

Polyvinyl-Alcohol-Modified Coal-Ash Mixtures for Productive Geotechnical Application

C. G. Robert^{1,a}, A. Ayob^{*1,b}, M. F. Mohammad Zaki^{1,c}, M. Z. A. Mohd Zahid^{2,d}, L. Ee Von¹

¹School of Environmental Engineering, Department of Civil Engineering, Kompleks Pengajian Jejawi 3, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia.

²Department of Civil Engineering Technology, Faculty of Engineering Technology, Universiti Malaysia Perlis, Pauh Putra, 02600 Arau, Perlis, Malaysia.

^ams.crystal_91@yahoo.com, ^b*afizah@unimap.edu.my, ^cfaizzaki@unimap.edu.my,

^dmohdzulham@unimap.edu.my

Abstract – Coal fly ash is an industrial by-product derived from coal combustion in thermal power plants. Productive reuse of these waste residuals is an essential component of the sustainable disposal and management of energy-related waste. The composition of coal-ash mixture (CAM) with different component percentages was modified with 2% of polyvinyl- alcohol (PVA), and examined in terms of pH, surface morphology, mineralogical-compound content, and engineering properties. PVA-modified CAM for all compositions exhibited high pH values within the range of 10.11–10.70. Scanning electron microscopy image exhibited agglomerated and strongly bonded PVA-modified CAM with FA (fly ash) 50-BA (bottom ash) 50 composition because of the effect of PVA that reacted with the coal ashes. Primary oxide content and the mineralogical contents of CAM did not show any significant correlation between unmodified and PVA-modified CAM samples. The insignificant shift in peak position of Si/Al-O stretches indicated electrostatic interaction between PVA and CAM based on Fourier transform infrared spectroscopy analysis. The FA content of PVA-modified CAM samples increased the gradient of stress-strain curves, which significantly improved the strength behavior of PVA-modified CAM for future applications in the geotechnical field. **Copyright** © 2015 Penerbit Akademia Baru - All rights reserved.

Keywords: Modified coal ash mixture, PVA, Strength, Geotechnical

1.0 INTRODUCTION

Coal consumption for energy production exponentially increases yearly. Coal combustion by-products are the materials produced when coal is burned to generate electricity in power plant. Consequently, the coal combustion by-products are wastes that should be disposed in an environmentally friendly way. However, most types of ash, including fly and bottom ash, are dumped in landfills because of the large quantity produced. This disposal method creates environmental, economic, and health problems [1,2]. Many factors, such as the particle size, initial concentration of trace elements, pH of extraction solution, leaching time, and solid/liquid ratio, effect the mobility of the trace elements in aqueous environment. The trace species readily leached from the dumped fly ash, thereby posing threats to the air, surface and ground water, soil and crop produce [3-5].

Recently, most aggressive efforts have been undertaken to recycle fly ash [6]. Productive utilization in bulk reduces the impact of waste disposal and causes a substantial reduction in the use of virgin material that leads to energy saving as well. In the US, about 118 million metric tons of coal combustion by-products are generated yearly, where only 44% are productively reused [7]. From this figure, fly ash, the fine particulate residual material, generates around 54 million tons. Approximately 38% of fly ash is productively recycled, predominantly as supplementary pozzolanic material in the concrete industry, making it the biggest fly ash reuse sector.

The fly ash particles are predominantly spherical in shape and consist of solid spheres, cenospheres, irregular-shaped debris, and porous unburnt carbon [5]. The partial replacement of Portland cement with fly ash reduces the heat of hydration and improves the workability and durability of the concrete. In addition to its incorporation in concrete construction, fly ash is also used in geotechnical application. Prashanth et al. (2001) [8] studied the potential of pozzolanic fly ash as a hydraulic barrier in landfill, and they concluded that fly ash possessed low shrinkage; thus, it did not crack. By contrast, bottom ash refers to the ash that is falling through the airflow to the bottom of the boiler and mechanically removed [9]. This ash does not possess the same enhanced workability. However, the chemical constituents of both two materials are very similar, with the main difference in their particle shape and size. The latter material is larger in size, irregular in shape, and contains pores and cavities [2]. Fly ash is not yet completely utilized; thus, large amount of bottom ash is still dumped. Nonetheless, recycling both the bottom ash and the fly ash in pavement and roadway construction applications has a benefit. The hydrated ash had stiffness equal to or greater than that of lime rock when used in both subgrade stabilization and base course application. Therefore, fly ash can be effectively utilized in civil engineering projects [5].

Fly ash alone cannot be used effectively in different fields of application. One of the most useful solutions to this problem is to modify fly ash with different admixtures. Many other materials, such as lime [10] and organic polymer [11], have been used as modifiers or additives. Several researchers have discussed aqueous polymer modification on polymer-soil interaction that defines the effectiveness of polymer solution in various applications [12, 13]. Meanwhile, utilizing fly ash as filler in different polymeric materials shows no binding between the polymer and individual fly ash, where the quality of the product is unsatisfactory [14]. Thus, a coal-ash mixture (CAM) is proposed to be a new material in productive geotechnical application. The spherical shape of fly ash and uneven surface of bottom ash facilitate dispersion and fluidity when modified with polymeric material. If the surface properties of fly and bottom ash can be modified in such way a new market for the utilization of CAM can be materialized. Therefore, this study reports on the characterization of CAM modified by polyvinyl alcohol (PVA) and investigates its polymeric effect on the geotechnical properties for productive application.

