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Micro-mechanical properties of alkali-activated fly ash evaluated by nanoindentation

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HIGHLIGHTS

- Nanoindentation combined with SEM-EDX were applied to study the micro-mechanical properties of AAFA.
- Three phases were identified, corresponding to three distinct peaks in the indentation results.
- The micro-mechanical properties of the gel phase were greatly affected by the pores between nano to micro scale.

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ABSTRACT

In this study, the micro-mechanical property of different phases in alkali-activated fly ash (AAFA) pastes was investigated by nanoindentation. The mechanical information of the gel phase in AAFA was then linked to the chemical and microstructural information provided by SEM-EDX, ATR-FTIR and N_2 adsorption, respectively. Three phases, i.e. aluminosilicate gel, residual fly ash particles and pores, were identified from the microstructural analysis of AAFA, corresponding to three distinct peaks in the indentation modulus frequency plots. The peak corresponding to the gel phase varied with curing age and activator content. The elastic modulus of aluminosilicate gel measured by nanoindentation was affected by the pores between nano to micro scale. The results of the chemical bonds of AAFA, however, cannot correspond well with the micromechanical results.

1. Introduction

Alkali-activated materials (AAM) have been extensively studied in the last few decades. Comprehensive reviews have been made by Provis and van Deventer and Pacheco-Torgal et al. [1–3]. The key driver for the increasing attention on AAM is its substantial reduction in CO_2 emission compared with Portland cement [4], as well as the high strength and excellent durability in aggressive environment [5,6]. However, in most cases, these excellent properties can be achieved only by optimizing the curing condition and mixture proportion with respect to a specific precursor. Variations of engineering properties were reported from different studies [7,8], which are attributed to different reaction products and microstructure formed in AAM by using chemically varied raw materials, different types and dosage of activator and curing conditions. Recently, advances in research have been made in our understanding on AAM [1], e.g. AAMs can be classified into three different systems according to the calcium content in binder: 1) high-calcium-based system, normally with slags as raw materials and calcium–silicate–hydrate (C–S–H) gel with a significant degree of aluminum substitution (C–A–S–H) as the main reaction product; 2) aluminosilicate-based (low-calcium) system, also called "geopolymers", with metakaolin or fly ash (class F) as raw materials and three-dimensional sodium aluminosilicate gel (N-A-S-H) as the main reaction product; 3) blended system by mixing high-calcium-based and aluminosilicate-based precursor; and in this system the types of reaction products were still under discussion (only C-A-S-H or a coexistence of C-A-S-H and N-A-S-H) [9–11]. Such classifications, to some extent, explain the different performance of AAM from scientific point of view. Different reaction products are responsible for the different microstructural evolution, thus presenting different engineering properties.

The characterization of C-A-S-H gel and N-A-S-H gel in AAM was extensively investigated by a variety of techniques, e.g. nuclear magnetic resonance (NMR), fourier transform infrared

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spectroscopy (FTIR), X-ray diffraction (XRD) etc. [12–15]. However, the results derived from the above techniques are mainly about chemical properties, and the mechanical contribution of the gel phase on the macroscopic properties of AAM is seldom reported. In some studies, the information from the atomic or molecular scale (nm length scale) was directly linked to the macro-mechanical property (cm-m length scale), which ignored the large gap between the scales. AAM present a heterogeneous structure at micro-scale, which is consisted of several different phases (e.g. gel, un-reacted particles, pores etc.). The macroscopic mechanical test can only describe the overall mechanical strength, and the mechanical information on individual phases is still missing. The application of nanoindentation allows the assessment of the mechanical property of individual phase on the nano or micro-scale. The principle of nanoindentation lies in forcing a very small tip (diamond) to material surface, the changes in the applied load and penetration depth are measured simultaneously [16]. This technique has been applied to cement-based materials and identified two types of C-S-H, namely high density C-S-H and low density C-S-H [17]. Studies on the micromechanical properties of individual phases in AAM, however, are limited. Recently, it has been argued whether nanoindentation can distinguish different phases in hardened cement paste [18–20]. It is recommended that the method of combining indentation with microstructural analysis (e.g. SEM-EDX) is a promising way to investigate local mechanical properties of materials with complex microstructure.

To this end, the micromechanical property of the individual phase in alkali activated fly ash (AAFA) pastes with different activator content (SiO_2 and Na_2O content) and curing age were identified and assessed with the aid of nanoindentation test and ESEM analysis in this study. By combining the nanoindentation results with SEM-EDX analysis, the mechanical information provided by nanoindentation can be directly compared to the chemical information provided by SEM-EDX. The chemical structure (Si/Al ratio) and pore size distribution of gel phase were investigated by ATR-FTIR and N_2 adsorption tests, respectively, and then linked to the micromechanical property of the aluminosilicate gel.

2. Materials and methods

2.1. Materials and mixture proportions of AAFA

Low calcium fly ash, Class F according to ASTM C 618, from The Netherlands, was used in this study. The chemical composition of fly ash is given in Table 1. The main chemical constituents of the fly ash were SiO_2 and Al_2O_3. Quartz (SiO_2) and mullite ($3Al_2O_3$ $2SiO_2$) were the main crystalline compounds in the fly ash (Fig. 1). The amorphous content of the fly ash, determined by the chemical dissolution treatment (EN 196, Part 2), was 69%. The density and mean particle size of the fly ash was 2.34 g/m^3 and 21.46 μm, respectively.

