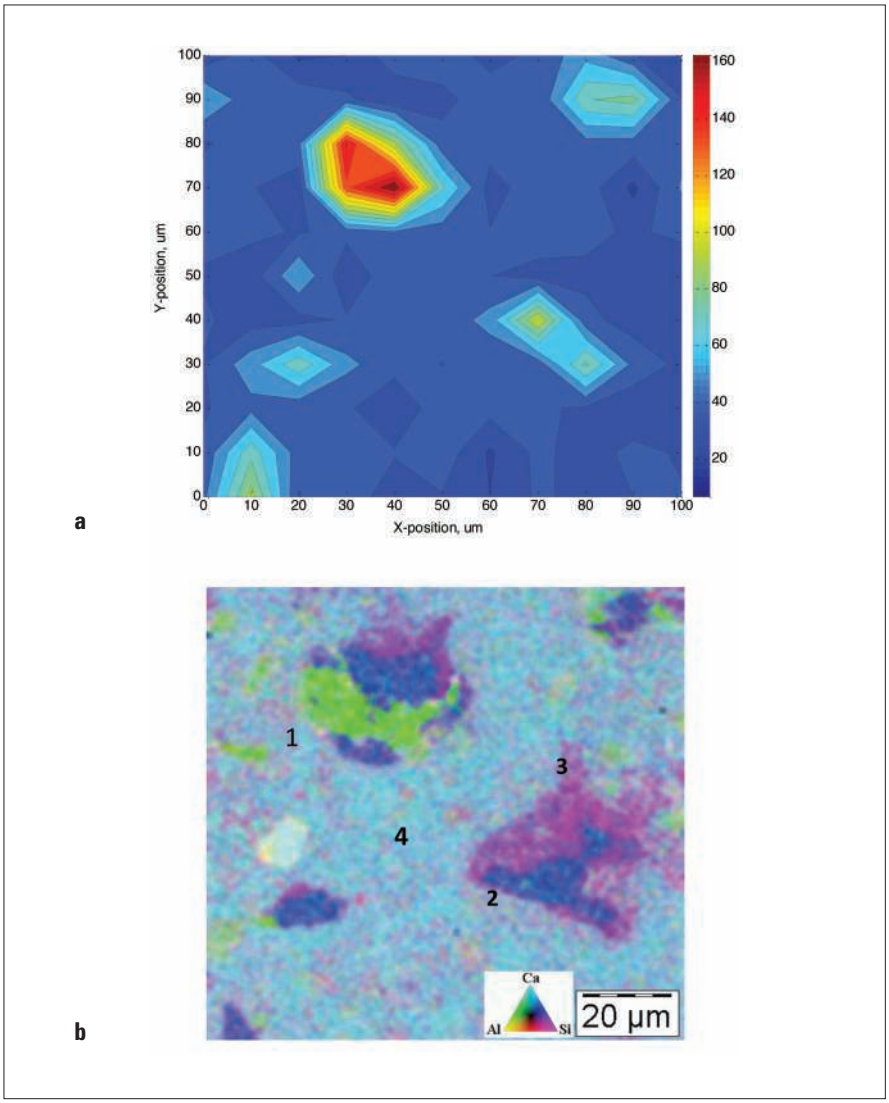


Figure 2. (a) Elastic modulus map (GPa), as obtained by the conventional CSM (10x10=100 indents matrix, spacing 10µm, indentation depth 100nm). (b) SEM-EDS map of the same area, where the green phase corresponds to C4AF clinker phases (label 1), the blue one to C3S clinker phase (label 2), the violet and light-blue to the HD and LD CSH, labels 3 and 4 respectively.

Experimental Details

Cement paste samples were produced from a commercial CEM I 52.5R Portland cement, using a w/b ratio of 0.36. After a curing time of 28 days under 100% humidity environment, samples were polished down to a surface roughness Ra < 20nm.

Nanoindentation tests are performed with an Agilent G200 NanoIndenter having CSM and Express Test, which includes NanoVision and a DCM II fitted with a Berkovich indenter. The standard material is fused silica.

In case of CSM tests, a grid of 20x20 indents was realized over a squared area of 200x200µm^2, with a spacing of 10µm and a maximum indentation depth of 100nm. CSM tests were useful to identify the best penetration gives which reduces both the effect of surface roughness (more evident at shallower depths) and the ones due to porosity (more important at larger depths) on the modulus vs depth profile: 100nm was found to be the optimal depth giving the most reliable evaluation of elastic modulus for such materials.