2.0 METHODOLOGY

CAM sample was obtained from the Jana Manjung coal power plant in Perak, Malaysia. PVA of MW=200 K that was fully hydrolyzed was purchased from MERCK and used as received. The mix proportions in percentage were denoted as BA100, FA25-BA75, FA50-BA50, FA75-BA25, and FA100 and measured by weight of the total CAM mixtures, and examined for its particle size distribution and specific gravity (G_s). pH values were determined after stirring the samples of unmodified and PVA modified CAM for 15 min to allow the pH of the slurry to stabilize. The PVA was dissolved in distilled water at 80 °C to prepare about 2.0 wt% solutions.

At 50 °C temperature, the CAM aqueous suspension containing PVA solution was stirred for 6 h by water bath shaker at 130 rpm. Thereafter, the samples were filtered with filter funnel, washed three times with distilled water, and poured into square molds of 100 mm × 100 mm × 100 mm, and left for ambient curing. After 48 h the samples were removed from the mold, wrapped in cling film, and left to cure for 14 and 28 days. The mineralogical and morphological characterizations of unmodified and PVA-modified CAM were studied through scanning electron microscope (JEOL JSM 6460 LA), X-ray fluorescence (MiniPAL 4), and FTIR (PerkimElmer Spectrum 65). For geotechnical properties, the strengths of the samples were determined through Proctor compaction and unconfined compression tests.

3.0 RESULTS AND DISCUSSION

3.1 Physiochemical characterization

3.1.1 Particle-size distribution

For particle-size distribution test, the grain size distribution is becoming well-graded with the increasing FA content (Fig. 1). The composition of fine grain is increasing from the mixtures that contain more fly ashes. Particle-size distribution of fly and bottom ash mixtures covers the range between clay to gravel, with the size ranging from 0.001 mm to 5.0 mm. The small size of spherical FA particles contributes to a better packing of the aggregate materials, which reduces porosity [15], and thus considerably improves the workability of CAM for geotechnical application.

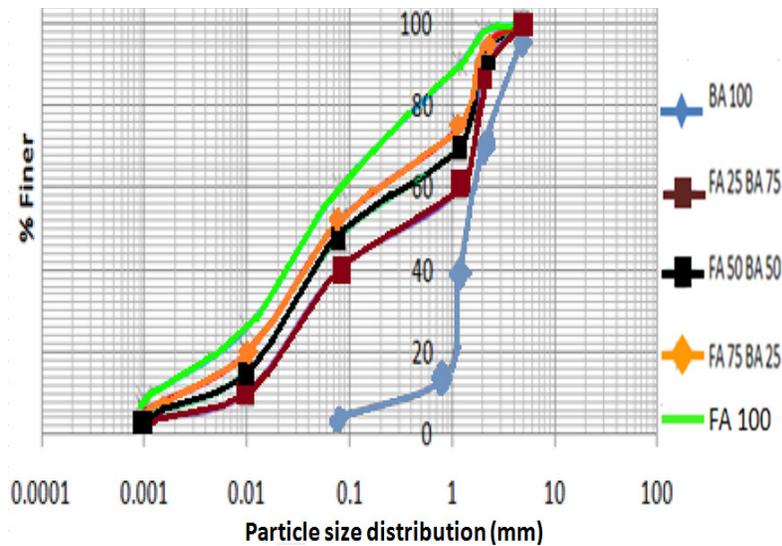


Figure 1: Particle-size distributions at different composition of FA and BA mixtures

Meanwhile, this silt-sized particle content of FA mixtures have certain advantages on the compressibility characteristics of soil. The compressibility of CAM increases with the increase of FA percentage composition [16]. The mixture that contains only BA100 can be classified as coarse-grained soil particle, which is distributed within the range of 0.08–5.0 mm.

3.1.2 Specific gravity and pH values

Table 1 shows the specific gravity (G_s) values for Jana Manjung CAM. The G_s value decreases as the FA content in the mixture increases. The range of the G_s value of fly and bottom ash mixture is between 2.10 to 2.50. However, a study from Pal and Ghosh (2010) [17] mentioned that no specific trend of relationship between particle-size distribution and G_s of FA mixture has been observed. The difference in the range of G_s value can be attributed to two factors: the chemical composition and presence of hollow FA particles or either BA particles with porous or vesicular structure [18].

Table 1: G_s and pH value of unmodified and PVA modified CAM

Composition (%)	G_s	pH value	
		Unmodified CAM	PVA modified CAM
BA100	2.50	9.20	10.60
FA25-BA75	2.42	9.28	10.11
FA50-BA50	2.32	9.41	10.42
FA75-BA25	2.21	9.60	10.53
FA100	2.10	9.80	10.70

Results show that the G_s value of BA is higher than that of FA. The composition of fly and bottom ash at different rates shows that the G_s value of the mixture depends on the grain size in mixture. The G_s value of FA is lower than that of the BA, which might be attributed to the higher contents of iron oxide and the larger BA particles.

Initially, FA consists of amorphous ferro-alumino silicate. In the coal ash composition, the aluminum, iron, and manganese oxides will sink and adsorb the trace elements. During the pH value measurement, the solubility of these oxides determined the release of elements to the solution. Both unmodified and PVA-modified CAM are alkaline, with the pH value ranging from 9.20 to 10.70 (Table 1), which is caused by the FA that contains higher free lime and alkaline oxides. The pH value of the ash-water system depends mainly on the Ca/S molar ratio in ash, although other minor alkalis or alkaline earth cations may also contribute to the balance [19-21]. Therefore, CAM application could improve the physical, chemical, and biological qualities of soils to which it is applied. This result is caused by the physicochemical properties of CAM, including silt- and clay-sized particles, low bulk density, higher water-holding capacity, favorable pH, and source of essential plant nutrients, thereby conferring it with potential soil-geotechnical application [22]. With regard to the productive geotechnical application, PVA-modified CAM is safe for use, and corrosion can be avoided even if the reinforcement bar is placed in the concrete during the construction work.

