INTRODUCTION

Textiles, decorative materials, and diversity of designs are widely used in buildings and residential interiors, which are susceptibility to flame and rapid spread of flames causing many fires leading to considerable loss of life and destructions of human life and buildings,\(^1,^2\) The upholstered furniture is a major threat for the initiation of fire,\(^3\) To slow or stop the spread of fire to reduce the fire intensity, textiles, decorative materials, and diversity of designs containing flame retardants are necessary to reduce the fire damage.\(^4,^5\) There are two kinds of fire retardants including char-forming fire retardants, such as inorganic acid, carbon-rich polymeric material, blowing agent, TiO\(_2\), SnO\(_2\), and gas phase flame retardants having halogen and phosphorus compounds, which have gas phase chemical mechanism and reduce the heat by scavenging free radicals.

Incorporation of aluminum hydroxide to the polymer makes four quantifiable contributions for fire retardancy including the heat capacity of the aluminum hydroxide prior to decomposition (9%), the decomposition endotherm (55%), the heat capacity of the decomposed aluminum hydroxide residue (13%), and the heat capacity of the water vapor in the flame layer (13%).\(^6\) Aluminum hydroxide is the most widely used fire retardant.\(^7\) However, high loading up to 65 wt.% causes negative impact to mechanical properties. Therefore, it is necessary to develop low loadings of aluminum hydroxide for better performance of the fire retardant. In this research, various amounts of AlCl\(_3\) were attached to uniform size of silica spheres and were converted to polyaluminum hydroxide by hydrolysis and condensation reactions. The resulting materials were analyzed with field emission scanning electron microscope (FESEM) images, Fourier transform infrared spectra (FTIR), and energy dispersive X-ray spectrum (EDS).
Ammonium hydroxide (28%), 3-mercaptopropyltrimethoxysilane (MPTMS, 95%), tetraethyl orthosilicate (TEOS, 98%), 2-propanol (99%), and AlCl₃ (99.99%) were purchased from Sigma Aldrich Co. Ltd and were used without further purification. Ammonium hydroxide (100 ml) and 2-propanol (100 ml) were charged in a 250 ml of round bottom flask. The TEOS (3.0 g) was added to the flask with vigorous stirring. Finally, the MPTMS was added to modify the surface of the spheres. The synthesized spheres were separated using centrifugal separator and washed with 2-propanol several times. Various amounts (40, 60, 80, and 100 mg) of AlCl₃ and 100 mg of silica spheres were added to deionized water, which was called as AlOH-40, AlOH-60, AlOH-80, and AlOH-100, respectively. The aqueous KOH solution (1:1 molar ratio between AlCl₃ and KOH) was slowly added to the AlOH-40, AlOH-60, AlOH-80, and AlOH-100 solutions with stirring at room temperature and ambient condition. Excess amount of KOH was added to the solution to hydrolyze the reacted Si–O–AlCl₂. The synthesized spheres and polyaluminum hydroxide (PAH) were separated by centrifuge and washed several times with methanol and water. The FTIR spectrum of the spheres-PAH was obtained with Nicolet iS5 FTIR spectrometer. FESEM images and EDS spectrum of the spheres-PAH were obtained with JEOL ISM-7401F field emission scanning electron microscope with the acceleration voltage of 5 and 15 kV, respectively.

Fire-safe polymers are the polymers that are resistant to degradation at high temperature, which need for fire-resistant polymers in the enclosed spaces including boats, skyscrapers, and airplane cabins. Until recent years, the majority of flame retardants have been halogen-containing compounds that releases volatile halogen radicals, which scavenges hydrogen radicals during the fire to produce non-flammable hydrogen halide gas to interrupt the flame cycle with the following reaction:

$$\text{X}^* + \text{RH} \rightarrow \text{HX} + \text{R}^*$$

where the RH represents the combustible gas or volatile part of the polymer during the thermal degradation. The halogen species act as a high efficiency of flame inhibition. Although halogen compounds slow down the flame spread and reduce the fire growth, they increase the release of toxic gases, such as CO and HX (hydrogen halide), are carcinogenic and toxic chemicals, and accumulate environment, which are more concern for protection of environment. Non-flammable filler incorporation to the polymer will reduce the flammability due
to the reduction of total amount of fuel and oxygen diffusion rate. Metal hydroxides including Al(OH)₃ and Mg(OH)₂ reduce heat and smoke during fire by releasing water at similar temperature compared with the decomposition temperature of the host polymers. The Al(OH)₃ is especially important due to its endothermical decomposition to form aluminum oxide with the following equation.

