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Original Article

Sodium Silicate Free Geopolymer As Coating Material: Adhesion To Steel

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Abstract: Geopolymer is a green and sustainable material synthesized by alkali activation of raw aluminosilicate rich materials. In this study class F-fly ash based sodium silicate free geopolymers were synthesized and used for coating application at 60^{o}C. Setting time and adhesion strength analysis were performed using Vicat needle and Elcometer 108 according to ASTM C 807-08 and D 4541 respectively. Infra Red spectroscopy was used to understand the degree of geopolymerisation by observing the vibration frequency of -Si-O-T bonds around 1000 cm^{-1}. A gradual increase in adhesion strength was observed with alteration of Na/Al ratio from 0.6 to 1.0. A maximum of 3.8 MPa adhesion strength was produced by geopolymer with Na/Al=1. Final setting time shows variation with varying Na/Al at a constant water content. It was found that geopolymers gained maximum strength within first 3 days and only partial changes has been noticed in terms of adhesion strength. Scanning electron microscopy of the final product revealed that the formation of geopolymer has occurred without addition of sodium silicate. It can be concluded that sodium silicate free geopolymer has the potential to be used as a sustainable and green coating material for metals protection.

Keywords: Geopolymer; Fly ash; Coating, Adhesion; Elcometer; FTIR; Microstructure

1. Introduction

Treatment and removal of fly ash as a waste from coal based power plants is going to be an uneconomical and environment unfriendly task. Reutilization is mostly focused as pozzolanic material and about 10-15% of fly ash is used by cement sector. Dumping in lowlands is the most common practice used for discarding of fly ash causing water, land and aerial contamination [1]. Geopolymer, an amorphous alumino silicate, is synthesized from fly ash in an environment friendly and green process compared to ordinary portland cement (OPC) [2]. This chemosynthetic material has many application including as binders, green and durable cements, encapsulating agent for hazardous waste, active catalyst and thermal resistant coating [3-7] .

Recently coating properties of this material has been explored by some researchers. Temuujin et.al. prepared fire resistant coating material from collie fly ash using geopolymer technology with a varying Si : Al and solid : liquid ratios and keeping a constant ratio of Na : Al equal to 1. Adhesion strength, a direct measure of the power of attachment of a coating with substrate, was determined using Elcometer 106 and maximum of 3.8 MPa of adhesion strength was attained. Mustafa et. al [8] studied flexural strength and thermal stability of geopolymer coated ceramics at different temperatures and a 3 time increase was found when temperature was increased from 600^{o}C to 1500^{o}C. Compared to (OPC), geopolymers offer improved properties at high temperature [9].

In most of the recent publications alkali silicate and alkali hydroxide based alkaline activators has been used for geopolymerisation process [4,10-12]. Alkali silicates are expensive and leading to shortening of setting time due to provision of soluble silica for chemical reaction. Preparation of sodium silicate free geopolymers are more economical and can be of great value as huger amount of waste ash can be utilized inside it.

This study aimed to synthesize sodium silicate free geopolymers with a varying Na/Al molar ratios and to study its effect on adhesion strength and final setting..

2. Results and Discussion

2.1. Adhesion study

Fig 1(a) shows adhesion strength analysis for 3, 7 and 28 days cured geopolymer samples coated on steel substrate. A maximum of 3.8 MPa strength was observed for AD 3. There is a gradual increase in adhesion strength with increase in Na/Al ratio from 0.6 to 1. whereas partial decrease was observed when that ratio was increased to 1.2. Geopolymerization process has reached to an end within first 3 days (Fig1.a).