3.1.3 FTIR analysis

Figure 2 presents the comparison of FTIR spectra for various compositions of unmodified and PVA-modified CAM at 28 day curing period. The stretching vibrations of Si–O–Al bonds mainly appear within the range of 1200–400 cm^{-1} [5,25,26].

All the dominant bands are centered at 1033, 1038, 1035, 1047, and 1051 cm^{-1} ; and 472, 472, 469, 471, and 471 cm^{-1} for the vibrations of Si–O/Al–O and Si–O bonds [27] respectively, for unmodified CAM at BA100, FA25-BA75, FA50-BA50, FA75-BA25, and FA100 composition (Figs. 3b, 3d, 3f, 3h, and 3j). However, the bands within the range of 1452–1460 cm^{-1} could be due to the stretching vibrations of O–C–O, which indicates the presence of carbonates and

possible traces of calcite, whereas the bands within the range of $3419\text{--}3447\text{ cm}^{-1}$ are ascribed to bending (H–O–H) vibrations of bound water molecules for all unmodified CAM sample (Figs. 2b, 2d, 2f, 2h, and 2j) [26].

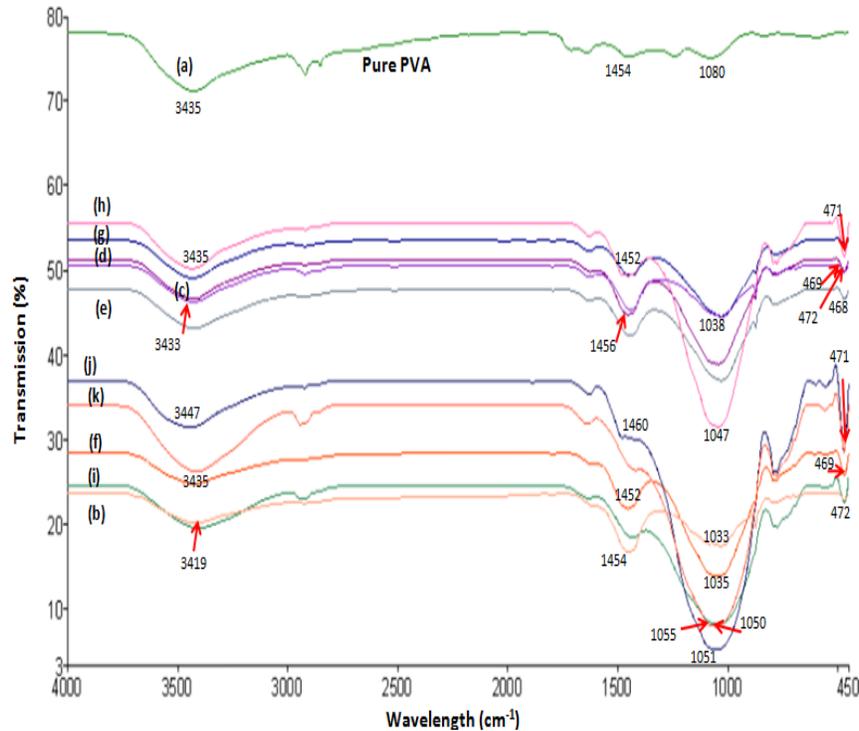


Figure 2: Comparison of FTIR spectra for various composition of (a) 2% pure PVA, unmodified CAM (b) BA100, (d) FA25 BA75, (f) FA50 BA50, (h) FA75 BA25, (j) FA100; and PVA modified CAM (c) BA100, (e) FA25 BA75, (g) FA50 BA50, (i) FA75 BA25, and (k) FA100 at 28 days curing period

Regarding the changes that occur in the PVA-modified CAM, the first observation is for the higher shifting bands of FA75-BA25 and FA100 compositions from 1047 and 1051 cm^{-1} (Figs. 2h and 2j) to wave numbers of 1050 and 1055 cm^{-1} , respectively (Figs. 2i and 2k). The other peaks shifted to slightly lower wave numbers of 1031 , 1031 , and 1032 cm^{-1} , respectively, for BA100, FA25-FA75, and FA50-BA50 composition of PVA-modified samples (Figs. 2c, 2e, and 2f). Similar to wave numbers assigned to Si–O group, the frequencies are unchanged for PVA-modified CAM of FA100 at 471 cm^{-1} (Figs. 2j and 2k). However, the wave numbers of PVA-modified CAM FA50-BA50 slightly shifted to higher frequency from 469 cm^{-1} (Fig. 2f) to 472 cm^{-1} (Fig. 2g); meanwhile, for BA100 and FA25-BA75, the wave numbers shifted to lower bands of 469 (Fig. 2c) and 468 cm^{-1} (Fig. 2e), respectively, from 472 cm^{-1} for both trends (Figs. 2b and 2d). All these shifts are significantly small, and the interaction between PVA and CAM could be attributed to electrostatic interaction.

The shifting to higher frequencies may result from the physical bonding between the Al–O/Si–O/other oxides in CAM with highly active polar group in PVA, such as –COOCH_3 group. However, the actions of physical bonding between hydroxyl (–OH group) in PVA and Al–O/Si–O/other oxides on CAM surfaces molecules shifted the band of related bonds to lower frequencies with reduction in the sharpness of peaks [25]. This phenomenon occurs under

atmospheric condition, when metal and metal oxides surfaces are well-known to be absorbed/adsorbed with –OH group or ions, thereby forming physical bonding with other substrates. The magnitude of the shift also depends on the amount of silica in the CAM. These changes could indicate the formation of a new product, an amorphous alum inosilicate (Al_2SiO_8) phase [26,28].