Ultra-fast tests were performed by prescribing arrays of 50x50 indents over an area of 100x100µm^2, by fixing a maximum depth of 100nm and a spacing of 2µm.

Express Test performs one complete indentation cycle per second, including approach, contact detection, load, unload, and movement to the next indentation site. In this way, quantitative maps of both the elastic modulus and the hardness of a surface can be realized in a reasonable time.

In this work, Fifteen different matrices were performed in a single day of testing (ten hours), being the overall number of performed tests equal to 37500.

Detailed microstructural and compositional observation of the same areas of the tests were finally performed by SEM-EDS analysis.

Results and Discussion

Figure 2 shows an optical micrograph where eight different maps (squared areas in dark grey) obtained by ultra-fast nanoindentation can be compared with the one obtained by conventional CSM nanoindentation (letter "A").

The elastic modulus maps obtained by both the conventional nanoindentation and the Express Test are reported in the Figures 3a and 4a, respectively. The corresponding SEM-EDS maps are also reported in the Figures 3b and 4b.

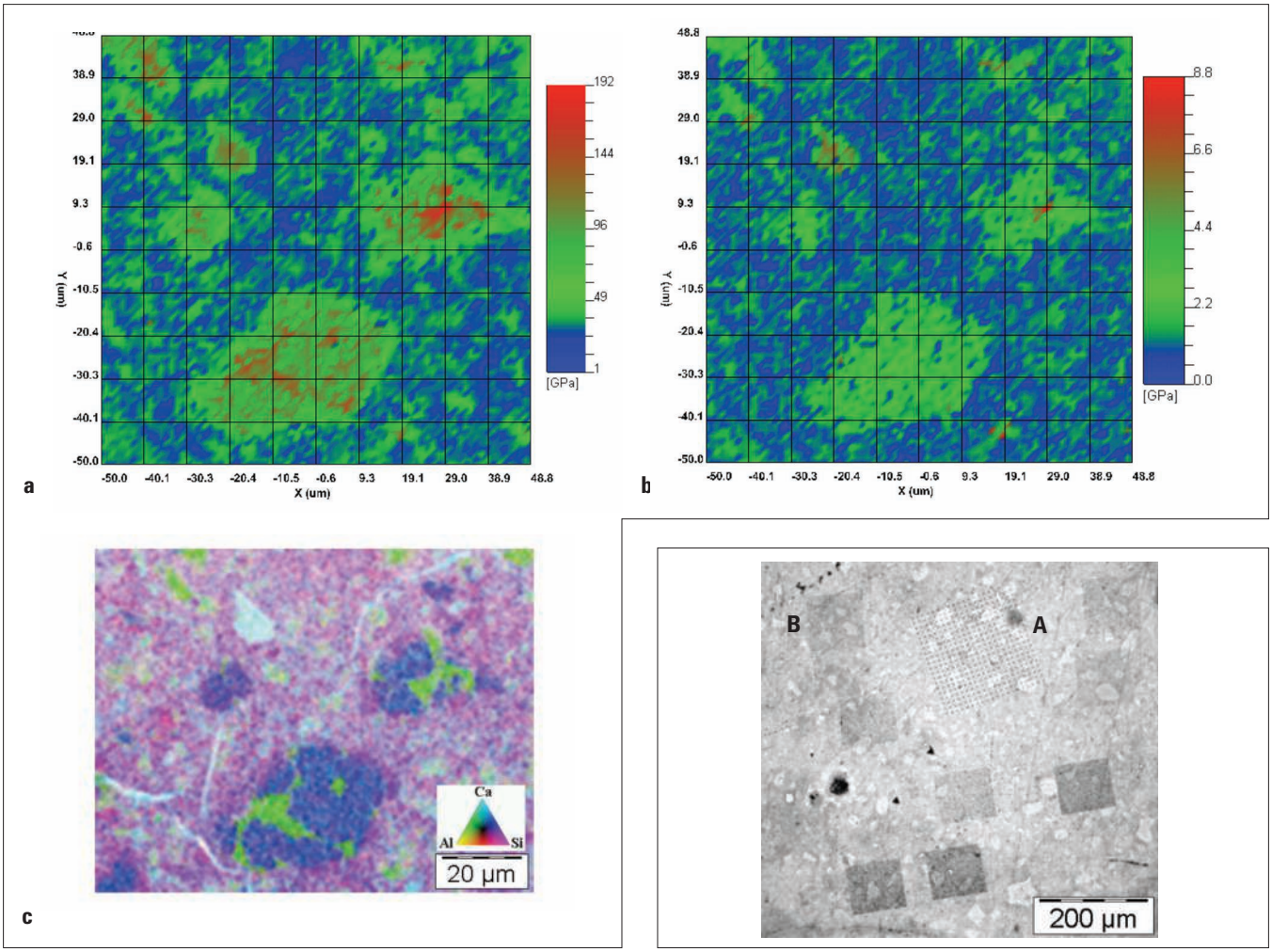