\[
2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}
\]  

Figure 1 shows synthetic processes of polyaluminum hydroxide on the surface of uniform size silica spheres. Initially, the AlCl₃ could be attached on the surface of the spheres with the Si–O–AlCl₂, which would be further proceeded hydrolysis and condensation reaction as shown in Figure 1.

Figure 2a–d show the FESEM images of synthesized silica spheres with 40, 60, 80, and 100 mg of AlCl₃, respectively. The amount of polyaluminum hydroxide increased with increasing the amount of AlCl₃ as shown in figures. The diameters of the spheres and polyaluminum hydroxides were approximately 400 nm and a few tens nanometers, respectively. Some polyaluminum hydroxide particles are on the surface of silica spheres and the others seem to be individually separated, which can be advantages when this material mixes with polymer having polar structure, such as polymethylmethacrylate, poly(ethylene naphthalate), poly(butylene terephthalate), and polycarbonate.

The FTIR spectrum of pure silica spheres is reported. Figure 3 shows the FTIR spectrum for pure silica spheres. The absorption peaks at 1,634, 1,094, and
836 cm\(^{-1}\) represent vibration mode of surface free water molecules, Si–O–Si stretching vibration mode, and Si–O stretching vibration mode, respectively. The strong and broad absorption peak at 3,400 cm\(^{-1}\) is due to the characteristic –OH stretching vibration mode. The absorption peak at 1,462 cm\(^{-1}\) represents the –CH deformation mode, and the FTIR absorption peak at 949 cm\(^{-1}\) causes by Si–O–C stretching vibration mode, which indicate possible existence of Si–O–CH\(_3\). Many researchers reported the FTIR spectrum for Si–O–Al and Al–OH.\(^{[13–16]}\) The broad –OH absorption peak at 3,400 cm\(^{-1}\) became two absorption peaks at 3,470 and 3,424 cm\(^{-1}\) representing Al–OH and Si–OH, respectively. Small absorption peaks at 1,462 and 3,424 cm\(^{-1}\) are attributed by Al–OH. The Si–O–C and free water absorption peaks reduced with increasing the amount of AlCl\(_3\). The –CH deformation mode completely disappeared for all four samples.

Figure 4 shows EDS spectrum for the sphere-PAH, which is comprised of oxygen 58.36, 5.10, 33.48, 2.39, 0.39, and 1.29 wt.% of aluminum, silicon, sulfur, chlorine, and potassium, respectively. The silicon is from silica spheres, and oxygen is from silica spheres and Al–OH. The existence of sulfur indicates the modification of sphere surface with MPTMS. The potassium is from the catalyst (KOH). There is small amount of chlorine, which indicates that most of the AlCl\(_3\) are hydrolyzed.

### FIGURE 4
Energy dispersive X-ray spectrum of SiO\(_2\)-polyaluminum hydroxide

Non-flammable filler incorporation to the polymer will reduce the flammability due to the reduction of total amount of fuel and oxygen diffusion rate. Metal hydroxides including Al(OH)\(_3\) and Mg(OH)\(_2\) reduce heat and smoke during fire by releasing water at similar temperature compared with the decomposition temperature of the host polymers. The Al(OH)\(_3\) is especially important due to its endothermic decomposition to form aluminum oxide. The surfaces of silica spheres were modified with aluminum hydroxide for application on fire safety. Various amounts of aluminum hydroxide were attached to the surface of silica spheres by hydrolysis and condensation reactions with KOH catalyst.

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## REFERENCES


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