

Effect of the additions of dehydrated geopolymer powders on compressive strength and integrity of the final geopolymer

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In this study, it is aimed to improve geopolymer compressive strength and integrity without causing any impurity. Thus, the effect of the additions of dehydrated geopolymer powders (0-40 wt.%) on compressive strength and integrity of the geopolymers cured with two different compositions was investigated. The powders were obtained by grinding of monolithic pure geopolymer which was dimensionally stabilised by thermally dehydration at 400 °C. Results of this study showed that when the powders were added at 10 wt.%, compactness of the microstructure and compressive strength of the samples increased. Additions of dehydrated geopolymer powder enhanced the integrity of the samples without changing the amorphous structure and typical FTIR spectrum of the pure geopolymers. Unlike the pure sample; after being thermally treated at 400 °C, the crack free samples, which had compressive strengths up to 51.65 Mpa could be obtained with the additions of the powders.

Key words: Geopolymers, Integrity, Ceramics, Compressive strength, Metakaolin.

Introduction

Geopolymers are known as fire-proof amorphous inorganic materials that can be generally produced with low CO₂ emission in mild temperatures by curing of alkali activated metakaolin or fly ashes [1-3]. These materials have various applications such as refractory for aluminium casting, dental materials, fire-resistant composites, green construction materials and advanced ceramic productions [1, 4-6]. Along with physical water, the cured geopolymers also contain structural water that dehydrates between 100 and 370 °C [3]. Irreversible excessive shrinkages occurring during the dehydration of structural waters cause the material to crack. This situation results in an integrity problem that restricts the applications [5-7]. To prevent drying cracks, the geopolymers have to be produced with dimensionally stable inert mineral filler additions such as silica sands [3, 5, 7]. Inert fillers increase the weight of the geopolymer products and cause thermal mismatch stresses in the structure. In addition to inert fillers; since various additives such as granulated blast furnace slag or organic resins also increase the compressive strength, they may also be included in the geopolymer compositions [8, 9]. Such types of additives cause the geopolymers to contain some impurities. Partial or full elimination of the said additives from the compositions becomes more important in thermal applications or in case the geopolymers are used as a

pre-shaped advanced ceramic precursor.

Y.M. Liew et al., reported that when the geopolymer powders obtained by the grinding of monolithic geopolymers were mixed with water, the powders set by continuing geopolymerisation reactions and they can be used to produce geopolymer cements in the “just adding water” concept [10, 11]. The effects of the geopolymer powder additions on properties of the cured geopolymers have not been reported. Unlike the additives used for the similar purposes [5, 7-9], the geopolymer powders are thought to have a potential to enhance the mechanical properties and integrity of the geopolymers without causing any impurity, thermal mismatch stresses, and excessive density. The effect of the powders of metakaolin based geopolymer, which dehydrated before grinding to obtain dimensionally stable powders, on integrity and compressive strengths of the cured geopolymers were investigated in this study.

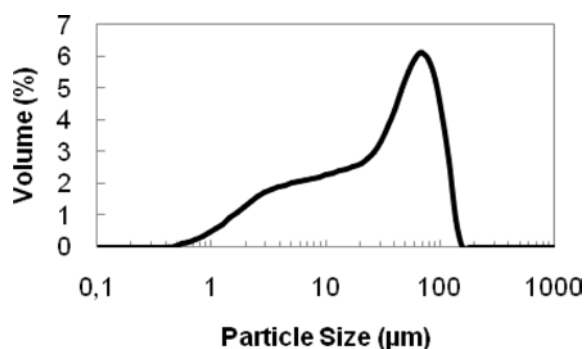
Experimental

Metakaolin (Si:Al = 1) was obtained by calcination of ultrafine kaolin (<2 µm) at 750 °C for 6 h. Alkaline activator solutions were prepared by mixing stoichiometric amounts of sodium hydroxide (Merck, 99 wt.% purity), Na-silicate solution (Merck, 8 wt.% Na₂O, 27 wt.% SiO₂, 65 wt.% H₂O), and distilled water. Geopolymer resins in two compositions were produced by mechanically mixing stoichiometric amounts of metakaolin and activator solutions until the homogenous pastes were obtained. Table 1 illustrates the molar ratios of the prepared resins. These

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Table 1. Molar ratios of the prepared resins.

