MICROMECHANICAL ANALYSIS OF HETEROGENEOUS STRUCTURAL MATERIALS

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1. Introduction

Micromechanical analysis of any material involves several subsequent steps that cannot be omitted. The first one includes microstructural observations and determination of phases. This step can be performed with the aid of many experimental techniques. Among others, the most common technique is electron microscopy (ESEM) and atomic force microscopy (AFM). These techniques allow qualitative as well as quantitative investigation of individual material phases at small volumes near or at the sample surface. As a complementary computational technique, image analysis can give valuable results for the phase distribution based on the separation of pixel colors.

The second step is the measurement of intrinsic properties of individual material phases. These measurements can be provided exclusively by nanoindentation which is a technique that can directly access mechanical properties at small dimensions starting from several tens of nanometers (depending on the sample and the probe).

The third step involves up-scaling of the properties to the higher level (mesolevel)[6]. Several analytical or numerical homogenization techniques can be employed to reach this goal.

2. Heterogeneity of structural materials

We can find several types of heterogeneity at microscale of structural materials. The first type of heterogeneity comes from mixing of components that do not chemically react in the matrix like sand, fibers, and other additives. Such heterogeneity is usually known in advance and is given by the mixing proportions. The second type of heterogeneity comes from chemical reactions that are evolving after the mixing of components. As a result of these reactions, new phases are produced and it is hard to rigorously define their volumes and distribution. Formation of the new phases includes fully reacted matrix, unreacted grains of the raw material and interfacial zones with different chemical and also mechanical properties[1,2]. Structural materials based on cement or waste materials (like fly-ash, furnace slag, etc.) usually include both types of the heterogeneity.

3. Test samples

As an example of structural materials, two types of samples were selected: cement paste (CP) and alkali-activated fly-ash (AAFA). Cement paste (as the main component of cementitious composites) is formed by mixing the cement powder (granulated clinker minerals) with water. Subsequent chemical reaction (hydration) follows to form new products. The main components that can also be distinguished in ESEM are hydrated products containing mainly calcium-silica hydrates (C-S-H gels) and calcium hydroxide $CaOH_2$ (CH, Portlandite), unreacted clinker grains and capillary pores (see Fig. 1). Samples used in this study were created from Portland cement CEM-I 42,5R, locality Mokrá, mixed with water in water-cement ratio = 0.5 by weight and cured in water for approximately 1 year.

The second samples were produced from granulated fly-ash (coal power-plant, Mělník) activated by addition of 6–10 % of Na_2O and cured 4–16 hours at 60–90 °C. After the

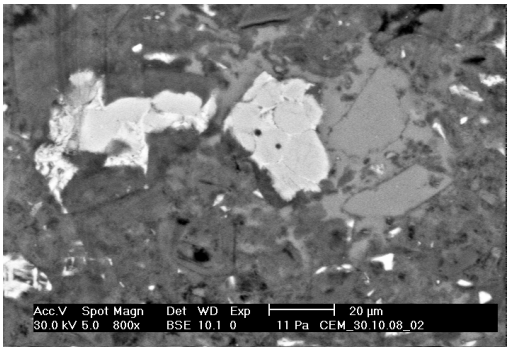

Figure 1. **ESEM image of hydrated cement paste.** Dark areas = pores; dark grey = C-S-H gels; light grey = Portlandite; light areas = unreacted clinkers

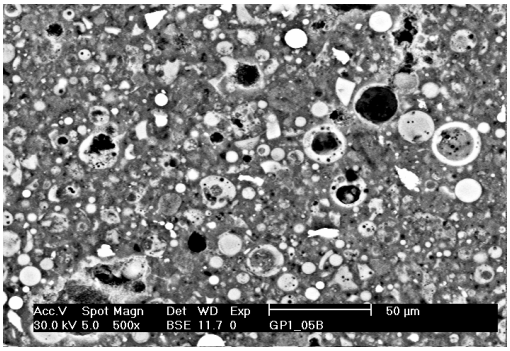

Figure 2. **ESEM image of AAFA.** Light and light grey areas = unreacted or partly reacted fly-ash grains; dark grey areas = polymer zone; dark areas = pores

activation, polymerization takes place to form 2–3 dimensional Si-O-Al-O chains as follow

$$M_n\left[-\left(Si-O\right)_z-Al-O\right]_n.wH_2O$$

The microstructure of resulting AAFA is shown in Fig. 2.

