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Effects of NaOH concentrations on physical and electrical properties of high calcium fly ash geopolymer paste

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ABSTRACT

The effects of sodium hydroxide (NaOH) concentration on setting time, compressive strength and electrical properties at the frequencies of 100 Hz–10 MHz of high calcium fly ash geopolymer pastes were investigated. Five NaOH concentrations (8, 10, 12, 15 and 18 molar) were studied. The liquid to ash ratio of 0.4, sodium silicate to sodium hydroxide ratio of 0.67 and low temperature curing at 40 °C were selected in making geopolymer pastes. The results showed that NaOH concentration had significant influence on the physical and electrical properties of geopolymer paste. The pastes with high NaOH concentrations showed increased setting time and compressive strength due to a high degree of geopolymerization as a result of the increased leaching of silica and alumina from fly ash. The dielectric constant and conductivity increased with NaOH concentration while $\tan\delta$ decreased due to an increase in geopolymerization. At the frequency of 10^3 Hz, the dielectric constants of all pastes were approximately 10^4 S/cm and decreased with increased frequency. The relaxation peaks of $\tan\delta$ reduced with an increase in NaOH concentration and ranged between 2.5 and 4.5. The AC conductivity behavior followed the universal power law and the values were in the range of 3.7×10^{-3}–1.5×10^{-2} at 10^5–10^6 Hz.

1. Introduction

Fly ash is an industrial by-product generated during the combustion of coal for energy production. Currently the annual production of coal ash worldwide is estimated around 600 million tons, with fly ash constituting about 500 million tons at 75–80% of the total ash produced [1]. In Thailand, the annual output of lignite fly ash from Mae Moh power station is around 3.0 million tons. Approximately 1.8 million tons are used as pozzolanic material in the cement and concrete industry. However, around 1.2 million tons are still left over and discarded at landfill site [2] which poses a serious environmental problem. This lignite fly ash contains a substantial amount of silica and alumina which can be used as a source material for making geopolymer [2–4]. The geopolymer materials have recently received considerable attention owing to their excellent fire resistance, excellent thermal properties, and environmentally friendly nature [5,6].

Aluminosilicate inorganic polymers, also called geopolymers, were firstly described by Davidovits as materials formed under high alkali condition from aluminosilicate solid and alkali silicate solutions [7]. The geopolymer is a type of cross-linked long chain inorganic polymer material between tetrahedral AlO_4 and SiO_4 units built in three dimensional structures. The linkages of AlO_4 and SiO_4 units require charge balancing from alkali ions such as Li^+, Na^+ and K^+. The mechanism of the existence of alkali ions in the molecular structure of geopolymer materials is not clearly understood at present. Usually the accustomed viewpoint is that the alkali metal ions play a charge balancing role or are actively bonded to the matrix. Therefore, the typical geopolymer composition is usually expressed as $n\boldsymbol{M}_2O\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$ where $\boldsymbol{M}$ is alkali metal element such as Li, Na or K [8]. Several materials containing silica and alumina can be used as starting source materials. These include the conventional starting materials viz., slag, metakaolin and class C fly ash [9,10]; other wastes or waste ashes such as rice husk ash, fluidized bed fly ash, glass cullet powder and waste concrete powder [11–14]; and Portland cement [15,16].

Recently it has been found that the chemosynthetic Al_2O_3–$2SiO_2$ geopolymer prepared by sol–gel method exhibits a high ionic electrical conductivity of about 1.5×10^{-6} S/cm in air at room temperature [8]. Such a high level of the ionic electrical conductivity observed in this geopolymer may be important properties as a promising fast-ionic conducting material for many applications such as solid-state batteries and other solid-state electrochemical

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parts. It has also been found that the water content does not directly affect the electrical conductivity of hardened geopolymer materials [8]. However, the free Na ions, water molecules and hydroxide ions are the major components determining the dielectric loss. The $2.4H_3PO_4–Al_2O_3–2SiO_2$ geopolymer can reduce the ion transfer due to the lack of free alkali cations within the structure. In addition, the heat treatment can reduce dielectric loss from 10^{-2} to 10^{-3} due to the decrease in water from the structure [17].