The –OH group has also been seen in fully hydroxylated silica powder, quartz, mullite, and glassy alumina-silicates in the PVA-modified CAM, approximately within the band of 469–472 cm^{-1} (Figs. 2c, 2e, 2g, 2i, and 2k). The –OH group present on the surface of the modified CAM has been attributed to the improved interfacial interactions with PVA chain by physical and/or chemical bonding. The distinct absorption peak at about 3403–3435 cm^{-1} for the PVA-modified CAM (Figs. 2b, 2d, 2f, 2h, and 2j) is for the –OH group due to the stretch of the hydrogen bond with OH groups. The stronger bands at these frequencies indicate a higher degree of water molecule retention in the mass of PVA-modified CAM.

3.2 Morphological characterization of PVA-modified CAM

SEM images show the morphologies of unmodified and PVA-modified CAM (Fig. 3) at 7 and 28 days of curing. SEM image shows that at BA100 composition of unmodified CAM, the particles are angular and irregular in shape, with rough and uneven surface texture for day 7 (Fig. 3a). The particle surface is also shiny, clean, and free of dust, which tends to be relatively inert due to the larger size and fused that attributes to less pozzolanic mechanism. However, as FA composition increases from 0% to 50%, the angular and irregular shapes are replaced by rounded and spherical particle shapes, respectively (Fig. 3b).

A distinct morphological difference between the two curing period is extended to particle agglomeration, which appears to be more prevalent at 28 days for the unmodified CAM at BA100, FA50-BA50, and FA100 composition, as shown in Figs. 3c, 3e, and 3g, respectively. The FA was well-rounded with thin wall, glassy spheres, and its surface appears to be very smooth. The particle morphology and size of a mixture play a vital role in the determination of its potential use in geotechnical engineering.

Meanwhile, the PVA-modified CAM is packed more closely and suggests more pozzolanic reaction, which will increase its cementing properties (Figs. 3d, 3f, and 3h). Pozzolanic reaction is important to improve the plasticity and strength characteristics of soil. Furthermore, the particles for PVA-modified CAM significantly agglomerated and strongly bonded similar to a popcorn shape because of the effect of PVA that reacted between the coal ashes. Therefore, this observation shows higher level of chemical interaction between the coal ash particles, which significantly enhances its mechanical engineering properties.

3.3 Mineralogical contents of PVA-modified CAM

Depending on the sensitivity of the measuring method, almost all known natural constituents can be detected in CAM. FA is consisted primarily of approximately 90%–99% of inorganic matter; its composition is mainly oxides of silicon, aluminum, and iron, with lesser contents of magnesium, sulfur, titanium, phosphorus, potassium, sodium, and manganese. In trace amount, a various heavy metals, such as arsenic, lead, zinc, selenium, chromium, and manganese, can also be found on coal-fired FA [7]. Table 2 shows the major element contents expressed as oxide from XRF analysis spectroscopy for unmodified and PVA-modified CAM.

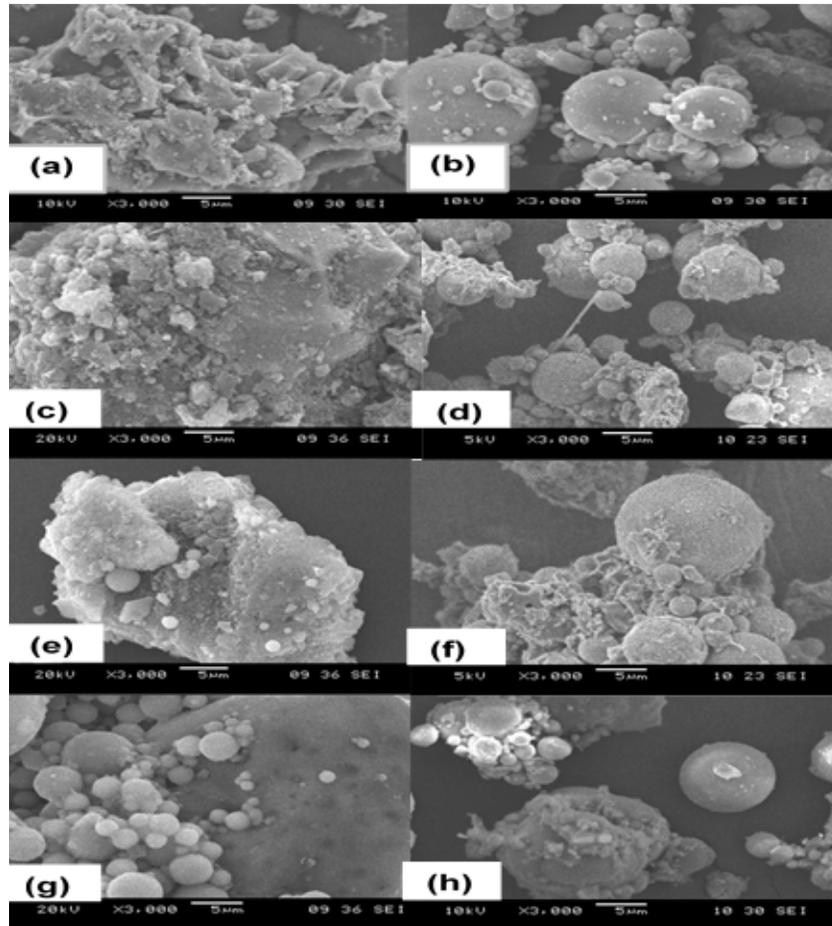


Figure 3: SEM surface morphology of unmodified CAM of (a) BA100; (b) FA50 BA50 at 7 days; for 28 days curing period of (c) unmodified BA100; (d) PVA modified BA100; (e) unmodified FA50 BA50; (f) PVA modified FA50 BA50; (g) unmodified FA100; (h) PVA modified FA100

The primary oxide content ($POC = SiO_2 + Fe_2O_3 + CaO + Al_2O_3$) is determined at 89.88% to 94.46% for both unmodified and PVA-modified CAM, where the percentages of POC did not change significantly. No apparent change in mineral phases is observed as a consequence of the modified CAM sample. Both POC and minerals of CAM samples clearly show no change in the mineralogical contents because of the modified surface.