4. Nanoindentation

In order to identify intrinsic material properties of the test samples, nanoindentation was employed. Two nanoindenters were used. Namely, Hysitron Tribolab was used for small indents (up to 10 mN) due to its high resolution and possibility of surface scanning and CSM Nanohardness tester was used for standard indentation with larger forces (up to 500 mN).

Since we are dealing with heterogeneous microstructure, interpretation of the results is more complicated than for a single phase material. We have to employ also special testing strategies to be able to correctly interpret experimental results. There are basically three strategies that can be used:

– Producing of large number of indents that are larger than the characteristic phase dimension with subsequent statistical evaluation of overall material properties of all affected phases that were indented (phase compound).
– Grid indentation in which indents are produced over a large area but the dimension of a single indent is smaller than the characteristic dimension of individual phase. Subsequent deconvolution techniques can be employed for assessment of the individual phase properties[3,4].
– Pointed indentation to a specific material phase with indent dimension smaller then the characteristic dimension of the tested phase. In this case, intrinsic properties of the phase (including intrinsic phase porosity) are obtained.

All three strategies were applied for the studied case and results compared.

The above mentioned deconvolution includes identification of the number of material phases (n) in the material. This number is usually known in advance from separate analysis (like EDX). Therefore, we are in fact looking for a finite number of n peaks in the histogram of mechanical properties from the whole set which serves like an overall probability function. We can deconvolute n probability functions from the overall one by defining n separate intervals with the individual probability function related to a single material phase. These functions are usually constructed using normal (Gauss) distribution[4].

5. Results on cement paste

A large grid of 100 indents was produced over the arbitrarily selected region of the cement paste. Relatively large indents possibly affecting more than one material phase were prescribed (maximum force 10 mN). The final depth of indents was around 700 nm (Fig. 3) which yielded in the surface dimension around 4 μm. Such indents' dimension causes physical homogenization (averaging) of properties in this volume. Since the majority of indents were performed in the hydrated products and indentation to clinkers was rare, indents lying in unhydrous phases were not considered for further evaluation. Thus, results are valid and identified for the hydrated phase compound. Overall modulus of elasticity for all the affected phases (mainly C-S-H gels and Portlandite) was measured to be 23.269±3.093 GPa. Properties of clinker minerals are usually measured separately in its pure unreacted state[8].

Although the results indicate small deviations, they must be considered as mean values of the whole compound. Identification of individual phases is not possible in this case.

Substantially larger number of indents is necessary to cover heterogeneity of the sample when using small indents. 400 indents in four series were prescribed to the maximum load of 2 mN (Fig. 4). On the other hand, we were able to identify individual material phases from histogram plotted for