In general, the ions that can conduct in ionic conductors are Li^+, Na^+, H^+, K^+, Ag^{2+}, O^{2-}, and F^- [18]. For geopolymer materials, free alkali metal ions are expected to play a role on the electrical properties. The concentrations of these free alkali metal ions are, therefore, closely related to the ionic electrical conductivity of fly ash geopolymer materials. Moreover, the electrical conductivity and dielectric constant of fly ash geopolymer pastes are dependent on the frequency range and liquid alkali to ash ratio [19].

In this study, the effects of NaOH concentrations on the physical and electrical properties, and the related dielectric response in fly ash geopolymer pastes (FAGP) were studied.

2. Materials and experimental procedures

2.1. Materials

Lignite high calcium fly ash from Mae Moh power plant in Thailand was used for this study. The median particle size was 23.5 μm and the percentage retained on sieve no. 325 was 40%. The chemical compositions were 35.21% SiO_2, 16.57% Al_2O_3, 25.52% CaO, 13.66% Fe_2O_3, 2.73% Na_2O and 6.31% other. The loss on ignition was low at 0.37. Sodium silicate with 32.39% SiO_2, 13.44% Na_2O and 54.17% H_2O by weight and NaOH solutions were used as alkali activators.

2.2. Geopolymer synthesis

The mixing procedure started with mixing fly ash (FA) and NaOH solution for 5 min. Sodium silicate solution was added and mixed for another 5 min. Liquid alkali solution to fly ash ratios (L/A) of 0.4 and sodium silicate to sodium hydroxide ratio of 0.67 were used. The concentrations of NaOH of 8, 10, 12, 15 and 18 molar were used. These values were selected based on the previous researches using the same lignite fly ash as source material [3,4,20]. The samples that contain the 8, 10, 12, 15 and 18 molar NaOH solutions are abbreviated as G8, G10, G12, G15, and G18 samples, respectively.

2.3. Sample preparation and testing

After being mixed, the fresh pastes were tested for setting times in a 25 °C room using standard Vicat needle apparatus in accordance with the ASTM C191 [21]. The reported results are the average of two tests.

The paste was then cast in a 3 cm diameter and 6 cm height plastic moulds for strength test. The cast samples were left standing in the 25 °C controlled room for 1 h. They were covered with clingfilm to avoid loss of water and put to cure in an electric oven at 40 °C for 24 h. After being cured, the specimens were left in the 25 °C controlled room until the age of 7 days. The compressive strength test was performed at the age of 7 days in accordance with the ASTM D1633 [22]. The reported results are the average of three specimens.

The microstructures of the pastes were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The broken portion of the compressive strength specimens were used for these analyses.

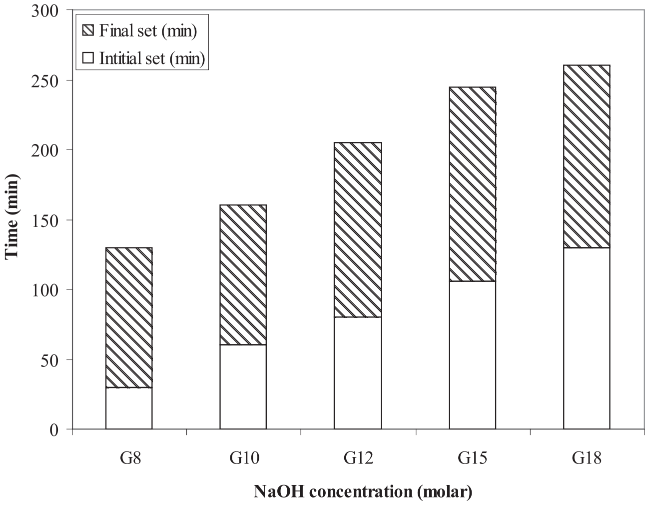

Fig. 1. Setting time of FAGP with various NaOH concentrations.

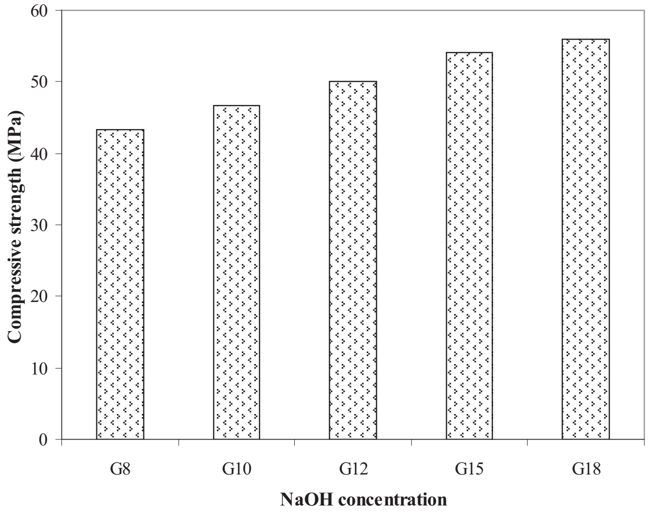

Fig. 2. Compressive strength of FAGP with various NaOH concentrations.