FA is classified into two classes, namely Class C FA and Class F FA, by ASTM Standard C618-08a (2008) [23]. These classes mainly differ in the amount of calcium, silica, alumina, and iron composition in FA. The chemical properties of FA are largely dependent on the chemical constituents of the burned coal, which is influenced by the type of coal used, combustion procedure, and the collector setup [5]. This burned coal could be anthracite, bituminous or sub-bituminous coal, or lignite. In this study, the Jana Manjung fly ash has 9.41%–19.90% of lime, which can be categorized as class C of the FA that forms from lignite or sun-bituminous coal (Table 2). This type of coal is calcareous and has some distinct self-cementing characteristics [14,24]. Therefore, Class C FA possesses latent hydraulic properties in addition to its pozzolanic properties; this class can be useful for productive geotechnical application, such as soil stabilization, because it may not require lime addition.

Table 2: Mineralogical compositions of unmodified and PVA modified CAM by XRF analysis

Com.	Coal ash composition									
	BA100	BA100 with PVA	FA25 BA75	FA25 BA75 with PVA	FA50 BA50	FA50 BA50 with PVA	FA75 BA25	FA75 BA25 with PVA	FA100	FA100 with PVA
SiO ₂	33.30	32.10	39.40	38.40	40.90	39.30	45.00	43.60	47.20	47.30
Fe ₂ O ₃	26.48	28.16	23.06	24.54	21.60	24.28	18.09	20.19	16.11	16.60
CaO	19.90	20.30	16.30	17.10	15.10	15.90	12.10	11.90	9.70	9.41
Al ₂ O ₃	10.20	10.00	14.70	14.10	16.00	14.80	18.70	18.70	20.50	20.80
SO ₃	2.66	1.90	2.02	1.20	1.97	0.88	1.55	0.48	1.210	0.44
K ₂ O	1.11	1.20	1.63	1.56	1.75	1.68	1.91	2.04	2.28	2.30
TiO ₂	1.13	1.08	1.28	1.32	1.49	1.34	1.46	1.57	1.64	1.69
V ₂ O ₅	0.06	0.05	0.06	0.05	0.09	0.06	0.06	0.07	0.07	0.07
Cr ₂ O ₃	0.04	0.10	0.04	0.05	0.04	0.08	0.03	0.08	0.03	0.07
MnO	0.15	0.16	0.13	0.14	0.19	0.14	0.10	0.17	0.09	0.14
NiO	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.03	0.02	0.03
CuO	0.05	0.06	0.06	0.06	0.06	0.06	0.05	0.06	0.05	0.05
ZnO	0.19	0.29	0.13	0.17	0.11	0.15	0.07	0.08	0.03	0.07
Rb ₂ O	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.03
SrO	0.17	0.19	0.18	0.18	0.18	0.19	0.18	0.20	0.19	0.20
ZrO ₂	0.07	0.08	0.08	0.08	0.07	0.08	0.07	0.09	0.08	0.09
RuO ₂	0.38	0.46	0.33	0.38	0.29	0.36	-	0.32	0.26	0.28
Eu ₂ O ₃	0.26	0.32	0.26	0.27	-	0.29	0.19	-	0.20	-
HgO	0.05	0.05	0.04	0.04	0.04	0.04	-	-	-	-
BaO	-	0.31	0.31	0.28	-	0.29	0.25	0.31	0.25	0.30
MgO	3.70	3.00	-	-	-	-	-	-	-	-
PbO	-	0.09	0.07	0.08	0.07	0.07	0.05	0.07	0.06	0.06
Y ₂ O ₃	-	-	-	-	-	0.01	0.01	-	0.01	0.01
Re ₂ O ₇	-	-	-	-	-	-	0.04	0.04	0.03	0.03
POC	89.88	90.56	93.46	94.14	93.60	94.28	93.89	94.39	93.50	94.11

POC = primary oxide content (SiO₂ + Fe₂O₃ + CaO + Al₂O₃)

3.4 Geotechnical properties of PVA-modified CAM

3.4.1 Maximum dry density (MDD) and Optimum Moisture Content (OMC)

Figure 4 shows the MDD and OMC values among the different compositions of unmodified and PVA-modified CAM. The highest MDD value of unmodified CAM was 1.2 g/cm³ for FA50-BA50 composition. Meanwhile, for PVA-modified CAM of BA100, FA25-BA75, and FA50-BA50 composition, the MDD value are significantly increased from 1.09 g/cm³ to 1.24 g/cm³ (Fig. 4a). Therefore, the PVA-modified samples had increased the maximum dry density in most of the FA composition when compared with the unmodified samples. This result is consistent with that of Ates (2013) [13] who studied the polymer-cement stabilization effect on the unconfined compressive strength of liquefiable soils. For PVA-modified CAM of FA100 composition, the MDD value decreases from 1.18 g/cm³ to 1.10 g/cm³.

Results of the Proctor compaction test show that the OMC values of PVA-modified CAM samples increased from 17.06%, 17.30%, and 18.91%, respectively for BA100, FA25-BA75, and FA50-BA50 composition (Fig. 4a). Therefore, when the content of the BA increases in CAM, it provides a well-graded size distribution, which significantly increases in MDD (Fig. 4a). However, a reverse pattern of MDD values for PVA-modified CAM at FA75-BA25 and FA100 composition is shown in Fig. 4a. This observation could due to fly and bottom ash particle that separated into two categories when they reached a certain level of mixing.

