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A multiscale investigation of reaction kinetics, phase formation, and mechanical properties of metakaolin geopolymers

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ABSTRACT

A multiscale study is presented of the reaction kinetics, phase formation, mechanical properties of metakaolin-based geopolymers by varying Si/Al ratios of 1.2–2.2 and Na/Al ratios of 0.6–1.2. Macro- and nano-mechanical properties of geopolymer samples were determined by unconfined compression testing and grid nanoindentation technique, respectively. The latter, in combination with statistical deconvolution, also enables the extraction of generally 4 distinct phases together with their nano-mechanical properties and volumetric fraction within the synthesized geopolymers. Moreover, the reaction kinetics, phase formation (particularly geopolymer gel development), and mechanical property development were investigated by characterizing geopolymers cured at the final setting time, 7, and 28 days. Phase formation was characterized by Fourier transform infrared spectroscopy (FTIR) via monitoring the evolution of the Si-O-T (T: Si or Al) and Al-O bonds. Results illustrate that the fraction of geopolymer gels dominantly governs the mechanical behavior, both of which increase with the Si/Al and Na/Al molar ratios, while the final setting time increases with the Si/Al ratio, but decreases with the Na/Al ratio. The chemical composition for the best mechanical performance of the studied geopolymers is a Si/Al ratio of 1.7 and Na/Al ratio of 0.9. The relationships among geopolymer chemical compositions, geopolymer gel formation rate, and macromechanical properties are also discussed.

1. Introduction

Geopolymer is potentially a sustainable and economical alternative to ordinary Portland cement because of its high mechanical strength, excellent durability, and low energy consumption and reduced CO_2 emission during its production [1–9]. Amorphous geopolymeric gel, composed of repeating units of -Si-O-Al-O-, -Si-O-Al-O-Si-O-, -Si-O-Al-O-Si-O-Si-O- in various forms [10], is the major constituent of the resulting geopolymer composites and plays critical roles in the development of their macro-mechanical properties. Therefore, it is important to understand the process of geopolymer gel formation and its characteristics at micro- or nano-scale [11–14]. Due to the high purity of metakaolin, Na- and K-metakaolin based geopolymers were often used to investigate geopolymerization kinetics, the development of chemical bonds, and changes in mineralogy [15–18]. Autef et al. [19] found that one or more geopolymeric networks were formed, depending on the reactivity of the metakaolins used, which also affect the mechanical properties of the geopolymers. Gharzouni et al. [20] also highlighted the crucial role of the reactivity of both metakaolin and the alkaline solution in the geopolymer formation and the mechanical strength of the resulting geopolymer samples. Lancellotti and his coworkers [21] observed that the geopolymerization processes and the water stability of the geopolymer were largely affected by curing temperature and the type of curing mold used, with the latter modifying the evaporation rate of alkali solution during the curing. White et al. [22] employed in situ X-ray pair distribution function analysis to track time-dependent nano-structural changes during the geopolymerization process. The X-ray pair distribution functions of metakaolin-based geopolymers indicate that free silica present in the activating solution enhances the dissolution of metakaolin during the initial stages of the reaction but reduces the extent of reaction significantly due to the denser morphology. However, most of these studies mainly focused on the reaction

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kinetics at early stages and the influence of curing conditions on geopolymerization. More importantly, a quantitative characterization of micro- and nano-mechanical properties of geopolymer gel and its fractions at different stages of polymerization cannot readily be obtained with common analytical techniques due to the amorphous nature of geopolymer gel, which is indistinguishable from other constituents in a geopolymer composite.

Recently, the grid nanoindentation technique has been applied to investigate the mechanical properties (e.g., Young's modulus and hardness) of heterogeneous materials, such as cement paste, rocks, and bones [23–25]. Based on grid indentation results, the volumetric fractions of multiple phases in a heterogeneous material can be resolved with the aid of statistical deconvolution analysis of the histogram of Young's modulus or hardness. Given that the sizes of geopolymer gels are in the order of several nanometers to micrometers [26], grid nanoindentation and deconvolution analysis were conducted on metakaolin- and fly ash-based geopolymers to probe the mechanical properties and volumetric fraction of geopolymer gels [27,28]. Beleña and Zhu [27] conducted grid nanoindentation on two metakaolin-based geopolymers with different curing procedures. Based on the statistical deconvolution analysis of $8 \times 15 (= 120)$ indents, they identified three phases in the two geopolymers: geopolymer gel, metakaolin, and crystalline minerals. They found that the Young's modulus and hardness of geopolymer gels varied in the range of 7–14 GPa and 0.2–0.5 GPa, respectively, while the fraction of geopolymer gels ranged from 83% to 89%, depending on synthesis conditions. Němeček et al. [28] applied the grid nanoindentation technique on a metakaolin-based geopolymer (MKG) cured at ambient temperature and two fly ash-based geopolymers (AAFA) cured at ambient temperature and 80 °C. They identified four phases in AAFA, which are N-A-S-H gels (also known as geopolymer gels), partially activated fly ash, non-activated fly ash, and non-activated compact glass in an ascending order according to the Young's modulus; and two phases in MKG, including geopolymer gels and unreacted metakaolin. They also found that the Young's modulus of geopolymer gels is irrelevant of the raw materials or curing temperature, which is around 17 GPa with a standard deviation of 3–5 GPa. The volumetric fraction of geopolymer gels, on the other hand, shows dependence on the curing temperature and raw materials, which is 50.7%, 77.5% and 97.2% in heat-cured AAFA, ambient-cured AAFA and heat-cured MKG, respectively. However, the correlation between geopolymer gel fraction and the mechanical properties of geopolymers at the macroscale was not established, nor did the influence of chemical compositions of geopolymer gels on the macromechanical properties of the resulting geopolymer composites.