Composition	Molar Ratios			
	Na ₂ O : Al ₂ O ₃ SiO ₂	: Al ₂ O ₃ H ₂ O	: Al ₂ O ₃ H ₂ O	: Na ₂ O
C1	1	4	16.3	16.3
C2	1.2	4	19.6	16.3

**Fig. 1.** Particle size distribution of the DGP powder.

compositions with two different fluid ratios are preferred since they present metakaolin based stable and high-strength geopolymers [3].

Primarily, dehydrated geopolymer powders (DGP powders) were obtained from the resin. Thus, the resin prepared in C1 composition was poured in cylinder moulds (40(ø) × 10 mm). Moulded resins were cured at 65 °C for 24 h in a hermetically sealed container. Cured resins were removed from the mould and dried at 85 °C for 24 h and then dehydrated at 400 °C for 2 h. Dehydrated monolithic solid consisting of drying cracks due to the unfilled production was milled in a laboratory type ring mill and geopolymer powders with the $d_{[0.5]}$ value of 33.96 μm were obtained. Fig. 1 illustrates particle size distribution of the powders obtained via mastersizer.

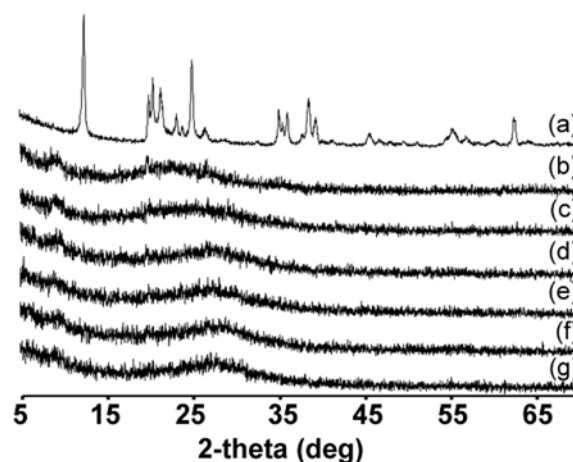
For the production of the samples, DGP powder were added to fresh resins (0–40 wt.%) prepared with C1 and C2 compositions and then mechanically mixed until homogenous mixtures were obtained. The mixtures were poured in cylindrical moulds (15(ø) × 30 mm for compressive strength tests, 40(ø) × 10 mm for other tests), and then vibrated for 10 minute to remove the air bubbles. Moulded mixtures were cured within a sealed closed container at 65 °C for 24 h and then the solids removed from the mould were dried at 85 °C for 24 h.

X-Ray Diffraction (XRD, Rigaku ultra iv, 5 to 70 ° of scanning angle, 2 °/min of scanning speed) was used to analyse phases. Particle size distribution analysis of the DGP powder was performed by using Malvern Mastersizer 2000 device. Ultimate compressive strengths of the samples were determined by using Zwick/Roell 600 kN universal testing machine with constant crosshead displacement of 1.00 mm/min. The densities of the samples were measured in accordance with Archimedes principle. The average values of three samples were

obtained for the density and compressive strength. BrukerIFS 66/S spectroscopy in a transmittance mode from 400 to 4000 cm⁻¹ was used to conduct Fourier Transform Infrared Spectrometer (FTIR) analyses. Scanning Electron Microscopy (SEM) examination was performed by using Carl Zeiss Ultra Plus Gemini FE-SEM. In order to examine the effect of powder additive on integrity, the samples prepared cylindrically at 40(ø) × 10 mm were firstly heated to 400 °C with a heating rate of 3 °/min and then they were dehydrated by keeping them at this temperature for 2 hours. The presence of cracks on the sample surface after the heat treatment was examined at room temperature by using a stereomicroscope.