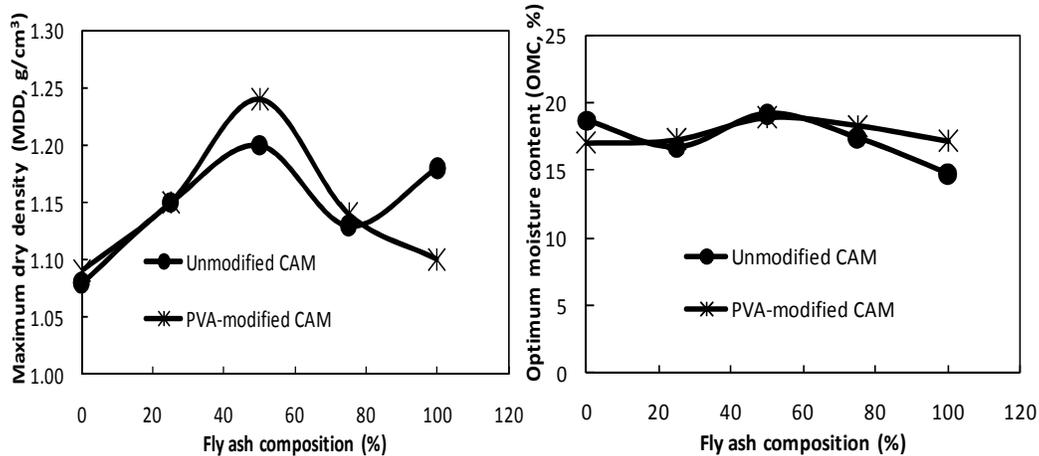


Figure 4: a) MDD; and b) OMC values for unmodified and PVA-modified CAM

Certain void between the CAM contained more water, but another part of the mixtures have smaller void filled less water, which result in lower MDD of 1.14 g/cm^3 and 1.10 g/cm^3 for FA75-BA25 and FA100 composition, respectively. This low MDD value is advantageous as a fill material for embankment in geotechnical application where the bearing capacity of bed-soil is sufficiently low [16]. Smaller ash particles within the range of $0.001\text{--}5 \text{ mm}$ give less amount of water for lubricating effect, which reduces OMC when mixed with PVA. This similar trend is consistent with that of Bhattacharyya and Pal (2013) [16] when they studied the influence of particle size on MDD and OMC values. However, for unmodified CAM of FA 100 composition, some weak, large cenosphere FA particles are crushed into finer particles during compaction, resulting in decreased air content because the fines occupy the voids between FA particles, thereby contributing to the increase in MDD value and decrease in OMC value (Figs. 4a and 4b).

The particle weight relates to the G_s value. The dry density of FA is mostly influenced by its G_s value. Generally, G_s proportionally relates to the dry density value of FA, regardless of the moisture contents and compaction energy [16]. In the present study, the BA100 has a G_s of 2.54 and MDD of 1.08 and 1.09 g/cm^3 for unmodified CAM and PVA-modified CAM, respectively, which is quite lower than the MDD value of FA100 (specific gravity, 2.22; MDD, 1.10 and 1.18 g/cm^3 for unmodified and PVA CAM, respectively; Table 1; Fig. 4b). Meanwhile, the FA50-BA50 composition at a G_s value of 2.36 contributes the highest MDD value of 1.20 and 1.24 g/cm^3 for unmodified and PVA-modified CAM, respectively. This phenomenon could be due to the equal composition of FA50-BA50, which allows the closely packed arrangement of the particles; thus, dry density level increased.

Particle structure could also affect the MDD and OMC values of CAM. Comparatively, the hollow FA particles with porous or vesicular textures have lesser MDD values than that of solid particles. The FA particles with irregular shape, holes, and crevices also resulted in the entrapped air in the sample mixture during compaction, which then could contribute to the decrease in the MDD value and increase in the OMC values in this present study. This result can be observed for the FA75-BA25 and FA100 composition (Figs. 4a and 4b). Similar trend was observed by Pal and Ghosh (2010) [17] when they concluded that particle structure affects the MDD and OMC values of Class F FA obtained from Kolaghat and Budge Budge thermal power plant.

3.4.2 Strength behaviour of PVA-modified CAM

The addition of polymer plays an important role in the development of the strength behavior of PVA-modified CAM. Results of unconfined compression strength (UCS) and undrained shear strength (USS) are summarized in Table 3, following Eq. 1.

$$S_u = q_u/2 \quad (1)$$

where q_u is the unconfined compression strength, and S_u is the undrained shear strength.

Table 3: Unconfined compression and undrained shear strength values for unmodified and PVA-modified CAM

Coal ash composition (%)	Unconfined compressive strength (kPa)	Undrained shear strength (kPa)
14 day curing		
Unmodified CAM		
BA100	-	-
FA25-BA75	14.26	7.13
FA50-BA50	14.26	7.13
FA75-BA25	15.34	7.67
FA100	13.29	6.64
PVA modified CAM		
BA100	13.16	6.58
FA25-BA75	17.46	8.73
FA50-BA50	40.37	20.19
FA75-BA25	17.46	8.73
FA100	39.85	19.93
28 days curing		
Unmodified CAM		
BA100	-	-
FA25-BA75	20.51	10.26
FA50-BA50	29.01	14.51
FA75-BA25	24.35	12.18
FA100	27.93	13.97
PVA modified CAM		
BA100	15.34	7.67
FA25-BA75	35.42	17.71
FA50-BA50	43.07	21.54
FA75-BA25	19.51	9.76
FA100	33.30	16.65

The UCS and USS values of both unmodified CAM and PVA-modified CAM for BA100, FA25-BA75, and FA75-BA25 composition increased starting from day 14 and 28 of the curing period. The highest UCS strength values recorded for PVA-modified FA50-BA50 composition significantly increases from 43.37 kPa on day 7 of curing to 43.07 kPa when curing is completed. This phenomenon is explained by the fact that PVA content resulted in enhanced bond mechanism of the FA–BA emulsion interface.