In this study, metakaolin-based geopolymers (MKG) were synthesized at different Si/Al and Na/Al ratios and cured at various durations of up to 28 days. They were characterized at multi-scales by macro-mechanical testing, micro- and nano-scale grid nanoindentation, and FTIR to: (i) determine the mechanical properties (i.e., Young's modulus and hardness) of geopolymer gels at nanoscale and extract the multiple phases of geopolymer composites; (ii) estimate the volumetric fraction of geopolymer gels and examine its effect on the macro-mechanical properties of geopolymer composites; and (iii) investigate the effect of chemical composition of raw materials on reaction kinetics, phase transformation, and macro-mechanical properties of geopolymer composites. The final setting time was measured by the Vicat needle test for each geopolymer sample to examine the effect of chemical composition on reaction rate. The results from this study reveal the influence of volumetric fraction and chemical bonds of geopolymer gels on the macro-mechanical properties of MKG at different reaction stages. This multi-scale study also sheds light on the relationship of chemical composition – formation of geopolymer gels – mechanical properties of geopolymer composites at the macroscale.

2. Materials and methods

2.1. Materials and geopolymer synthesis

Relatively pure, powdery metakaolin (MK) from Advanced Cement Technologies, LLC was selected in this study to minimize the intervening effect of impurities in other raw materials (e.g., fly ash, furnace slag) on geopolymer synthesis and subsequent nanoindentation testing. Its chemical composition and physical properties are summarized in Table 1. The dominant constituents in the metakaolin are SiO_2 and Al_2O_3, most of which are amorphous as a result of high-temperature calcination (e.g., above 550 °C [29–31]) of kaolin. According to the XRD characterization of the MK, the main remaining crystalline phases after the calcination are Quartz, Kaolinite and Anatase. The XRD spectrum was shown in our previous study [32], which is not repeated herein for clarity. In addition, the platy-shaped, fine MK particles have a high specific surface area, enabling fast reaction with the alkali activator. A sodium hydroxide solution (50 wt% NaOH and 50 wt% water) from Fisher Scientific, Inc. and a reagent-grade sodium silicate solution (10.6 wt % Na_2O, 26.5 wt% SiO_2, 1.39 g/mL at 25 °C) from Sigma Aldrich, Inc. were mixed with deionized water at predesigned mix ratios to prepare alkali activators that also adjusted the Si/Al and Na/Al molar ratios of the geopolymer precursors.

The Si/Al and Na/Al molar ratios of the raw materials resulting in metakaolin based geopolymer with high mechanical strength were found to be around 1.9 [33] and 1.0 [1], respectively. In this study, the Si/Al and Na/Al molar ratios higher and lower than the recommended values [1,10,33,34] were chosen to assess how the chemical composition of raw materials affects the development of geopolymer gel and the mechanical properties of geopolymer samples. Thus, MKG samples were prepared at 7 Si/Al molar ratios and 4 Na/Al molar ratios, ranging from 1.2 to 2.2 and 0.6 to 1.2, respectively (Table 2). The Si/Al or Na/Al ratio is used to designate different MKG sample sets, represented by SA and NA respectively, followed by an integer that is 10 times the respective molar ratio in geopolymer synthesis (Table 2). The sample sets with varying Si/Al ratios have a fixed Na/Al ratio of ~1.0, which is the theoretical Na/Al ratio for geopolymers [33,35,36], and those with varying Na/Al ratios have a fixed Si/Al ratio of 1.7. The sample sets with a Na/Al ratio of 1.1, designated as SA17 or NA11, were chosen as an

Table 1
Chemical composition and physical properties of the metakaolin sample.

Chemical composition (wt%)	
SiO_2	52.20
Al_2O_3	43.11
Fe_2O_3	1.53
CaO	0.07
MgO	0.06
Na_2O	0.07
K_2O	0.22
SO_3	0.99
Moisture content	0.33
Loss on ignition	0.18
Physical properties	
Percent passing No. 325 mesh (wt%)	92.9
Blaine Fineness (m^2/kg)	2690