Results and Discussion

Fig. 2 illustrates the XRD patterns of the starting materials and products. Only kaolinite peaks were detected in the kaolin (Fig. 2a), which transformed into amorphous metakaolin by calcinations (Fig. 2b). The produced DGP powders (Fig. 2c) and pure samples (Fig. 2d and 2f) were amorphous. Although it was reported [10, 11] that the monoliths obtained by mixing the geopolymer powders with water included zeolitic phases, the samples produced by the addition of 10 wt.% DGP powder to geopolymer resin maintained

**Fig. 2.** XRD patterns of the (a) kaolin, (b) metakaolin, (c) DGP powder, (d) Pure C1, (e) C1 + 10 wt.% DGP powder, (f) Pure C2 and (g) C2 + 10 wt.% DGP powder.**Table 2.** Compressive strengths (Mpa) and densities (gr/cm³) of the samples (densities are given in brackets under the compressive strength values).

Composition	wt.% DGP Powder Addition				
	0%	10%	20%	30%	40%
C1	19.41 (1.31)	37.64 (1.37)	20.35 (1.35)	11.79 (1.29)	8.74 (1.26)
C2	46.95 (1.41)	51.65 (1.42)	36.95 (1.39)	27.20 (1.37)	14.48 (1.37)

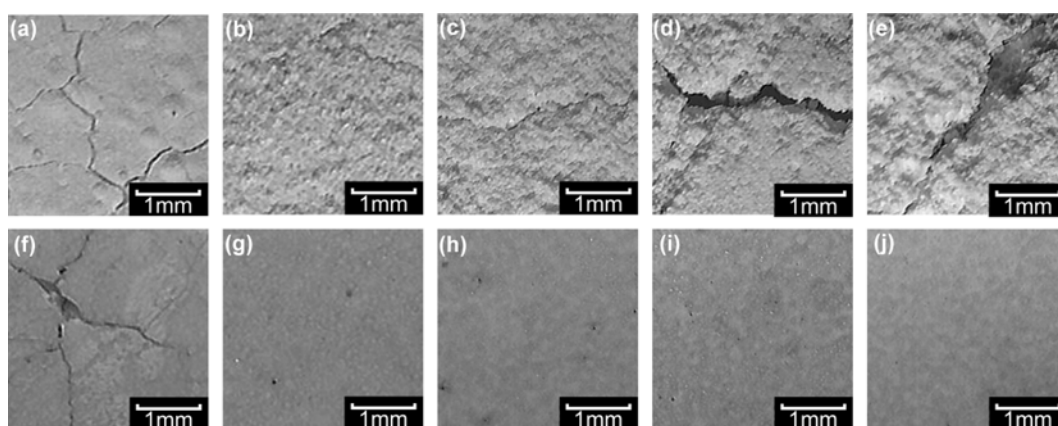


Fig. 3. The stereo microscopy images of the (a) 0, (b) 10, (c) 20, (d) 30, (e) 40 wt.% DGP powder added samples with C1 composition and (f) 0, (g) 10, (h) 20, (i) 30, (j) 40 wt.% DGP powder added samples with C2 composition.

their amorphous structure (Fig. 2e and 2g).

Table 2 illustrates the densities and the compressive strengths of the sample. As compared to pure samples, higher density values were observed in 10 wt.% DGP powder added samples independently of resin compositions. It is known that the geopolymers have permanent porosity at the nano-size level [12]. Due to its hydrophilic structure, it is an expected result that DGP powders detained the fluid of the mixture into its pore structure up to a certain addition ratio, approached solid components to each other and consequently increased the density. When the additions were more than the values of 10 wt.%, the densities of the samples decreased dramatically. Sharp decrease in the density was more significant in the samples having C1 composition with less water ratio. Since the amount of liquid to cause the fluidity to be insufficient was absorbed by added powders in order to place solid components as void-free and elimination of air-bubbles, it was estimated that the density decreased in the samples having an addition over 10 wt.%.