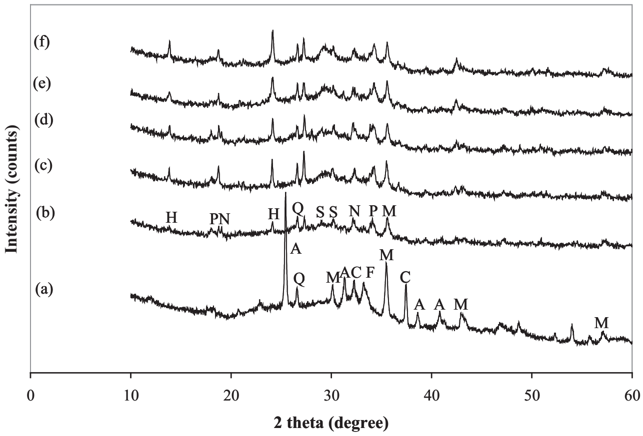

Fig. 3. XRD pattern of fly ash and FAGP with various NaOH concentrations (a) fly ash, (b) G8, (c) G10, (d) G12, (e) G15 and (f) G18.

For dielectric measurement, discs of 19 mm diameter and 2 mm thickness were cast and prepared in the same manner as the strength specimens. At the age of 7 days, the samples were

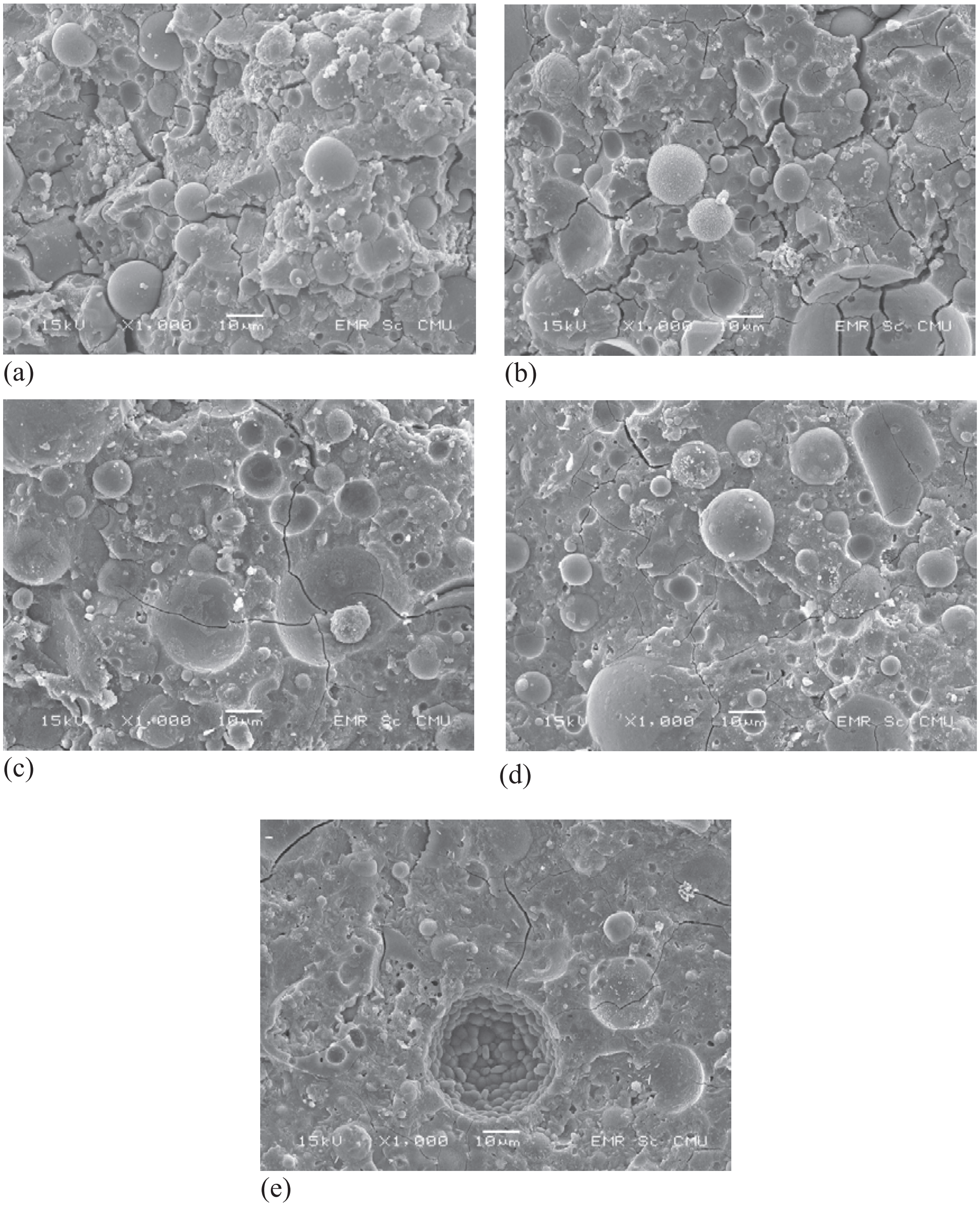

Fig. 4. SEM images of FAGP with various NaOH concentrations (a) G8, (b) G10, (c) G12, (d) G15 and (e) G18.

electroded by silver paint on both sides of the disk-shaped samples. The capacitance, dissipation factor, and electrical responses of the samples were measured with the use of a Hewlett Packard 4194A impedance gain phase analyzer over the frequency range of 102–106 Hz at room temperature and at oscillation voltage of 1.0 V. The relative permittivity or dielectric constant (εr) and dielectric loss (ε_r'') were calculated from Eqs. (1) and (2) [23,24]

$$\varepsilon_r = \frac{Ct}{\varepsilon_0 A} \tag{1}$$

where C is the capacitance of the sample, t is the thickness, ε_0 is the permittivity of free space constant (8.854×10^{-12}), and A is the electrode area;

$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r} \tag{2}$$

where ε_r is the relative permittivity, ε_r'' is the dielectric loss, and $\tan\delta$ is the loss tangent.

3. Results and discussion

3.1. Setting time of geopolymer paste

The results of setting time are shown in Fig. 1. The initial and final setting times increased with an increase in NaOH concentration. The final setting times were 130, 160, 205, 245 and 260 min

