Studies on the modification of fly ash structure with alkaline pre-treatment as a green composite flame retardant filler

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Abstract. A green composite made up of renewable and recyclable materials has become one of the advanced material’s attractive topics. The smooth fly ash surface used in the green composite for flame retardancy enhancement are hard to bind with hydrophobic polymer. Thus, the surface modification of this filler is needed to increase its surface roughness and pore size to be more compatible with its polymer matrix. In this research study, the alkaline pre-treatment of fly ash has been performed by using sodium hydroxide solution (NaOH) with various concentrations (5 w/w%, 10 w/w%, 15 w/w%, 20 w/w%). For pore size and morphological of the filler’s evaluation, few analyses such as Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), Barret-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) pore size and volume analysis were conducted. Treated fly ash with 20 w/w% sodium hydroxide concentration gives the better morphological structure in terms of pore diameter, volume, area and high composition of aluminium, silicon with lower calcium and sulphur contents compared to others. Hence, the potential of the physiochemical properties of the green composite produced by using this modified filler will be improved as the adhesiveness of the filler with its matrix increased.

1. Introduction
As for thermal stability enhancement, the flame retardants (FRs) will be used as it gives a significant impact on suppressing flame to prevent fire spread. Flame retardants have been used in a wide range of applications such as in the manufacturing process [1]. Fly ash is an example of an inorganic material which is suitable to be used as a filler flame retardant material in bio-composite. Fly ash is a waste generated by electric power plant through the coal combustion process. In this process, the pulverized solid fuels consist of combustible organic matter with different composition of minerals will be consumed [2–8].

Around 1.5 billion tonnes of fly ash have been produced worldwide and the percentage of fly ash utilization is approximately 40% [3]. According to [4], the estimated fly ash generated for every year is approximately 600 million tonnes and only 110 million tonnes in India. However, the huge amount of non-utilized fly ash waste is classified as a hazardous material and becomes a serious issue towards the environmental problem if the fly ashes are directly dumped as a landfill material [3,8]. The fly ash waste will also cause air and water pollution containing dust [9]. Thus, utilizing the fly ash in a good way will bring more benefits as nowadays many researchers are interested in exploring the high filler application in polymeric materials to enhance its thermal stability and any useful applications [2,3].
The presence of –OH group in fly ash’s surface will enhance the compatibility between the inorganic material and polymer substrate as the functional group of -OH becomes the active sites for functional chain polymer structure to be bonded chemically [1,8]. The addition of fly ash is one of the effective additives for flame retardancy to improve the efficiency of the composite [1]. There is also a study conducted by (Porąbka et al. 2015) regarding the fly ash that is used as a reinforcement filler for low-density polyethylene [9]. The research on nanostructured fly ash as a flame retardancy enhancement for polyvinyl chloride (PVC) is also reported by (Patil et al. 2016) [6]. In addition, the fly ash is reported to be used as a flame retardant to enhance the flame retardancy of several polymers such as polycarbonate, polyvinyl chloride, epoxy resins, epoxy, polypropylene blends, rigid polyurethane foam (RPUF) synergetic with ammonium phosphate (APP) and pentaerythritol (PER) is also reported by (Dong et al. 2015)[3]. The modification of low-density polyethylene by adding fly ash is a suitable and effective solution [9]. Therefore, in this research study, the fly ash treated with various concentration of an alkaline solution (NaOH) (5,10,15 and 20 wt/wt%) with a ratio of fly ash/NaOH 1:1.2 for fly ash activation [5] have been performed to study the morphological structure, pore diameter, area and volume of the fly ash produced.

2. Experimental

2.1. Materials
The fly ash was collected from Jimah power station located at Port Dickson, Negeri Sembilan, Malaysia. Sodium hydroxide, pallets for analysis was purchased from Emsure.

2.2. Methods
2.2.1. Treated Fly Ash (Alkaline pre-treatment). The raw fly ash will be treated by using NaOH solution within the range concentration of 5 to 20% (by weight). The fly ash will be immersed in NaOH solution at room temperature and stirred for approximately 30 minutes with the speed of 750 rpm by using FAVORITE Stirring Hotplate (HS0707V2). The ratio of fly ash to sodium hydroxide used is 1:1.2 (for fly ash activation). Then, the fly ash will be filtered by using a vacuum pump and dried at oven by using a temperature of 115°C for 5 hours.

2.3. Characterization process for the structural of fly ash
Characterization process by using Scanning Electron Microscopy – Energy Dispersive X-Ray (SEM-EDX) (Cambridge S200, microscope), Brunauer-Emmett-teller (BET) and Barret-Joyner-Halenda (BJH) (TrisStat 3000 analyzer) analysis were conducted to determine the best the morphological structure, pore diameter, area and volume distribution of the fly ash.