Furthermore, the adsorption mechanism of PVA emulsion will possibly bond to fine FA composition than to the BA particles. The PVA is also categorized as cationic polymer. Thus, the PVA molecules can easily form an electrostatic bond with the FA particles. The retention on FA occurs mostly through sorption of polymer molecules on both internal and external pore surfaces or microscopic interlayer spaces, which causes higher cohesion of particles in FA and

increase in UCS value [12]. The adsorption causes the PVA to change in conformation; thus, it tends to exist as random coils in solution, and uncoils and spreads out at the solid interface.

However, for the FA100 composition of PVA-modified sample, the unconfined compressive strength and undrained shear strength significantly decreased from 39.85 kPa to 33.30 kPa and 19.93 kPa to 16.65 kPa, respectively. This condition could be due to the interlocking between the FA particles created from the chemical reactions. FA particles gain higher unconfined compressive strength from the cementitious reaction or via hydrolysis process of the particles on day 7 of the curing period (Table 3).

Observing the stress–strain plots on days 7 and 28 of the curing period, the gradient of stress–strain curves significantly increases with an increased fly ash composition from 0% to 50% of the PVA-modified CAM samples (Figs. 5a and 5b).

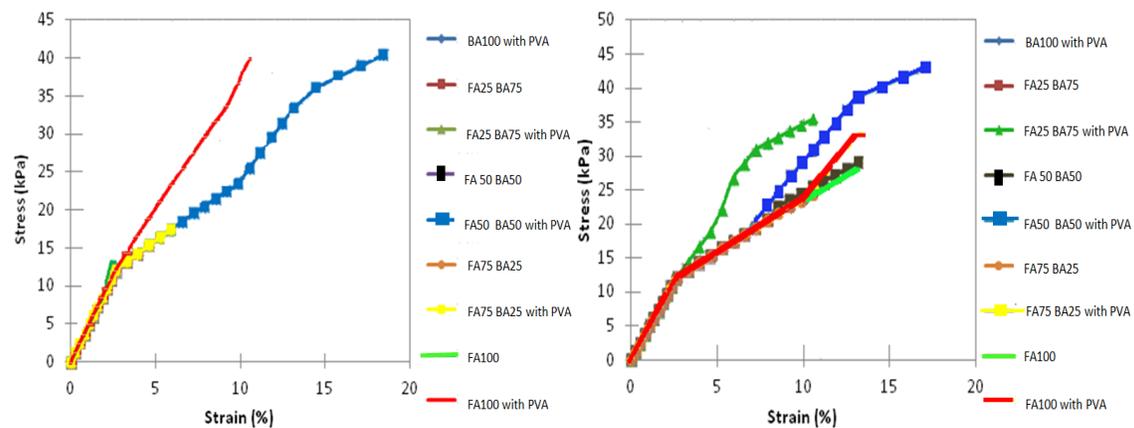


Figure 5: Stress and strain behaviour for unmodified and PVA modified CAM after (a) 14 days and (b) 28 days curing period

Meanwhile, the lowest strength observed for PVA-modified BA100 composition is 15.34 kPa, which is due to its low cohesive characteristics. This results means that with PVA addition, the modified CAM shows a better strength at the same strain level. Modification by PVA also leads to an increase in the stiffness trends for the CAM. The undrained shear strength of that particular composition is determined at 21.54 kPa. In this case, PVA binds the coal ash particles; thus, the shear strength of the polymeric-modified CAM is increased, and its geotechnical properties are enhanced for further application.

4.0 CONCLUSION

We investigated CAM, whose FA is fine and has nearly spherical particles mostly within the range of 0.001–5.0 mm; the BA is composed of coarse-grained soil particles within the range of 0.08–5.0 mm, and the G_s value is between 2.10 to 2.5. Although the chemical composition of the PVA-modified CAM investigated in this current study is not altered extensively, significant changes could be observed in its physiochemical properties. The PVA-modified CAM for all compositions exhibit higher pH values within the range of 10.11–10.70 than the unmodified samples at 9.20–9.80. SEM image shows that the PVA-modified CAM at FA50-BA50 agglomerated and strongly bonded because of the effect of PVA that reacted between the coal ashes, which significantly enhances the pozzolanic chemical reaction, and thus the

mechanical engineering properties. The possibility of interaction between CAM and PVA could be deduced from the FTIR analysis, because of the small shift in peak positions of the Si/Al–O stretch, which may be indicative of the electrostatic interactions rather than the bonding interactions between CAM and PVA. As the FA composition increases from 0% to 50% in the PVA-modified CAM samples, the gradient of stress–strain curve significantly also increases, consequently enhancing the shear strength and giving possibility for further geotechnical applications.

ACKNOWLEDGEMENT

This research was funded by Research Acculturation Grant Scheme grant no. RAGS 9018-00078.