Figure 3. (a) Elastic modulus map (GPa), as obtained by the express test (50x50=2500 indents matrix, spacing 2µm, indentation depth 100nm). (b) Hardness map (GPa) from the same test, (c) SEM-EDS map of the same area, where the orange phase corresponds to C4AF clinker phases, the light-blue to C3S clinker phase.

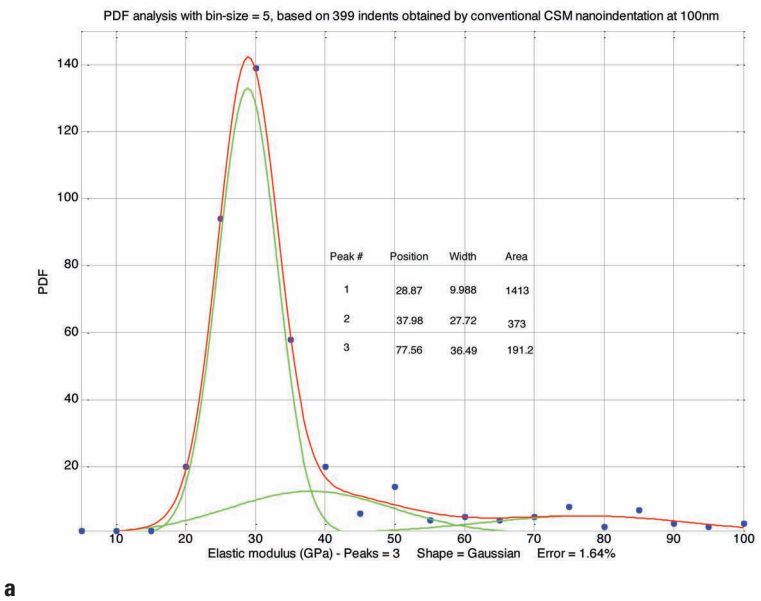
Figure 4. Optical micrograph where eight different maps (squared areas in dark grey) obtained by ultra-fast nanoindentation can be compared with the one obtained by conventional CSM nanoindentation (label "A"). Results of map "B" are those reported in the Figure 3a–c.

In both cases, a good correspondence between the elastic modulus maps and the SEM-EDS observations is observed.

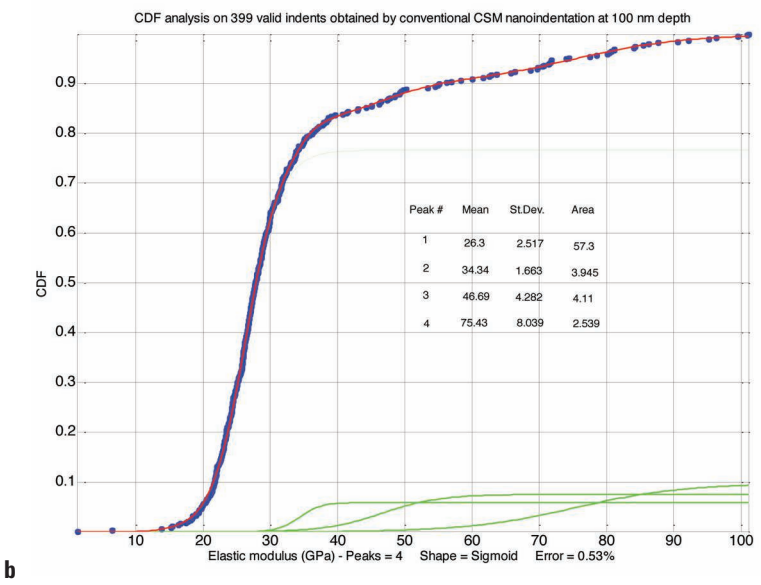
In case of the conventional map (Fig. 3a), the positions of the un-hydrated clinker grains are clearly identified, but no distinction is possible among the tri- and di-calcium silicates (C2S and C3S), the Calcium aluminate and ferrite (C3A and/or C4AF). The SEM-EDS maps reported in the Figure 2b show the presence of a C3S clinker grain (bottom right), a mixed C3S/C4AF grain (top left), a magnesium oxide (MgO) particle (white particle) and three smaller C3S grains. The inner product of hydration (HD-CSH) is clearly recognizable as the violet (Si-rich) crown around the un-hydrated C3S grains. The LD-CSH (Ca-rich) is the light blue matrix. The elemental distribution in the EDS maps was not observed previously.