3. Results and discussion

3.1. Structural surface of untreated and treated fly ash by using Scanning Electron Analysis (SEM)
The surface morphology of raw/untreated fly ash in figure 1 (a) shows the smooth surface which leads to difficulty for a binding process with the polymer substrate. Thus, modifying the raw fly ash surface with alkaline treatment will eventually increase the roughness and forming an active group of the surface to increase the adhesiveness of the fly ash with its polymer substrate [1,2].

As shown in figure 1 (b), (c), (d) and (e), the morphological surface of the treated fly ash by using sodium hydroxide with various concentration which is 5, 10, 15 and 20 (wt/wt%) seems to be rougher and smaller compared with raw or untreated fly ash. This research work is aligned with (Anh et al. 2019; Nguyen et al. 2019), according to them, the rougher and smaller particle size presented on the treated fly ash surface is due to the abrasive condition during the treatment process [1,2]. This reaction of sodium hydroxide with oxide of fly ash makes the surface of fly ash cracked and aluminium silicate formed. Besides, according to (Mukherjee & Borthakur, 2004), the dissolution of sulphate and other
water-soluble components in the fly ash sample is one of the reasons for fly ash size reduction with alkaline treatment [10]. The alkaline solution will react with the alumina and silica presented in the fly ash hence forming the soluble silicate and aluminates compounds. The simple reactions of the fly ash with sodium hydroxide described by (Mukherjee & Borthakur, 2004) are as equations (1) and (2) below [10]. The sodium silicate and aluminium silicate are indeed formed during the alkaline treatment of fly ash by using sodium hydroxide solution [1,2,10]. A high concentration of sodium hydroxide used will form a formation of hydroxysodalite as described in equation (3) [10].

\[ SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \]  
\[ Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \]  
\[ Na_2(SiO_3)_6 + 2[Na_2(AlO_2)_3] + 2(NaOH) + 2(H_2O) \rightarrow Na_8[AlSiO_4]_6(OH)_2 + 2(H_2O) \]  

Based on the structural surface of the fly ash in figure 1, the treated fly ash with 20 wt/wt% of sodium hydroxide gives the best images compared to untreated fly ash and treated fly ash with various concentration of sodium hydroxide 5, 10 and 15 (wt/wt%) in term of having more smaller particles and even agglomeration of the particles in the fly ash. The smallest particles detected on the treated fly ash with 20 wt/wt% of sodium hydroxide surface by using Scanning Electron Analysis (SEM) is between 1.0 to 1.4 µm. Similar morphology of the treated fly ash with alkaline treatment is also found in (Yang, Gai, Cai, & Chen, 2006) research work [11]. As the concentration of sodium hydroxide used increased, the amount of silicate and aluminate will also be increased and resulted in producing aluminosilicates and hydroxysodalite [10,12]. The treated fly ash is also expected to have a better adhesive process with the polymer substrate when the fly ash is used as a filler for the polypropylene polymer matrix [11]. Therefore, having a rougher surface and smaller particles with even agglomeration such as a structural image of treated fly ash with 20 wt/wt% of sodium hydroxide will be more compatible with its polymer matrix.
3.2. Element quantification of fly ash by using Energy Dispersive X-ray analysis (EDX)

Figure 2 shows the electron images for the element quantification by using Energy Dispersive X-Ray (EDX) method. The list of elements quantities such as carbon, oxygen, sodium, magnesium, aluminium, silicon, potassium, phosphorus, sulphur, calcium, titanium, iron and platinum presented in the fly ash is tabulated in table 1. The platinum detected in both untreated fly ash and treated fly ash due to the coating method for SEM analysis purposed. Hence, the quantity of platinum detected for both samples can be neglected.

Figure 1. Surface morphology by SEM by 3.0kx magnification scale for (a) Untreated fly ash (b) Treated 5wt/wt% NaOH (c) Treated 10wt/wt% NaOH (d) Treated 15wt/wt% NaOH (e) Treated 20wt/wt% NaOH.

