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Effective properties of a fly ash geopolymer: Synergistic application of X-ray synchrotron tomography, nanoindentation, and homogenization models

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ABSTRACT

Microstructural and micromechanical investigation of a fly ash-based geopolymer using: (i) synchrotron X-ray tomography (XRT) to determine the volume fraction and tortuosity of pores that are influential in fluid transport, (ii) mercury intrusion porosimetry (MIP) to capture the volume fraction of smaller pores, (iii) scanning electron microscopy (SEM) combined with multi-label thresholding to identify and characterize the solid phases in the microstructure, and (iv) nanoindentation to determine the component phase elastic properties using statistical deconvolution, is reported in this paper. The phase volume fractions and elastic properties are used in multi-step mean field homogenization (Mori–Tanaka and double inclusion) models to determine the homogenized macroscale elastic modulus of the composite. The homogenized elastic moduli are in good agreement with the flexural elastic modulus determined on macroscale paste beams. The combined use of microstructural and micromechanical characterization tools at multiple scales provides valuable information towards the material design of fly ash geopolymers.

1. Introduction

Alkali-activated binders are a class of environmentally friendly materials with comparable mechanical and durability performance to that of conventional ordinary Portland cement (OPC)-based binders. Industrial waste/by-product materials including fly ash, blast furnace slag, and clays can be activated using alkaline media to produce such binders [1–4]. Geopolymers belong to the class of alkali-activated binders and are based on fly ash or metakaolin, resulting in an alkali aluminosilicate reaction product that is morphologically and behaviorally different from the calcium (alumino) silicate gels resulting from OPC hydration [5]. Several studies have evaluated the reaction kinetics, microstructure and mechanical properties of geopolymer systems in detail [3,4,6–8].

Similar to conventional OPC-based binders, geopolymeric systems are also inherently porous and heterogeneous, and display widely differing mechanical and durability properties depending on the material's microstructure. Thus, proper characterization of the pore-and-microstructure is critical for a fundamental understanding of material behavior, as well as developing methods for adequate material design. Recent studies have evaluated the pore structure of fly ash geopolymers using mercury intrusion porosimetry (MIP) [8,9], which is a common method for conventional cementitious systems. An empirical approach to evaluate the fluid transport through fly ash geopolymer is reported in Ref. [9] wherein the Katz–Thompson model is used in conjunction with pore structural information from MIP [10–13]. Scanning electron microscopy (SEM) on two-dimensional images also are used for pore structure characterization [14,15]. The drawback of these methods (assumption of pore shapes, inconsistencies in pressurized mercury intrusion, having to deal with a large number of 2D images, inadequacy in determining phase connectivity information etc.) in probing the pore structure of heterogeneous materials can be alleviated to a large extent through the use of X-ray microtomographic (XRT or μCT) techniques. A few studies have evaluated the pore structure of cement-based and alkali-activated systems using this technique, thus helping to understand several characteristics such as distribution of air voids [16] spacing of fibers in 3D [17], leaching and sulfate attack in cement pastes [18,19], and pore network tortuosity [20,21].

While the pore structure of the material is important in dictating the transport behavior and, thus, the durability characteristics, the mechanical properties of a heterogeneous material are also influenced significantly by the individual phase amounts (both solids and pore) and their properties. The individual phase elastic properties can be obtained

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using nanoindentation experiments, as has been reported for cement-based materials [22–25]. Micromechanical homogenization models are in-turn necessary to estimate the composite properties at the macro-scale. The response of the heterogeneous material at the micro-scale is averaged through analytical models, generally based on Eshelby's method [26–28], that replace the microscopically inhomogeneous strains and stresses by homogeneous values. The successful implementation of this approach demands accurate quantification of the phase volume fractions. The use of empirical models to determine the reaction product and pore volume fractions in highly heterogeneous systems containing multiple phases such as fly ash-based geopolymers, is unlikely to yield satisfactory results in a consistent manner. Moreover, it has been reported elsewhere that the classification and identification of different solid phases in the fly ash-based geopolymer using synchrotron XRT is challenging due to the low absorption contrast of different solid phases in the available X-ray energy range [21].

This study reports a comprehensive investigation of a fly ash-based geopolymer using 3D X-ray synchrotron imaging, nanoindentation on the individual constituents in the geopolymer, and image analysis on backscattered scanning electron micrographs, to culminate in reliable micromechanics-based prediction of macroscale mechanical properties. Such a comprehensive effort towards effective property prediction, considering the synergistic applications of complementary methods, is novel. Synchrotron XRT is used to interrogate the pore structure using a pixel size of 0.74 μm, which is supplemented by MIP for the detection of smaller pore sizes. The 3D pore structural information from XRT is utilized in a numerical Stoke's solver [29–31] to develop a realistic assessment of saturated fluid permeability. Phase quantification of the heterogeneous microstructural features was accomplished using a multiple-thresholding image analysis procedure implemented on several high resolution backscattered SEM images. The quantified solid phase fractions are also validated through the frequency of occurrences of different solid phases in the statistical nanoindentation technique. The microscale properties are up-scaled using mean field homogenization schemes including Mori–Tanaka and double inclusion methods [27,28,32–36] to extract the homogenized Young's modulus, which is validated through macro-scale experiments. Linking the microstructure and micromechanical properties of a heterogeneous material, and using this information to predict the macroscopic mechanical performance, provides efficient means of optimizing the material design and mechanical behavior of fly ash-based geopolymers. The synergistic use of these advanced tools also opens up avenues for performance prediction of similar materials.