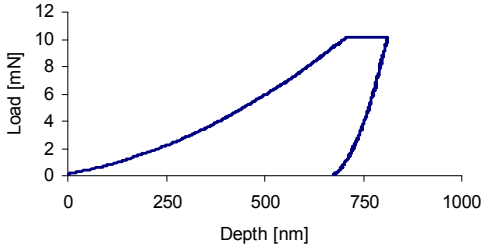

Figure 3. **Large indent (10 mN) into hydrated compound of cement paste**

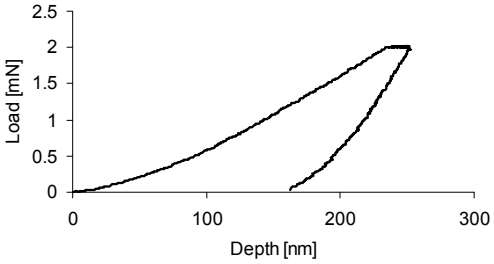

Figure 4. **Small indent (2 mN) in cement paste**

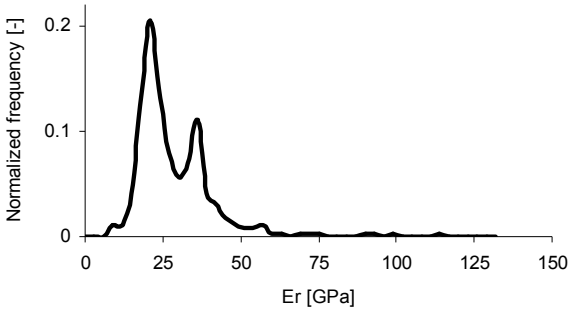

Figure 5. **Histogram of reduced moduli in cement paste**

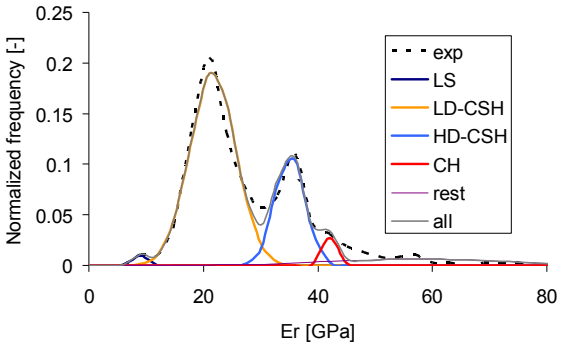

Figure 6. **Deconvolution of individual phases in cement paste**

reduced modulus[5], for example (Fig. 5). Several identifiable peaks can be found in this histogram that can be attributed to individual phases.

We decided to apply deconvolution into 5 phases in Fig. 5. These phases were following: low stiffness phases (LS); low density C-S-H gels (LD-CSH); high density C-S-H gels (HD-CSH); Portlandite (CH) and the rest (rest). Experimental histogram of all phases as well as individual phase distributions are depicted in Fig. 6. Mean values and standard deviations of normal distributions for individual phases can be found in Tab. I.

Pointed indentation to a specific phase is in general possible based on the assumption that the phase can be distinguished in optical microscope or in a scanner prior to indentation. In case of cement paste, such a phase can be a clinker or high density C-S-H gel that is formed mainly as a rim around the clinker grain. Other phases cannot be found in such a way. Therefore, we tried to identify directly HD C-S-H by pointed indentation. Small deviations were found which shows on indentation to a homogeneous-like phase. The results of reduced moduli were 38.6±2.57 GPa. This value corresponds fairly well with results obtained by deconvolution from histogram (Tab. I).

Table I
Results from deconvolution and image analysis of cement paste

	LS	LD-CSH	HD-CSH	CH	Rest
Mean E_r, GPa	7.45	20.16	33.59	40.74	55.75
s.d.	0.85	3.90	2.47	0.92	14.62
f_j , %	1	64	24	3	8
f_j^{IA} , %	7.9±6		82±5.3	4.6±2.8	5.5±2.4

E_r stands fro reduced modulus; f_j stands for volume fraction received from deconvolution; f_j^{IA} stands for volume fraction received from image analysis

6. Results on alkali-activated fly-ash

Similar approach was used also for the investigation of AAFA samples. First, a matrix of 100 large indents to 100 mN was prescribed. Second, matrices with 100 indents up to 2 mN were tested on four arbitrary places (i.e. 400 indents all together). The difference of the histogram of reduced moduli is depicted in Fig. 7. It can be seen that the distribution of large indents is much narrower and some of the peaks are missing. It clearly shows physical homogenization produced already during the indentation. Obtained results are moreless mean values of the polymer and fly-ash compound. On the other hand, histogram of small indents is wider and contains results from several individual phases.

We decided to apply deconvolution into 5 phases in Fig. 7. These phases were following: low stiffness phases (LS); polymeric phases (GP); partly polymerized zones (partGP); partly activated fly-ash (partFA); and the rest, mainly nonreacted fly-ash (rest). Experimental histogram of all phases as well as individual phase distributions are depicted in Fig. 8. Mean values and standard deviations of normal distributions for individual phases can be found in Tab. II.

Pointed indentation was not possible in case of AAFA because we were not able to distinguish a specific phase prior to indentation.