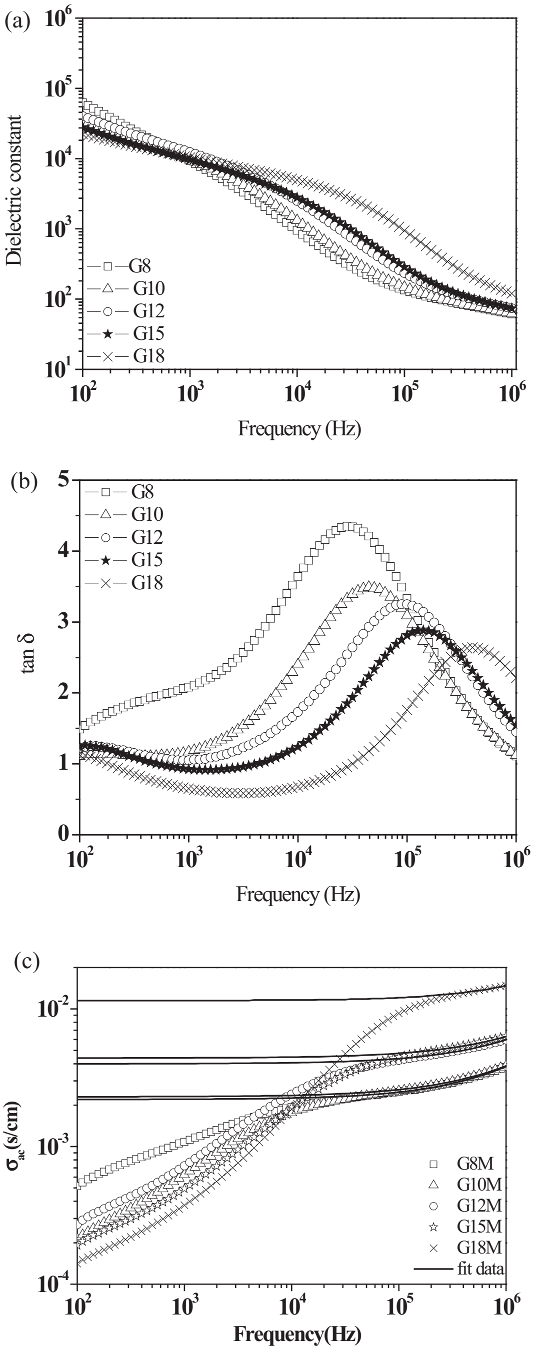

Fig. 5. Electrical properties of FAGP with various NaOH concentrations (a) dielectric constant, (b) tan δ, (c) AC conductivity (σ_{ac}).

Table 1
Parameters obtained from fitting universal power law curves of FAGP with various NaOH concentrations.

NaOH concentrations	σ_0 (S/cm)	A	n
8 M	0.0022	5.1×10^{-8}	0.75
10 M	0.0023	6.5×10^{-8}	0.73
12 M	0.0040	7.2×10^{-8}	0.74
15 M	0.0044	8.5×10^{-8}	0.72
18 M	0.0115	9.1×10^{-8}	0.76

for G8, G10, G12, G15, and G18 pastes, respectively. At low NaOH concentration, the leaching out of silica and alumina was low [20]. The leaching out of Ca^{2+} to the solution was not interrupted and the solution was thus filled with calcium. The amount of calcium was sufficient for the precipitation and reacted to form calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH). This resulted in the setting of paste and the setting time was thus short [25,26]. The setting time of geopolymer paste was thus related to the amount of the available calcium [27].

At high NaOH concentration, the leaching of silica and alumina was much better. The leaching out of calcium was hindered and the amount of calcium in the solution was limited. The setting of the paste was controlled by the normal geopolymerization process and the setting time was increased.

3.2. Compressive strength of geopolymer paste

The results of compressive strength are shown in Fig. 2. The compressive strength was increased with an increase in the NaOH concentration. They were 43.3, 46.7, 50.0, 54.1 and 56.0 MPa for the G8, G10, G12, G15, and G18 pastes, respectively. When the NaOH concentration was high, the dissolution of Si^{4+} and Al^{3+} ions from fly ash increased and the formation of sodium alumino-silicate was enhanced leading to an increase in strength [20,28,29].

The XRD patterns of fly ash and FAGP with various NaOH concentrations are shown in Fig. 3(a–f). The fly ash consists of an amorphous phase as indicated by the broad hump around 20–38° and crystalline phase as indicated by the sharp peaks of quartz (SiO_2), hematite (Fe_2O_3), anhydrite ($CaSO_4$), magnesioferrite ($MgFe_2O_4$) and calcium oxide (CaO). When the fly ash was activated with the alkali solutions, the glassy component was the first to dissolve and formed a new phase of alkaline aluminosilicate gel with apparent shift of broad hump around 25–38° [19,20,28,30]. Moreover, the peaks of quartz and magnesioferrite were still present from the remain of the unreacted or partially reacted fly ash with the disappearance of anhydrite. The new phases were portlandite ($Ca(OH)_2$), sodium sulfate (Na_2SO_4) and hydrosodalite ($Na_4Al_3Si_3O_{12}(OH)$). As discussed, the presence of $Ca(OH)_2$ affected the setting time of the paste. Moreover, the fly ash with high calcium oxide reacted with silicate compounds to form CSH similar to the hydration of Portland cement. The broad hump, therefore, included the geopolymeric gel and CSH gel [2,28]. A higher NaOH concentration had better ability to dissolve fly ash particles which resulted in better geopolymerization. The peaks of hydrosodalite and CSH increased with the increase in the NaOH concentration resulting in the increase in strength of paste.

Fig. 4(a–e) show the morphology of FAGP when activated by NaOH with various concentrations. The unreacted and/or partially reacted grains of fly ash and a continuous mass of alumino-silicate were easily detected. With increasing NaOH concentration, the unreacted fly ash particles were less abundant and the matrices looked rather dense. The findings were similar to the previously published results [31]. When the alumino-silicate source material came into contact with the alkali solution, the leaching of both silica and alumina started [32]. The increase in the NaOH concentration in the system resulted in the increase in leaching of silica and alumina from the fly ash particles to the solutions [20]. This resulted in a dense and strong geopolymer matrix which increased compressive strength of the paste.