It was found that the compressive strengths of the samples with C2 composition were higher than the samples with C1 composition (Table 2). Excess Na^+ cations in the samples with C2 composition may have provided more geopolymer transformation in the highly reactive alumina silicate solid precursor. The peak compressive strengths of the samples were obtained at the addition ratios of 10 wt.%. It was considered that DGP powders optimised the solid/liquid ratio in the matrix in terms of compressive strength for the addition of 10 wt.%. Because of emergence of the samples with more porosity due to high viscosity in the resin of samples added with over than 10 wt.% DGP powder, the compressive strengths of samples decreased with addition ratio over than 10 wt.%. Another possible explanation that describes the decrease of compressive strength by the addition of DGP powder over 10 wt.% was that the diffusion capability of the reactants in the solution that was trapped in the pore structure of the powders at this

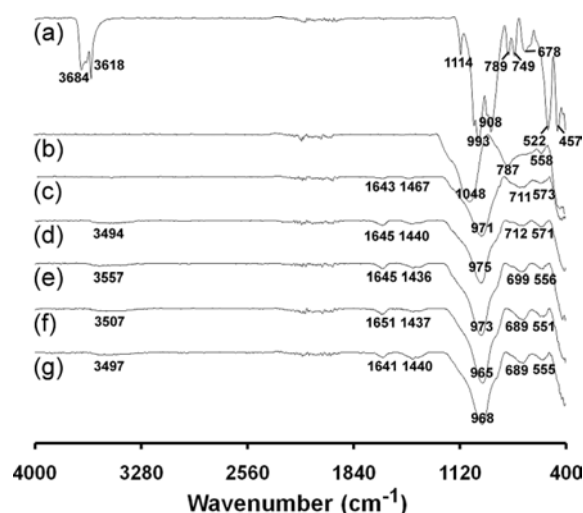


Fig. 4. IR spectra of (a) kaolin, (b) metakaolin, (c) DGP powder, (d) Pure C1, (e) C1 + 10 wt.% DGP powder, (f) Pure C2 and (g) C2 + 10 wt.% DGP powder.

additive ratio was insufficient for the reactions. This situation was observed as a result of sharp decrease of compressive strengths of samples with increasing addition ratios even though there was no significant difference in densities of samples having C2 composition and 30 wt.% and 40 wt.% powder addition.

Fig. 3 illustrates the macroscopic images of the sample surfaces after the heat treatment at 400 °C. Pure sample with C1 composition was cracked after the heat treatment (Fig. 3a). While the amount of cracking decreased with 10 wt.% and 20 wt.% DGP powder addition to C1 composition (Fig. 3b and 3c) the addition of the powders over than 20 wt.% affected the integrity negatively due to poor mechanical properties of the samples (Fig. 3d and 3e). Although pure sample with C2 composition was cracked (Fig. 3f), crack free samples were obtained with the addition of 10 to 40 wt.% DGP powders (Fig. 3g, 3h, 3i and 3j). The fact that powder added samples with C2 composition had higher strength allowed samples to be dehydrated

as crack-free by increasing the resistance against stresses causing crack formation in the samples. It should be noted that samples with C2 composition also offered shiny and air bubble free surfaces. It seems that higher water including composition of the samples with C2 composition can tolerate the hydrophilic DGP powder addition.

Fig 4 illustrates IR spectra of the starting material and the products. In kaolin spectrum, characteristic peaks known for the kaolinite mineral were determined (Fig. 4a). Peaks at 3684 cm^{-1} and 3618 cm^{-1} in the kaolin spectrum belonged to the OH^- stretching vibration [10, 13]. Peaks at 1114 cm^{-1} and 993 cm^{-1} showed the Si-O bonds [10, 13]. Peaks at 908 cm^{-1} wave number expressed the Al-OH vibrations [10, 13]. Peaks at 789 cm^{-1} , 749 cm^{-1} , 678 cm^{-1} and 457 cm^{-1} belonged to the Si-O bonds [10, 13] and the peak at about 522 cm^{-1} showed the Si-O-Al^{vi} bonds [10, 13]. Because dehydroxylation and degradation occurred in the kaolinite due to the heat treatment, the peaks caused by the OH^- molecules in the metakaolin spectrum disappeared (Fig. 4b) and the peaks showing the Si-O, Al-O and Si-O-Al bonds were observed respectively at 1048 cm^{-1} , 787 cm^{-1} and 558 cm^{-1} [10].