In contrast with the conventional low-resolution maps, an almost perfect correspondence is noticed between the mechanical maps (Fig. 4a-b) and the SEM-EDS map (Fig. 4c) when using the express test. Also in this case, C3S, mixed C3S/C4AF and MgO particles are identified by EDS analysis (Fig. 4c). Those particles are all clearly defined by the Express Test mapping, where the elastic modulus gradients inside single phases are also well-defined. In particular, higher modulus is found for the C4AF and MgO grains with respect to the C3S clinker grains. Clear distinctions in terms of hardness are also observed.

EDS maps showed a higher Si/Ca ratio for the HD-CSH, even though a more



a



b

Figure 5. (a) Gaussian Distribution (PDF) analysis with bin-size = 5 GPa, based on 399 indents obtained by the conventional CSM method at 100 nm depth (b) Cumulative Distribution Function (CDF) analysis on 399 indents obtained by the conventional CSM method at 100 nm depth.

homogeneous Si distribution is observed on this area. The two C-S-H phases identified (LD, HD-CSH), corresponds to two different packaging densities of the basic building block. This suggest that the local Si ion mobility could be reduced in correspondence of the clinker/matrix interface so to give a Si-rich phase.

It is important to note that the Elastic Modulus map obtained by ultra-fast indentation is also able to identify the LD and HD-CSH phases directly on the map.

The use of the ultra-fast nanoindentation approach is a real enabling technology for this application, as it allows to achieve real micron-scale spatial resolution for mechanical property mapping.

This is further confirmed by the statistical deconvolution analysis reported in the Figures 5 and 6.
On one hand, deconvolution from 399 valid conventional tests gives unstable results when using the PDF approach for data analysis.

In fact, a significant effect of the adopted bin-size on the results was observed when using the PDF approach: this is clearly due to the low peak intensity for the secondary phases, which is of the same order (or even lower) than the average noise associated to the experiments (roughness and other edge effects). The example reported in the Figure 5a is the one which gives the lowest fitting error.

Note that previous literature studies report extremely similar data [5], thus meaning that quantitative evaluation of the secondary phases is very difficult by using a conventional nanoindentation approach, or at least it is strongly affected by the noise associated to measurements.

On the other hand, the analysis of 33134 valid tests obtained by the Express Test method give extremely robust results irrespective of the adopted deconvolution approach (PDF and CDF):

in all cases, peaks corresponding to the four main phases are identified in a reproducible way, being ALL peak intensity significantly higher than the noise associated to measurements. So, the most reliable mechanical properties of the cement paste are those given in the Figure 4a–b: four main phases are identified, namely the LD-CSH, HD-CSH and two peaks corresponding to the two main un-hydrated clinker grains (C3S and C4AF).

Finally, it is interesting to make a quantitative comparison between the average elastic moduli of the hydrated phases, as obtained by the conventional and Express Test methods.

As reported in Figures 5–6, the Express Test seems to overestimate the elastic modulus of the CSH phases, in comparison with the conventional nanoindentation.

This is likely due to the significant strain-rate sensitivity of cement-based materials, which was already reported in previous papers. The higher elastic moduli obtained by the express test are then simply related to the higher strain-rate during testing.

Conclusion

In this work, the hydration mechanisms of a commercial cement paste have been investigated by the use of an innovative statistical ultra-fast nanoindentation method.

The two-dimensional analysis of mechanical phases, coupled with SEM-EDS maps, revealed the presence of two distinct hydrated phases (low density and high-density CSH). High-density and low-density phases correspond to the inner and outer products of hydration, respectively. By correlation with SEM-EDS observations, different packing densities were also correlated to different Si/Ca ratios. Gradients of elastic modulus inside the clinker grains are also resolved by this method.