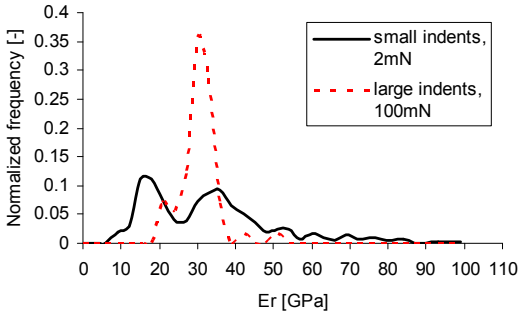

Figure 7. **Histogram of reduced moduli in AAFA**

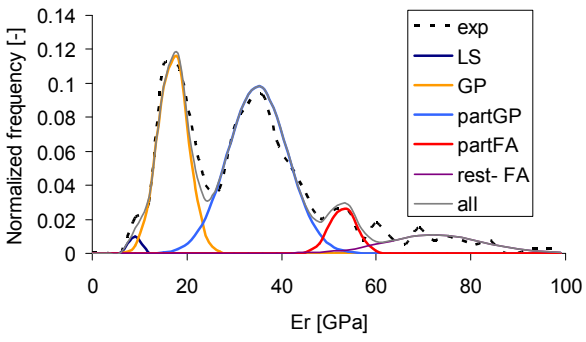

Figure 8. **Deconvolution of individual phases in AAFA**

7. Validation of results using image analysis

In order to validate our results from deconvolution, we employed also image analysis. Our aim was to separate material phases from ESEM images based on the pixel color. Multiple back-scattered electron images were taken in ESEM and thresholded (20 images for CP and 4 images for AAFA). Results of thresholding is summarized in Tabs I and II. It can be concluded that good correlation in terms of similar volume fractions was obtained for cement paste samples but for the low stiffness phase. However, results from image analysis include (*i*) pores that cannot be mechanically determined and (*ii*) deviation of the value indicate large scatter in the set of 20 images. That means that irregular pore structure cannot be sufficiently determined by means of mechanical testing. For the AAFA samples, the correlation is good for the main phases (GP, partGP) but again LS phase is not in good agreement with results from image analysis in which a pore structure is determined rather than the solid phase. It also seems that image analysis overestimates fly-ash phases (partFA and rest). This can be attributed to not sufficiently high number of images (only four were analyzed).

Table II
Results from deconvolution and image analysis of AAFA

	LS	GP	part GP	part FA	Rest
Mean E_r, GPa	7.15	15.53	33.50	51.49	70.85
s.d.	0.65	3.01	6.18	2.76	10.29
f_j , %	1	32	51	7	9
f_j^{IA} , %	4.2±1.5	23.7±2	45.3±4	26.8±2	

E_r stands fro reduced modulus; f_j stands for volume fraction received from deconvolution; f_j^{IA} stands for volume fraction received from image analysis

8. Conclusions

Micromechanical analysis using different testing strategies was demonstrated on two examples- cement paste and alkali activated fly-ash. For both cases, grid indentation using large indents give mean values with small deviations of a material compound. Mechanical properties are homogenized by the indenter from several phases. In case of using small indents, intrinsic phase properties are obtained in the form of property histogram. Subsequently, individual phase properties can be deconvoluted from this histogram.

Pointed indentation to a specific material phase is the best solution but it can be performed only if the following conditions are satisfied: the phase is easily identifiable in optical microscope or it can be morphologically determined before indentation (e.g. by surface scanning). Otherwise, indents cannot be pointed to this phase even if the indent‘s size is smaller than the measured volume.

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Micromechanical Analysis of Heterogeneous Structural Materials

This contribution is dedicated to the methodology used in the micromechanical analysis of heterogeneous materials. It is applied to two cases of structural materials: cement paste and alkali activated fly-ash. The paper contains several approaches how to test and evaluate data from nanoindentation. It is shown that different size of indents must be followed by different interpretation of results. In case of using small size indents it is possible to derive individual material phase properties by means of deconvolution from property histogram. Indentation to a specific phase can be used only in limited number of cases provided this phase can be determined optically or by scanning before the test. Nanoindentation results were also compared with similar results obtained from image analysis.