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The effects of phase changes on the bonding property of geopolymer to hydrated cement

Huajun Zhu [a], Zuhua Zhang [b,*], Fenggan Deng [a], Yalong Cao [a]

[a] *Key Laboratory for Ecology and Pollution Control of Coastal Wetlands (Environmental Protection Department of Jiangsu Province), Yancheng Institute of Technology, Yancheng 224051, China*
[b] *Centre of Excellence in Engineered Fibre Composites (CEEFC), Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba 4350, Australia*

HIGHLIGHTS

- The bonding between geopolymer binder and cement paste is 1.2–2.5 MPa in tension.
- Under 80 °C curing conditions geopolymers tend to crystallize into zeolite structure.
- Under 80 °C curing conditions cement C–S–Hs become more ordered and porous.
- The phase changes towards more ordered structures cause bond strength loss.

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ABSTRACT

Using geopolymers as bonding materials could be an alternative solution to the concrete repair. This study reports the effects of phase changes on the bonding property of geopolymer to hydrated cement. A geopolymer binder was prepared by activation of heated kaolin with sodium silicate solution, bonded with 28 days aged cement paste and cured under different conditions. The experimental results demonstrated that under the 20 °C air curing conditions, the bond strength achieved 1.3 MPa at 7 days and increased to 1.5 MPa at 28 days. While under the 80 °C steam and water curing conditions, the bond strength decreased by 31% and 37% respectively. The XRD, FTIR and SEM analysis of the geopolymers and hydrated cement pastes show that the strength loss is due to two factors: (1) the increased porosity in cement paste due to the water loss and/or crystallization of C–S–Hs; and (2) the mineralogical change (crystallization) in geopolymer binder which becomes more ordered structures. The increased porosity and the crystallization either in cement or geopolymer generate local stress and weak regions at the interface. This study suggests that the stability of metakaolin-based geopolymers should be taken into consideration when they are used as bonding or coating materials for concrete repair, particularly at the conditions with elevated temperatures.

1. Introduction

The most widely used bonding materials for concrete repair have been shifted from the conventional cement in the early half of the last century towards the polymer modified cementitious materials and pure resins today [1,2]. However, in many cases, such as at extreme temperatures, high abrasion and aggressive conditions, the durability of organic bonding materials is seriously questioned, particularly given the limited modulus and fast ageing of polymers at these conditions [3,4]. The development of durable and compatible bonding materials is important for successful repair, and is attracting wide interest.

Geopolymer, also known as ‘inorganic polymer’, has emerged as a ‘green’ binder with wide potentials for manufacturing sustainable materials for environmental, refractory and construction applications. It is formed by dissolution of aluminosilicate solid materials, usually metakaolin and fly ash, in a strong alkaline activator solution, polymerization, gelation and/or crystallization [5]. Laboratory researches have demonstrated their unique properties, such as high modulus [6–8], chemical resistance [9] and fire resistance [10,11]. The development of geopolymer coating and bonding materials to replace organic repairing materials for protecting and strengthening the aged concrete structures have been reported in previous studies [12–14]. This highly promising technology has been highlighted in a review paper by Pacheco-Torgal et al. [15].

Two key technical factors that affect the application of geopolymer as a bonding material are the durability and the bonding strength to concretes. The excellent durability of geopolymers has been well demonstrated under ambient weathering and various aggressive conditions [9,16]. However, the bonding properties have only obtained limited attention. The bonding properties, in

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[*] Corresponding author. Tel.: +61 7 46311335.
E-mail address: Zuhua.zhang2@usq.edu.au (Z. Zhang).

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terms of bond strengths in tension, shearing and compression, are even more important than the durability, as they determine the possibility for this application purpose. It is reported that geopolymer can successfully bond carbon fabrics to reinforced concrete beams, even better than the organic polymers [7]. It is well known that assessments by different testing methods give different ranges of bond strength [17]. In the compression pattern, the shear bond strength of slant prisms with geopolymer and concrete joints at a 60° angle of cross section is 10–20 MPa [14,18]. In the tension pattern, it is reported the bonding between geopolymer mortar and concrete is very low (pull strength <0.2 MPa [19]). Zhang et al. [16] reported that the testing of the 'dog-bone' specimens and the pull-off bond strength between the geopolymer and cement mortars is 0.5–2 MPa, which is consistent with the results by Hu et al. [12], who used a similar testing method. Behind these specific data, one of the most concerned issues is the bonding mechanisms of geopolymer to hydrated cement, as this issue relates to both the bonding strength and its durability.

Zhang et al. [20] proposed a chemical bonding mechanism that involves the surface dissolution of hydrated cement and the formation of new calcium containing geopolymeric gels. The chemical bonding brings benefits to the integrity of the bonding interface; however, the transformation in interface may cause more significant influences on the bonding properties. This is based on the fact that geopolymers have zeolite-like local structures [21,22], which tend to transform into crystalline phases, depending on the activator type, ageing temperature and humidity conditions [23,24]. The transformation of geopolymer gels towards zeolites or more ordered structure cause re-organization of local structure, which has been noticed to have different influences on the mechanical properties [25,26]. Lloyd [26] concluded that amorphous geopolymer gels synthesized from metakaolin formed crystalline zeolites upon hydrothermal ageing (95 °C), accompanied by major restructuring of the gel and loss of compressive strength. In comparison, much less of the gel in a geopolymer derived from fly ash was converted to zeolite phases during high temperature ageing, corresponding with negligible strength loss. To date, the effects of phase transformation on the bonding properties have not gained much attention and remain unclear. This study aims at investigating the bonding properties and the interface by examining the change in metakaolin-based geopolymers under different curing conditions.