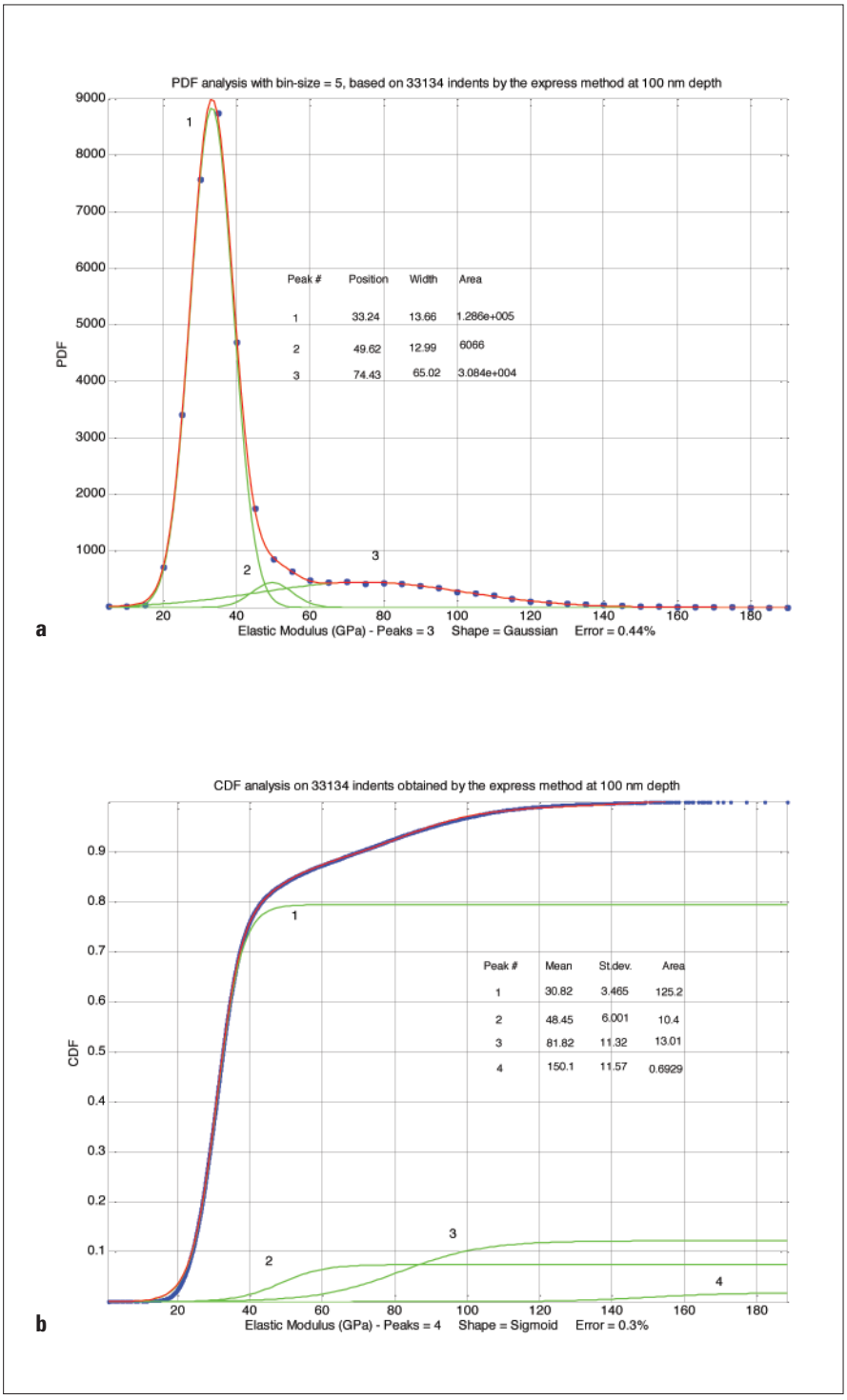


Figure 6. (a) Gaussian Distribution (PDF) analysis with bin-size = 5, based on 33134 indents by the express method at 100 nm depth (b) Cumulative Distribution Function (CDF) analysis on 33134 indents obtained by the express method at 100 nm depth.

The adopted ultra-fast indentation method also allows to distinguish between the different phases that are present inside single grains of un-hydrated phases. This gives unprecedented resolution in mapping the mechanical properties of cement, if compared to conventional nanoindentation mapping. This experimental tool can be an enabling technology for the design of innovative cement formulations, e.g. by tailoring the relative content of the constituents and/or addition of nano-additives.

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Published in USA, October 15, 2013
5991-3389EN

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