In DGP powders (Fig. 4c) and all the monolithic geopolymer samples (Fig. 4d, 4e, 4f and 4g), the metakaolin structure was degraded by geopolymerisation and a characteristic spectrum that was compatible with the previously reported ones for the geopolymers produced from metakaolin was observed [10, 14]. The only significant difference between the spectra of DGP powders and monolithic samples was that DGP powders did not contain wide bands caused by the OH^- vibration at around 3500 cm^{-1} due to dehydration and the peak of H_2O stretching at about 1645 cm^{-1} had low intensity compared to the other spectra [10]. Peaks within range of the 1436 cm^{-1} and 1467 cm^{-1} in the spectra belonged to NaCO_3 formed by the sodium carbonation that remained from the reactions [14]. Peaks within range of 965 cm^{-1} and 975 cm^{-1} belonged to the Si-O-(Al or Si) bonds that were characteristic for the geopolymers [10]. Peaks within range of 711 cm^{-1} and 689 cm^{-1} showed Al-O-Si stretching vibration and the peaks observed between 551 cm^{-1} and 573 cm^{-1} showed Al-O-Si bending vibration [14]. The absence of a significant change in the spectra as a result of addition of the DGP powders in the pure samples showed that DGP powder additive did not change the absolute geopolymer structure.

Fig. 5 illustrates SEM images of the samples. The loose microstructure of the pure samples with C1 composition (Fig. 5a) that included porosities was densified significantly with 10 wt.% DGP powder addition (Fig. 5b). Densification of the microstructure of the samples with C2 composition involving 10 wt.% DGP powder addition was not as significant as the samples with C1 composition due to its higher aqueous

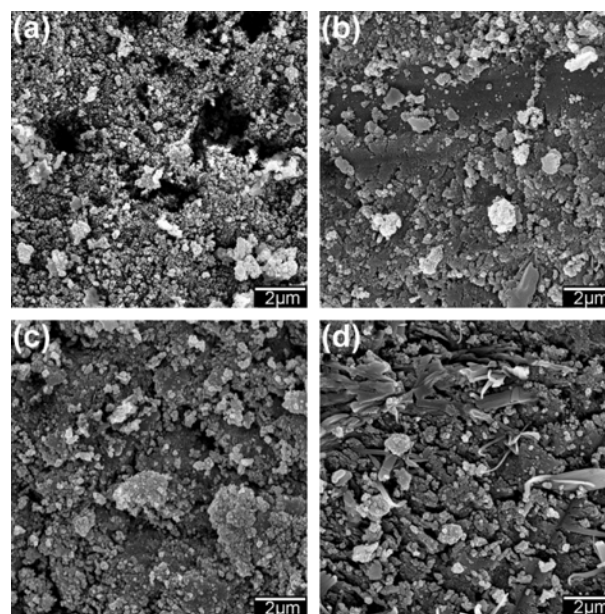


Fig. 5. SEM images of the (a) Pure C1, (b) C1 + 10 wt.% DGP powder, (c) Pure C2 and (d) C2 + 10 wt.% DGP powder.

composition (Fig. 5c and 5d). Increased compactness of the microstructures of both samples with the powder addition reflected on compressive strength values as an increase (as seen in Table 2).

Conclusions

In this study, it was concluded that the integrity and compressive strength of the geopolymers improved with addition of DGP powders without causing any impurities. Xrd analyses showed that the added powders did not degrade the amorphous structure. In the FTIR analyses, it was determined that the added DGP powders did not cause a significant change in the spectrum. Compressive strength increased with the addition of 10 wt.% DGP powders. Doping at higher ratios negatively affected the compressive strength. Due to the water absorption property of DGP powders, the samples with higher surface quality and integrity were obtained from the composition containing higher water quantity. After dehydration performed at $400\text{ }^{\circ}\text{C}$ with addition of DGP powder made to this composition, samples containing no crack at addition ratios from 10 wt.% to 40 wt.% were obtained. It is expected that in order to offer a crack free products after dehydration, geopolymers which need no or less inert mineral fillers in terms of dimensional and drying parameters may be producible with the dehydrated geopolymer powder additions for various applications.

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