Figure 2. Electron images for Energy Dispersive X-Ray (EDX) quantification (a) Untreated fly ash (b) Treated 20wt/wt% NaOH region A (c) Treated 20wt/wt% NaOH region B.
### Table 1. Weight percentages of elements detected on untreated fly ash and treated fly ash with 20 wt/wt% of sodium hydroxide.

| Element     | Carbon (wt/wt%) | Oxygen (wt/wt%) | Sodium (wt/wt%) | Magnesium (wt/wt%) | Aluminium (wt/wt%) | Silicon (wt/wt%) | Potassium (wt/wt%) |
|-------------|-----------------|-----------------|-----------------|-------------------|-------------------|-----------------|-------------------|
| for untreated fly ash | 9.315           | 39.197          | -               | 0.261             | 1.525             | 4.689           | -                 |
| for treated fly ash with 20 wt/wt% NaOH (region A) | 3.547           | 51.351          | 1.063           | 0.314             | 5.588             | 26.041          | 1.410             |
| for treated fly ash with 20 wt/wt% NaOH (region B) | 3.124           | 55.537          | 3.716           | 0.972             | 5.848             | 14.974          | 0.330             |

| Element     | Phosphorus (wt/wt%) | Sulphur (wt/wt%) | Calcium (wt/wt%) | Titanium (wt/wt%) | Iron (wt/wt%) | Platinum (wt/wt%) |
|-------------|---------------------|-----------------|-----------------|-----------------|--------------|-------------------|
| for untreated fly ash | 10.250             | 0.819           | 25.670          | -               | 2.460        | 5.814             |
| for treated fly ash with 20 wt/wt% NaOH (region A) | -                   | -               | 0.570           | 0.721           | 2.129        | 7.265             |
| for treated fly ash with 20 wt/wt% NaOH (region B) | -                   | -               | 5.882           | 0.472           | 5.196        | 3.949             |
Based on the elements presented in table 1 above, the carbon, oxygen, sodium, magnesium, aluminium, silicon, potassium, phosphorus, sulphur, calcium, titanium, iron elements are detected in the fly ash composition. However, the most important elements to be discussed for flame retardancy enhancement filler are silicon and aluminium. The treated fly ash with 20 wt/wt% of NaOH gives the highest silicon and aluminium contents in the fly ash. It is perhaps due to the effect of the alkaline treatment conducted to change the morphological surface of the fly ash. Based on the equation (1) and (2), the aluminosilicate is formed after performing the alkalinisation process by using sodium hydroxide for the fly ash. Excessive sodium hydroxide concentration will make the hydroxysodalite being formed too as described in equation (3) [1,2,10]. Hence, this formation makes the aluminium and silicon content increased for treated fly ash with 20 wt/wt% NaOH. According to (Provis & Deventer, 2002), the best flame retardance filler should be contained with the high composition of aluminosilicate [13]. Furthermore, having the high content of silicon in the polypropylene polymer will reduce the heat release, burning rate and mass loss rate as measured by using nitrogen gasification devices and increase the polymer melt viscosity [14]. Thus, based on the result obtained, the treated fly ash with 20 wt/wt% NaOH gives the best silicon and aluminium composition to act as a flame retardant filler for green composite.

In addition, the treated fly ash with 20 wt/wt% NaOH also gives the lowest value of calcium content compared with the untreated fly ash. According to (Provis & Deventer, 2002), the low calcium content of the fly ash is suitable to be used as a flame retardance filler [13]. Having lower calcium content is more preferable as the high calcium content will make difficulties in the polymerisation process [15]. Low calcium content in the fly ash will also be a good trait for the fly ash to resist the acid attack [15]. Hence, based on the result obtained, the treated fly ash with 20 wt/wt% NaOH gives the best calcium content composition for the better flame retardancy enhancement filler for the composite.

As for the content of sulphur, the sulphur content for treated fly ash with 20 wt/wt% NaOH is not detected in that specific region. The alkaline treatment by using sodium hydroxide has made the sulphur content in the fly ash is being removed. The desulphurization process is increased with an increase in the concentration of the alkaline solution [10]. The sulphur content is good for water and acid resistance but it will not perform well when the fire contact is involved [16]. Thus, zero content of the sulphur element is important for the flame retardance filler. Also, the exposure of sulphur dioxide will cause severe injuries including respiration, irritation, inflammation and eyes burning injuries [17]. Although, the sulphur content for untreated fly ash is less than 1% and might not give a significant impact on the environment. However, having zero content of sulphur in the flame retardant filler is better to prevent environmental pollution. Based on the result obtained, the treated fly ash with 20 wt/wt% NaOH seems suitable to be used as a flame retardancy filler for composite.

3.3. The pore size distribution of untreated fly ash and treated fly ash with 20 wt/wt% filler as NaOH with BJH Analysis

The comparison data for untreated and treated fly ash with 20wt/wt% NaOH data for the particle size distribution including the pore diameter, area and volume by using BJH Analysis is illustrated in figure 3 below. Based on that figure, the range of pore diameter of untreated and treated fly ash with 20 wt/wt% NaOH are between 1.7142 to 177.1200 nm. The overall pattern for both types of fly ash shows that the pore volume keeps decreasing with increment in pore size diameter. The pore volume of untreated fly ash is higher in the range of 1.7142 to 2.6116 nm compared to treated fly ash with 20 wt/wt% NaOH. The depth of the pore for untreated fly ash is deeper compared to treated fly ash in the range of 1.7142 to 2.6116 nm.