Both the XRD and the SEM analyses reinforced the finding that the increase in compressive strength of high calcium fly ash ash geopolymer paste was due to the increase in NaOH concentration. The presence of calcium in substantial quantity in the system led to the formation of hydration products of CSH. At the same time, the high NaOH concentration of the system enhanced the leaching of silica and alumina and resulted in increased geopolymerization and formation of NASH gel. The CSH co-existed with NASH gel and increased the strength of paste [33].

3.3. Electrical properties of geopolymer pastes

Fig. 5 shows the electrical properties of FAGP with various NaOH concentrations. The results showed a decrease in dielectric constant (Fig. 5a) and increase in conductivity (Fig. 5b) with an increasing frequency which was indicative of a region of dispersion resulting from relaxation of a polarization process within the system [34]. For dielectric constant (Fig. 5a), the FAGP showed high dielectric constant values of 10^4–10^5at the low frequency range of 10^2–10^3 Hz which were the results of electrode/sample interfacial polarization and double-layer polarization on fly ash surface [33,34]. At the frequency of 10^3 Hz, the dielectric values of all samples were high at approximately 10^4. At the higher frequency, the dielectric values decreased and depended on the NaOH concentration. The dielectric values decreased less with the increase in NaOH concentration since the samples contained less unreacted fly ash and were denser than those of the low NaOH concentration mix.

For tan δ (Fig. 5b), the relaxation peaks of all samples were clearly observed and the trend of results was related to the dielectric constant values. The peak values of tan δ ranged between 2.5 and 4.5. When the NaOH concentration increased, the peak height decreased and the peak position shifted towards a higher frequency. This phenomenon was related to the denseness of structure. At high NaOH concentration, the leaching of alumina and silica was enhanced and the geopolymerization and formation of geopolymer gel increased [20] which led to a dense structure.

For the AC conductivity (Fig. 5c), the FAGP showed low conductivity in the range of 1.4×10^{-4}–5.2×10^{-4} at a low frequency as a result of electrode effect. At a high frequency, the conductivity increased with the increased frequency and NaOH concentration which was related to the increased geopolymerization. At 10^5–10^6 Hz, the AC conductivity values were 3.7×10^{-3}–1.5×10^{-2} S/cm. At a high frequency, the AC conductivity behavior follows the universal power law [35] as shown in Eq. (3).

$$\sigma(\omega) = \sigma_o + A\omega^n \tag{3}$$

where $\sigma(\omega)$ is the total conductivity, σ_0 is the DC conductivity, A is the pre-exponential factor, ω is the angular frequency, and n is the fractional exponent between 0 and 1.

The values of σ_0, A and n were obtained from Eq. (3) and shown in Table 1. The DC conductivity clearly increased with the increase in NaOH concentration which was due to the increase in geopolymerization.

4. Conclusions

Based on the results of the tests, the following conclusions can be made.

1. The NaOH concentration had significant influence on the physical and electrical properties of geopolymer paste. With an increase in NaOH concentration, the setting time and compressive strength increased resulting from a dense matrix with less unreacted fly ash in the microstructure.
2. The dielectric constant, loss and conductivity of geopolymer pastes were also affected by the NaOH concentration. At the low frequency range of 10^2–10^3 Hz, the geopolymer paste showed high dielectric constant values of 10^4–10^5. At the frequency of 10^3 Hz, all dielectric values of pastes were approximately the same at 10^4. At higher frequencies, the dielectric values decreased substantially and were related to the NaOH concentration. The decrease was less with the increases in NaOH concentration and strength of paste.
3. The relaxation peaks of tan δ of geopolymer paste ranged between 2.5 and 4.5, and were related to the dielectric constant values. When the NaOH concentration increased, the peak height decreased and the peak position shifted towards a higher frequency due to the increased denseness and strength of pastes.
4. For the AC conductivity, the geopolymer paste showed low conductivity of 1.4×10^{-4}–5.2×10^{-4}at a low frequency. At higher frequencies, the conductivity increased with the increased NaOH concentration. At 10^5–10^6 Hz, the AC conductivity values were 3.7×10^{-3}–1.5×10^{-2} S/cm. It was also found that the AC conductivity values of high calcium fly ash geopolymer pastes followed the universal power law.
5. It has been demonstrated that the physical and electrical properties of the high calcium fly ash geopolymer materials can be improved by using a suitable NaOH concentration.

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