2. Materials and experimental procedure

2.1. Materials and mixture proportions

A Class F fly ash conforming to ASTM C 618 was used as the starting material. The chemical composition of fly ash, determined using X-ray fluorescence is shown in Table 1. Eight molar NaOH solution was used to activate the fly ash. The liquid-to-powder ratio (mass-based) used was 0.40. The alkaline solution was added to fly ash, and mixed for 4 minutes in a laboratory mixer. The mixtures were then filled in molds and subjected to heat curing in a laboratory oven at 60 °C for 48 hours, in sealed conditions. This curing process was previously shown to provide a compressive strength of 25–30 MPa [2], which is commonly adopted for many types of structural concretes. Though longer curing durations and higher temperatures can result in lower porosities and higher strengths, the focus of this work is not on development of geopolymer mixtures, but on the use of advanced techniques in combination for property prediction.

Table 1
Chemical composition and physical properties of fly ash.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI	Median particle size
58.4%	23.8%	4.19%	7.32%	1.11%	0.44%	1.43%	1.02%	0.5%	19 μm

2.2. Synchrotron X-ray tomography

Synchrotron X-ray tomography (XRT) was performed at the 2-BM beamline of the Advanced Photon Source (APS) at Argonne National Laboratory. Details of APS beamline 2-BM have been described elsewhere [37,38]. A monochromatic beam with energy of approximately 27 keV was focused on samples of approximately 1.5 mm in size. The transmitted X-rays were converted to visible light using a LuAG:Ce scintillator screen coupled with an objective lens and CoolSnap K4 CCD camera to achieve a pixel size of 0.74 μm. 2D projections were acquired at angular increments of 0.12° over a range of 180°. The 2D projections were then reconstructed to 3D using fast Fourier transform (FFT)-based Gridrec algorithm [39–41]. XRT has been employed in the analysis of pore-structure of cementitious materials, and synchrotron microtomography is considered highly suitable for the evaluation of pore structure that is influential in dictating the transport properties and material durability [21,42–44].

2.3. Mercury intrusion porosimetry (MIP)

The pore structure of the fly ash-based geopolymer pastes was also evaluated using mercury intrusion porosimetry (MIP) to examine the pores in the smaller size ranges that were not able to be probed by XRT. A porosimeter that can detect minimum pore diameter of 0.0036 μm was employed for this study. This test was performed in two steps: (i) evacuation of gasses and filling the sample holder with mercury in the low-pressure run that increases the pressure from ambient to 345 kPa, and (ii) intrusion of mercury into the sample at high pressure (maximum pressure of 414 MPa). A solid–liquid (pore wall-mercury) contact angle of 130° and a mercury surface tension of 485 mN/m were used to interpret the results using the Washburn equation [13,45,46].

2.4. Nanoindentation

For nanoindentation, a cylindrical sample of 25 mm in diameter and 75 mm in height was prepared and heat cured at 60 °C for 48 hours. A cubic piece with 4 mm sides was cut and polished to a 0.04 μm colloidal silica finish. The nanoindentation measurements were carried out on the polished sample in a commercial Nanoindenter (MTS Nanoindenter XP) using a Berkovich tip. Samples were mounted on aluminum stubs for nanoindentation testing using superglue. Indentations were carried out at initially at ~10 μm spacing in a grid on an area approximately 250 μm × 250 μm in size, which is considered representative for cementitious materials [21,47]. All the indentation locations were carefully selected prior to testing to ensure that the pores or cavities are not encountered in the process. Thus, the indentation experiments were carried out mostly on the solid phases, which resulted in very few spurious peaks in the modulus frequency distribution curves. The depth of penetration was chosen to be 500 nm which is smaller than the characteristic size of unreacted fly ash inclusions in order to avoid phase-interactions during penetration. Continuous stiffness measurement (CSM) technique [48–51] was employed here to measure the contact stiffness. While the traditional Oliver–Pharr methodology [52] measures the contact stiffness only at the point of unloading, the CSM technique allows measurement of contact stiffness at any point of the loading curve corresponding to any depth of penetration. CSM is accomplished by imposing a harmonic excitation of constant amplitude and frequency to the normally increasing load on the indenter. For any excitation frequency, the displacement response of the indenter and the phase angle are measured continuously as a function of the penetration