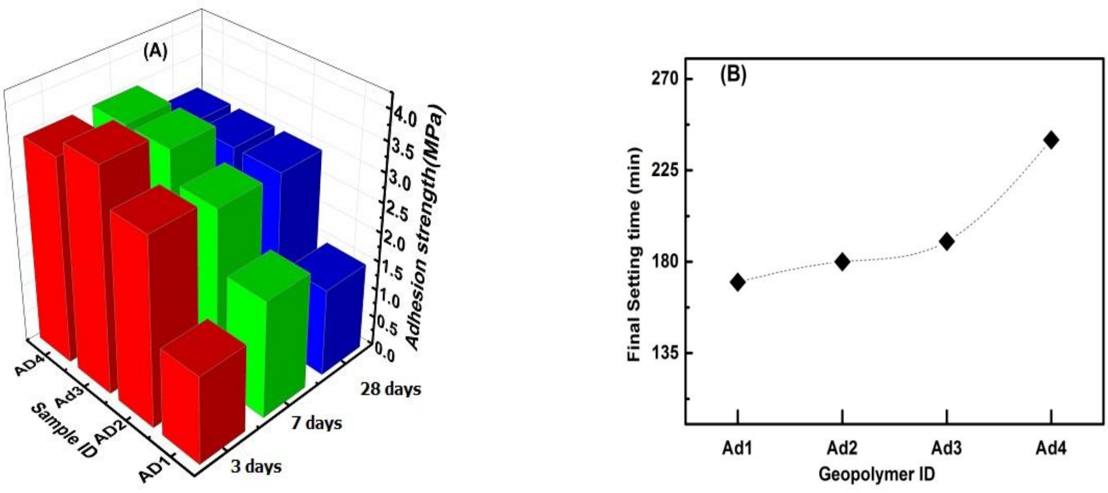

Fig 1.(A) Adhesion strength of geopolymers to steel (B) final setting time of geopolymers

Temuujin reported a maximum adhesion strength of 3.5 MPa for collie fly ash based geopolymer at Si/Al= 3.5 and water/solid ratio of 0.35. Whereas at Si/Al molar ratio equal to 2, the adhesion strength was reduced to 0.5 MPa [10]. This variation can be explained on nature, particle size, chemical composition and reactive phases of fly ash. Silica and alumina content of Collie fly ash is lower than the ash used in this study [13].The degree of geopolymerisation is influenced by amorphous alumina and silica content of the starting raw material. Silica to alumina ratio is another factor responsible for higher adhesion strength in this study.

2.2. Setting time analysis

Setting time of geopolymer is important because it provides information about its application and curing time. Fig. 1(b) shows the longevity of final setting time of geopolymer with gradual increase in sodium hydroxide content. A final setting of 240 minutes was observed in sample AD4 having the highest Na/Al ratio compared to other samples. It is assumed that all these samples can handled for at least 150 minutes after mixing. These results are in agreement with the previously reported work[14]. Wang et al produced geopolymers were set in 65 min at 60^{o}C. The difference between the two studies is because of use of different starting materials and their composition. Si/Al ratio used by Wang et.al was 2.27 that may be leading to a shorter setting time [15].

2.3. FTIR analysis

Fig. 2 represents FTIR analysis of fly ash and geopolymer samples. Absorbance at 3445cm^{-1} and 1634cm^{1-} can be attributed to (-O-H) asymmetric stretching due to water and silanol groups. Broad peak centred around 1000cm^{-1} is assigned to Si-O-T (T= Si or Al) vibrations in fly ash and geopolymers. Si-O-T bonding vibration provides valuable information about geopolymerisation. In fly ash the maximum value of the broad peak is 1080cm^{-1} whereas in geopolymer samples this peak has shifted towards 990cm^{-1}. This new peak formation can be explained on transformation of Si-O-Si bonds of amorphous silica into Si-O-Al bonds of poly sialate. A shoulder at 1050cm^{-1}in geopolymer samples is due to presence of quartz. All geopolymer samples have nearly similar spectra with a minor variation in broadening of peak.

Catherine et.al used in situ ATR-FTIR for early stages study of geopolymer. Si-O-T absorption peak of fly ash at 1050 cm^{-1} was found to transform into a new peak at 960 cm^{-1} due to Si-O-Al bonds formation. In lower silicates the peak position is centred around 990cm^{-1}[16,17]. Similar results were also obtained by Ailar et.al. The Si-O-T peak at 1099cm^{-1} in fly ash was disappeared and a new peak at 964cm^{-1} appeared due to geopolymerisation [18].