The alkali activators were prepared by mixing sodium hydroxide (analytical grade, >98% purity) with distilled water and sodium silicate solution (Na_2O: 8.25 wt%, SiO_2: 27.50 wt%). Na_2O and SiO_2 contents supplied by the activator were 1.0 mol or 1.5 mol per 1000 g fly ash, as described in Table 2. The alkali activators were previously optimized to yield good mechanical property after curing at 40 °C for 7 days and 28 days [8], respectively (Table 2). The water/binder ratio was kept constant at 0.35. All alkali activators were prepared one day before sample preparation.

For sample preparation, fly ash was mixed with the activator in a mixer for 4 min. After mixing, the pastes were poured into plastic bottles with a diameter of 35 mm and height of 65 mm. The bottles were vibrated for 2 min to remove air bubbles and then sealed with a lid. The sealed bottles were cured in an oven at 40 °C for 7 days and 28 days, respectively.

2.2. Nanoindentation

At each curing age, the specimens were cut into slices with a thickness of around 10 mm. In order to obtain a very flat and smooth surface (“mirror-like”), specimens need to be well ground and polished. To prepare the samples, the surfaces of the specimens were first ground on the middle-speed lap wheel with the aid of SiC papers with different finer grades: p320, p500, p800, p1200 and p4000. The samples were then polished on a lap wheel with diamond abrasive cloth: 6, 3, 1 and 0.25 μm. Ethanol was used as the lubricant during the grinding and polishing procedure. After polishing, the specimens were cleaned in an ultrasonic bath to remove the dust and diamond particles left on the surface. Nanoindentation measurements were performed on the top surface of the specimens. The distance between individual indents was 10 μm. Information about the elastic properties was obtained from a matrix of minimum 240 indents covering a representative area of at least $50 \times 390\ \mu m^2$ on the surface. Two or three representative areas were selected for each AAFA specimen in this study. In total around 720 indents were measured and analyzed for each AAFA sample.

Nanoindentation tests were conducted by using Agilent Nano Indenter G200, equipped with a berkovich tip to determine the elastic modulus (E) of different phases (e.g. un-reacted fly ash particles and aluminosilicate gel). All tests were programmed in such a way that the loading was applied when the indenter contacted with the surface of the sample until a specified maximum penetration depth (h_{max}) was reached (1000 nm in this study). Afterwards, the load was maintained for 10 s to allow the material to creep, and then followed by the unloading process. The holding period is important for unbiasing the unloading stage. Fig. 2a shows a typical load-time diagram of the indentation test. It needs to be emphasized that the loading and unloading indentation rates applied in this study were not constant (Fig. 2a). This is different from the previous studies [21,22] in which a linear loading was normally applied until a maximum load was achieved. The above load-controlled setup of the instrument led in a varied h_{max} of the indenter, depending on the hardness of the indented material. In this study, a displacement-controlled setup was used with a constant h_{max} (1000 nm) for all the phases. Such setup was also applied in the previous reported studied [23,24] to investigate the micromechanical property of cement-based materials. The mechanical response for each indent was estimated as 3–4 times of the penetration depth (hmax) [25]. At this scale, it is possible that the derived elastic modulus is affected by other phases within the interaction volume underneath the indenter. Thus the derived elastic modulus for each indent is an average mechanical response of the interaction volume. In the present study, the mean particle size of the fly ash particle was 21.46 μm, which is 10 times larger than the maximum indentation depth (1 μm). Thus it is regarded that the unreacted fly ash particle phase and gel phase can be distinguished by nanoindentation. A typical load-penetration (P-h) curve is shown in Fig. 2b. The Continues Stiffness Method (CSM Method) developed by Oliver and Pharr [26] was applied to calculate the indentation (reduced) modulus E_r, as shown in Eq. (1):

$$E_r = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{Ac}} \tag{1}$$

where S is the contact stiffness evaluated as the initial slope of the unloading curve at the peak load and maximum depth h_{max}, i.e. $S = (dP/dh)_{h=hmax}$; A_c is the contact area at the maximum depth h_{max}. The effect of non-rigid indenter can be accounted by the following equation:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \tag{2}$$

where E and ν are the elastic modulus and Poisson's ratio of the tested material, respectively. In this study, Poisson's ratio ν was assumed to be 0.18 for all measurements. E_i and ν_i are the elastic properties of the diamond indenter (E_i = 1141 GPa, ν_i = 0.07).

The histograms of the elastic modulus E can be constructed from the measurements, as shown in Eq. (3):

$$p_i^{exp} = \frac{f_i^{exp}}{N^{exp}} \cdot \frac{1}{b} \quad i = 1, 2, \ldots, N^{bins} \tag{3}$$

where N^{exp} is the number of the measurements, which is equally spaced into N^{bins} bins with the bin size b; f_i^{exp} is the frequency of occurrence of each bin. In this study, the bin size b was chosen as 2 GPa. The hardness of AAFA mixtures can also be derived from the nanoindentation results. As they showed the same trend as the elastic modulus results, the hardness results were not involved in this paper.

Table 1
Chemical composition and physical properties of the fly ash used in this study.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	SO_3	L.I.
Weight (%)	48.36	31.36	4.44	7.14	1.35	1.64	0.72	1.24	1.90	1.18	4.89

L.I. = loss on ignition.