REFERENCES

- [1] C. Alkan, M. Arslan, M. Cici, M. Kaya, M. Aksory, A study on the production of a new material from fly ash and polyethylene. *Resources Conservation Recycle* (13) (1995) 147-154.
- [2] C. Chindaprasirt, C. Jaturapitakkul, W. Chalee, U. Rattanasak, Comparative study on the characteristics of fly ash and bottom ash geopolymers. *Waste Management* (29) (2009) 539-543.
- [3] N. Saikia, S. Kato, K. Kojima, Compositions and leaching behaviors of combustion residue. *Fuel* (85) (2006) 264-271.
- [4] S.M. Nyale, C.P. Eze, R.O. Akinyeye, W.M. Gitari, S.A. Akinyemi, O.O. Faoba, L.F. Petrik, The leaching behavior and geochemical fractionation of trace elements in hydraulically disposed weathered coal fly ash. *Journal Environmental Science Health A* (49) (2014) 233-242.
- [5] Z.T. Yao, X.S. Ji, P.K. Sarker, J.H. Tang, L.Q. Ge, M.S. Xia, Y.Q. Xi, A comprehensive review on the applications of coal fly ash. *Earth-Science Review* (141) (2015) 105-121.
- [6] M. Ilic, C. Cheeseman, C. Sollars, J. Knight, Mineralogy and microstructure of sintered lignite coal fly ash. *Fuel* (78) (2003) 331-336.
- [7] N.N.N. Yeboah, C.R. Shearer, S.E. Burns, K.E. Kurtis, Characterization of biomass and high carbon content coal ash for productive reuse applications. *Fuel* (116) (2014) 438-447.
- [8] S. Prashanth, P.V. Sivapullaiah, A. Sridharan, Pozzolanic fly ash as hydraulic barrier in landfill. *Engineering Geology* (60) (2001) 245-252.
- [9] Z.T. Yao, Generation, characterization and extracting of silicon and aluminium from coal fly ash, In Saker PK (Ed). *Fly Ash Sources: Applications and Potential Environmental Impacts*. Nova Science Publishers (2013) 3-58.
- [10] D. Dermatas, X. G. Meng, Utilization of fly ash for stabilization/solidification of heavy metals contaminated soils. *Engineering Geology Issue 3-4* (70) (2003) 377-394.

- [11] S.M. Lahalih, N. Ahmed, Effect of new soil stabilizers on the compressive strength of dune sand. *Construction Building Material Issue 6-7 (12) (1998) 321-328.*
- [12] S.A. Naeini, B. Naderinia, E. Izadi, Unconfined compressive strength of clayey soils stabilized with waterborne polymer. *KSCE Journal Civil Engineering Issue 6 (16) (2012) 943-949.*
- [13] A. Ates, The effect of polymer-cement stabilization on the unconfined compressive strength of liquefiable soils. *International Journal Polymer Science (2013).*
- [14] D.C.C. Nath, S. Bandyopadhyay, A. Yu, D. Blackburn, C. White, High strength bio-composite films of poly(vinyl alcohol) reinforced with chemically modified-fly ash. *Journal Material Science, doi.1007/s10853-009-4091-6 (2009).*
- [15] S.C. Kou, C.S. Poon, A novel polymer concrete made with recycled glass aggregates, fly ash and metakolin. *Construction Building Material (41) (2013)146-151.*
- [16] A. Bhattacharyya, S.K. Pal, Compaction and consolidation characteristics of fly ash mixed with locally available soil of Tripura. *Processing Indian Geotechnical Conference (2013) 1-8.*
- [17] S.K. Pal, A. Ghosh, Influence of physical properties on engineering properties of Class F fly ash. *Indian Geotechnical Conference (2010) 361-364.*
- [18] N.S. Pandian, Fly ash characterization with reference to geotechnical application. *Journal Indian Institute Science (84) (2004)189-216.*
- [19] C.R. Ward, D. French, J. Jankowski, M. Dubikova, Z. Li, K.W. Riley, Element mobility from fresh and long-stored acidic fly ashes associated with an Australian power station. *International Coal Geology (80) (2009) 224-236.*
- [20] J.L. Kolbe, L.S. Lee, C.T. Jafvert, I.P. Murarka, Use of alkaline coal ash for reclamation of a former strip mine, *Proceedings 2011. World Coal Ash (WOCA) Conference (2011).*
- [21] X. Querol, A. Alastuey, A. Lopez-Soler, F. Plana, Synthesis of zeolite from coal fly ash: an overview. *International Journal Coal Geology (50) (2002) 412-423.*
- [22] V.C. Pandey, N. Singh, Impact of fly ash incorporation in soil systems. *Agriculture Ecosystem Environment (136) (2010) 17-27.*
- [23] ASTM Standard C618-08a. 2008. ASTM International, West Conshohocken, PA, Retrieved 10 Dec 2014, <http://www.astm.org/Standard/C618.htm>. doi:10.1520/C0618-08.
- [24] E.A. Okunade, Geotechnical properties of some coal fly ash stabilized Southwestern Nigeria lateritic soils. *Modified Applied Science Issue 4 (12) (2010) 66-73.*
- [25] D.C.C. Nath, S. Bandyopadhyay, S. Gupta, A. Yu, D. Blackburn, C. White, Surface-coated fly ash used as filler in biodegradable poly(vinyl alcohol) composite films: Part 1- The modification process. *Applied Surface Science (256) (2010) 2759-2763.*
- [26] S. Onisei, Y. Pontikes, T. Van Gerven, G.N. Angelopoulos, T. Velea, V. Predica, P. Moldovan, Synthesis of inorganic polymers using fly ash and primary lead slag. *Journal Hazard Material Issue 205-206 (2012) 101-110.*

- [27] K. Somna, C. Jaturapitakkul, P. Kajitvicyanukul, P. Chindaprasirt, NaOH-activated ground fly ash geopolymer cured at ambient temperature. *Fuel* (90) (2011) 2118-2124.
- [28] A. Fernandez-Jimenez, A. Palomo, Mid-infrared spectroscopic studies of alkali-activated fly ash structure. *Microporous Mesoporous Material* (86) (2005) 207-214.