The BJH model that has been developed by Barret-Joyer-Halenda in 1951 is based on the Kelvin equation and multilayer adsorption. This method is widely used to calculate the pore size distribution within the mesoporous and microporous range [18]. Hence, the pore volume is determined by using the BJH method is by the multilayer of N2 gas filling inside the pore. Thus, the N2 gas filled up inside the pore indicates the pore depth. However, for the pore volume for the particle diameter size of fly
ash between 3.3274 to 177.1200 nm, the pore volume of treated fly ash with 20 wt/wt% NaOH has a higher volume compared to untreated fly ash. This data shows that the pore size diameter for treated fly ash with 20 wt/wt% NaOH is deeper compared to untreated fly ash.

As for the pore area perspective, the overall pattern for both types of fly ash shows that the pore area is kept decreasing with increasing pore size diameter. The pore area for untreated fly ash is higher compared to treated fly ash in the range of 1.7142 to 12.4934 nm. However, the pore area for the treated fly ash is relatively higher compared to untreated fly ash in a range pore diameter of 14.2805 to 177.1200 nm.

In short, based on the results obtained for the pore volume, area and diameter for both types of the pore. The untreated fly ash will have bowl shape pore meanwhile the treated fly ash is needle shape type for diameter pore size of 1.7142 to 12.4934 nm and 14.2805 to 177.1200 nm. The images of the pore for both types of fly ash are illustrated in figure 4 (a), (b), (c) and (d) based on the pore volume, area and diameter data obtained in the BJH Analysis.

Therefore, based on the overall data pattern, the treated fly ash with 20 wt/wt% NaOH has a better structural image in terms of the pore size distribution, volume and also area compared to untreated fly ash. The pore area of the larger particle size of treated fly ash is larger compared to untreated fly ash. Thus, treated fly ash with sodium hydroxide indeed improved the structural image for the fly ash to get better adhesiveness with its polymer matrix.

![Figure 3](image-url)

**Figure 3.** The distribution comparison of pore volume, pore diameter and pore area of untreated and treated fly ash with 20 wt/wt% of NaOH.
Figure 4. Illustrated image for untreated fly ash for pore diameter of (a) 1.7142 to 12.4934 nm, (b) 14.2805 to 177.1200 nm. Illustrated image for treated fly ash with 20 wt/wt% NaOH for pore diameter of (c) 1.7142 to 12.4934 nm, (d) 14.2805 to 177.1200 nm.

3.4. The specific surface area of untreated and treated fly ash by using BET Analysis

| Sample                    | Specific surface area (m²/g) |
|---------------------------|-----------------------------|
| Untreated fly ash         | 7.0331                      |
| Treated 20wt/wt% NaOH     | 1.0181                      |

Based on the data tabulated in table 2 above, the specific surface area of untreated fly ash is larger compared to treated 20 wt/wt% of fly ash with NaOH. The treated fly ash with 20 wt/wt% NaOH is having a small BET specific surface area perhaps due to an increase of hydroxysodalite crystallinity. According to (Astuti, Wahyuni, Prasetya, & Bendiyasa, 2012), the small pore size of hydroxysodalite will cover the treated fly ash particle partially including the amorphous component [19]. This statement is related to the relationship of the pore diameter of the fly ash particle with its specific surface area. Increasing hydroxysodalite particles will decrease the specific surface area of the fly ash [19]. The increasing in hydroxysodalite particle will be a good influence in the compressive strength of the geopolymer composite [20]. The optimal thermo-mechanical properties will also be achieved in a high amount of hydroxysodalite produced [13]. Therefore, using treated fly ash with 20 wt/wt% NaOH as a flame retardant filler for a composite might give a good result in thermal and mechanical properties as small BET specific surface area is influenced by the hydroxysodalite component.

4. Conclusion

In a conclusion, the treated fly ash with 20 wt/wt% NaOH gives a better structural and morphological image in terms of pore diameter, volume, area and composition compared to untreated fly ash. The pore area for the large pore diameter size of the particles in treated fly ash is higher compared to untreated fly ash. Having a high pore area at a large particle size of the fly ash will be benefited to enhance the compatibility of filler with its polymeric matrix. In addition, the high composition of the aluminium, silicon and low calcium and sulphur contents in the treated fly ash also gives the positive traits for better flame retardancy enhancement filler with its composite.

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