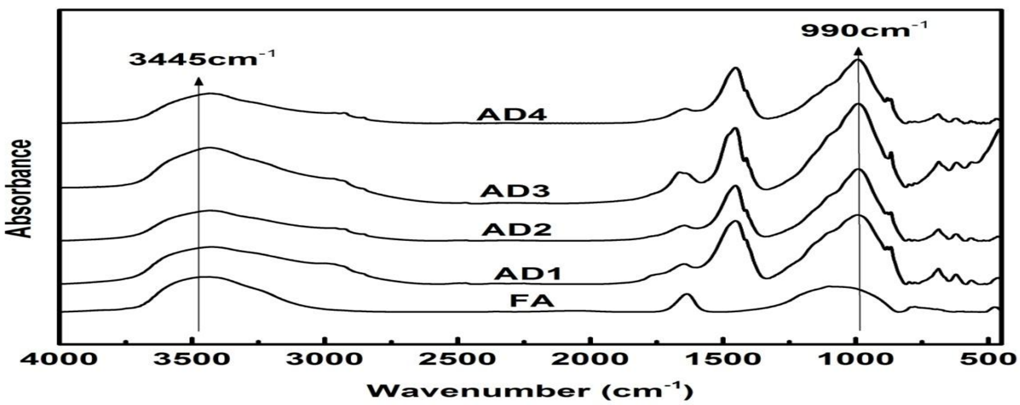

Fig 2. FTIR spectra of fly ash and geopolymer sample (28 days curing)

2.4. Microstructure analysis

FESEM is a universally used technique for micro structural study of geopolymers. Fig. 3 shows microstructure of AD 1, 2, 3 and 4. Fly ash is a multi component material composed of particles of different diameter and composition [19]. Presence of fly ash particle in geopolymer samples shows that part of these particles did not take part in chemical reaction. Larger fly ash particles (> 10um) with cracks and voids are clearly visible in AD 01 indicating that such particle offer resistance to alkali leaching. Porous texture with large sphere of unreacted and partially reacted fly ash represents a poor geopolymerisation in AD 01 leading to weaker adhesion. AD2 and AD4 is having a smooth surface without any cracks. Both of these samples have similar FTIR spectra and adhesion strengths. The Sodium hydroxide content has a direct relation with smoothness of surface and adhesion strength. These results are in agreement with the previous results [20]. Fly ash particles are dissolved by NaOH activator and higher Na/Al ratio will lead to more geopolymerisation.