2. Experimental

2.1. Materials

The geopolymer binder was synthesized by activation of metakaolin with sodium silicate solution. The metakaolin was obtained from Fujian province, China. It is a product of 750 °C × 2 h heated kaolin powder. The metakaolin powder has a BET surface area of 12 m^2/g, and the particle size distribution determined by a laser particle sizer is shown in Fig. 1. The cement used for making substrates was a 52.5 Portland cement. Table 1 gives the chemical composition of the metakaolin and cement as determined by X-ray fluorescence (XRF). The technical requirements for the cement are also listed. As sand or coarse stone gravels may introduce complexities in the interfaces, in this study, only pastes were prepared, bonded and tested.

The alkaline activator was a mixture of chemical grade NaOH solution (12 M) and commercial liquid sodium silicate (original modulus was 3.33, Na_2O 8.29 wt%, SiO_2 29.91 wt%). The mass ratio of NaOH solution and the liquid sodium silicate was 0.7, giving a molar ratio SiO_2:Na_2O of 1.2 in the mixture. Distilled water was then added to adjust the concentration to 35 wt% ($Na_2O + SiO_2$) and the molar ratio of H_2O/Na_2O was 15.2.

2.2. Specimen preparation and testing

2.2.1. Specimens for bond strength testing

The moulds for bonded specimen preparation and testing are shown in Fig. 2. Cement paste at a water/cement ratio of 0.32 was cast in one half of the cavity, set and aged for 28 days at 20 ± 2 °C, relative humidity of 95 ± 5%. This ageing was believed be able to guarantee the cement paste get a high hydration degree because of the relatively quick strength development of this cement. A longer curing should provide a more mature paste, for example, 90 days at room temperature [27]; however, it is difficult to define a 'suitable' hydration degree to stimulate the concrete repair. To minimise the influences of cement hydration on bonding, this study adopted the 28 days curing procedure. Afterwards the other half was filled with geopolymer paste, which was prepared by mixing metakaolin with the alkaline activator solution at a liquid/solid ratio of 0.65 mL/g. This mixture had a stoichiometric composition of $2.5Na_2O \cdot 4.1Al_2O_3 \cdot 12.4SiO_2 \cdot 38.7H_2O$, regardless of the trace composition in metakaolin. After 1 day setting and hardening at 20 ± 2 °C, relative humidity of 95 ± 5%, the bonded specimens were removed from moulds and put in the following three conditions for ageing:

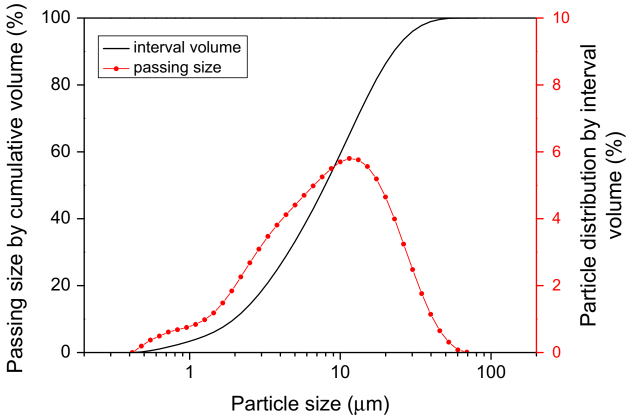

Fig. 1. Particle size distribution of metakaolin.

Table 1
Chemical composition of metakaolin and the 52.5 Portland cement, and the technical requirements of the cement as per GB175-2007.

	Metakaolin	Cement
SiO_2	55.87	20.3
Al_2O_3	42.25	5.5
Fe_2O_3	0.38	3.3
CaO	0.04	63.9
MgO	0.04	1.6
Na_2O	0.26	0.3
K_2O	0.31	1.3
SO_3	0	1.02
TiO_2	0.20	0
Loss on ignition	0.61	2.3
Initial setting (min)		$\geqslant 45$
Final setting (min)		$\leqslant 390$
3 days Bending strength (MPa)		$\geqslant 4.0$
3 days Compressive strength (MPa)		$\geqslant 23$
28 days Bending strength (MPa)		$\geqslant 7.0$
28 days Compressive strength (MPa)		$\geqslant 52.5$

(1) AC – 20 °C air curing at relative humidity of 95 ± 5%;
(2) SC – 80 °C sealed curing in plastic bags; and
(3) WC – 80 °C water curing in water bath.

The 7 days and 28 days bond strengths were tested on a RG-3010 universal mechanical testing machine in a tension pattern. The pulling rate was 0.2 mm/min.

2.2.2. Specimens for compression testing

The cement paste and geopolymer paste were cast into cubic specimens of size 20 × 20 × 20 mm and allowed to harden at the AC conditions. In parallel with the bonding testing, all of the cement specimens were also aged for 28 days. The 'old' cement specimens and 1 day aged geopolymer specimens were put in the above three conditions for further curing until testing. The compressive strength testing was performed on a RG-3010 universal mechanical testing machine, at a load rate of 0.5 mm/min.

2.2.3. XRD, FTIR and SEM-EDS analysis

The compression fractured specimens at different ages were collected and stored in acetone. The samples were grounded and dried at 65 °C for 24 h for XRD and FTIR analysis. The XRD analysis was performed using a DX-2700 X-ray