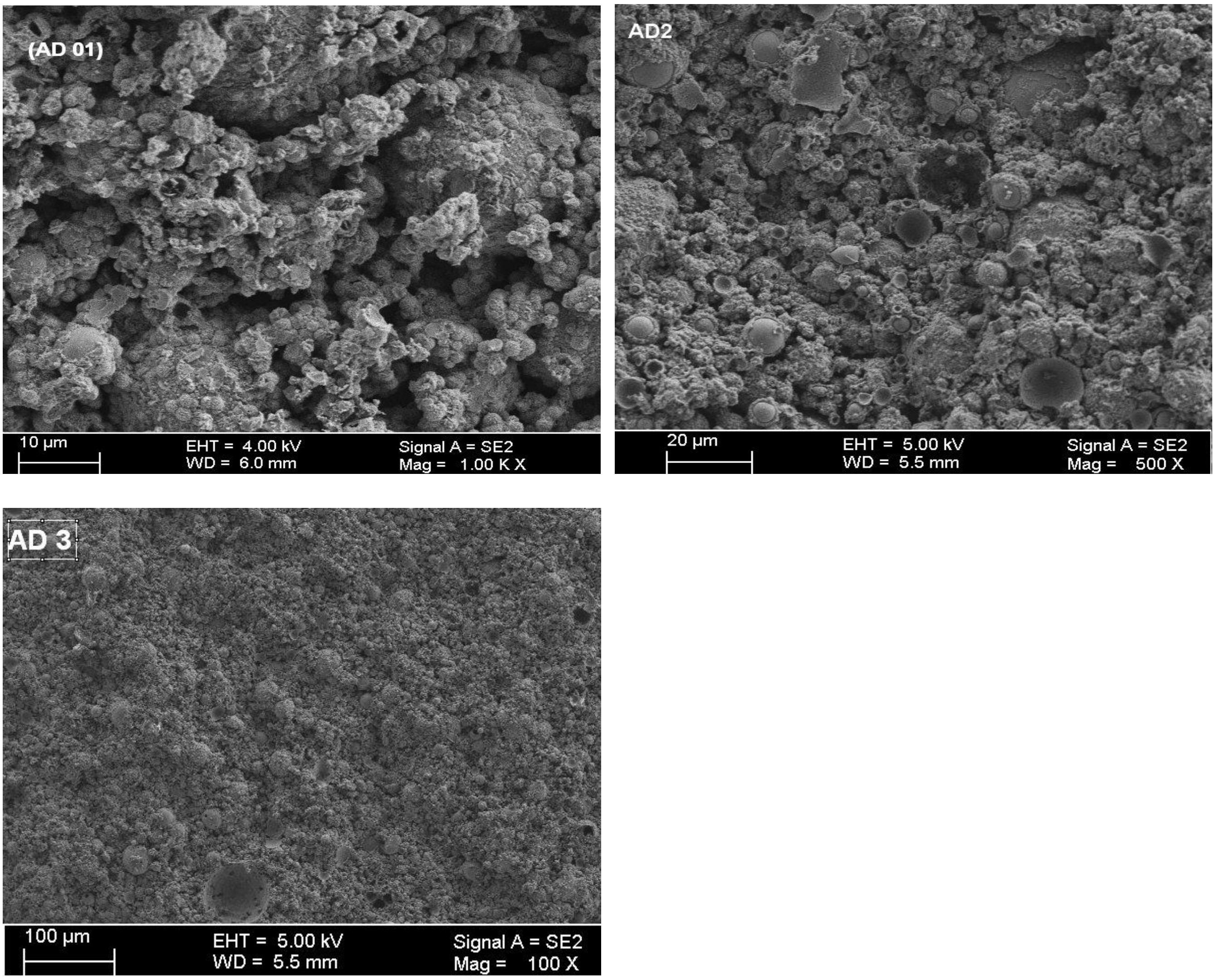

Fig3. FESEM micrographs of geopolymer samples

3. Experimental Section

3.1. Material

Sodium hydroxide (NaOH) was procured from Merck Millipore. Class f- fly ash was obtained from a local power plant and was sieved through a 45 µm sieve using RETSCH vibratory sieve shaker AS 200 basic. Mild steel bars (3mm x 50mm x 127mm) were purchased from TSA Sdn. Bhd. Malaysia. Demineralized water, was used throughout the experiments.

3.2. Methods

Fly ash was mixed with sodium hydroxide solution (prepared independently for every formulation) according to Table 1. Sodium silicate solution was not used in this experiment. All samples were uniformly homogenized with an over head mechanical stirrer for 5 minutes. Cleaned and pretreated steel plates were coated with geopolymer paste using dip coating and were oven cured at 60^{o}Cfor 28 days period.

Part of the sample was placed in the sample holder for setting time analysis at the constant temperature.

Table 1: Mix design for geopolymer synthesis

Sample ID	**Si: Al ratio**	**Na: AL ratio**	**Water :solid ratio**	**Curing temp.**	**Curing time**
AD 01	1.78	0.6	0.33	60^{o}C	28 days
AD 02	1.78	0.8	0.33	60^{o}C	28 days
AD 03	1.78	1.0	0.33	60^{o}C	28 days
AD 04	1.78	1.2	0.33	60^{o}C	28 days

3.3. Characterization

Adhesion strength of the coating material was determined using Elcometer 108 according to ASTM D 4541. Dolly fixed with coating surface by epoxy was cured in the oven for 24 hours and pulled with Elcometer. Adhesion strength of 3, 7 and 28 days was recorded.

Setting time analysis was performed using Vicat apparatus according to ASTM C 266-13. Samples were placed under Vicat apparatus and setting time was recorded with needle having 1.13 mm diameter and fixed on a 300g movable rod

Coating material was microscopically analyzed using variable pressure field emission electron microscope (VPFESEM), model Zeiss Supra 55 VP. Perkin Elmer Spectrum One, Fourier Transform Infra Red spectrometer (FTIR) was used to determine IR analysis of the geopolymer using KBr pellet.

4. Conclusions

A sodium silicate free, geopolymer synthesized from Fly ash produced a maximum adhesion strength of 3.8MPa. Na/Al ratio has a vital influence on adhesion property and setting time of geopolymers. Optimum value of Na/Al ratio for fly ash based geopolymer as coating material was found to be 1. Setting time show increase with increase in Na/Al ratio. Larger fly ash particles are less reactive and remain unreacted or partially reacted leading to reduction in adhesion strength of geopolymer based coating.. It was revealed from FTIR analysis that quartz is not taking part in geopolymerisation.

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Conflicts of Interest

No conflict of interest.

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