

Synthesis and Characterization of New Eco-Friendly Fire-Retardants Based on Soda-Silicate Glass

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Fire-retardants (FRs) are additives used to improve the fire-resistance of combustible materials. New generations of FRs must be effective and eco-friendly. Traditional inorganic FRs are non-hazardous but have limited fire-retardancy. Here, we aim to develop an innovative way to enhance the fire-retardancy of inorganic FRs. We synthesized a new type of FRs, called mATH, whose compositions are similar to soda-silicate glass ($x\text{Na}_2\text{O}\cdot y\text{K}_2\text{O}\cdot z\text{SiO}_2\cdot t\text{Al}_2\text{O}_3$). When applied to unsaturated polyester resin, mATH showed a much better performance than traditional aluminum trihydroxide (ATH). The better performance of mATH originated from its new working mechanism. Dehydrated mATH, as a soda-silicate glass, melts under the heat of the fire, which causes heat sink and produces a molten glass. The molten glass forms a charred insulating layer that prevents oxygen from contacting the interior combustible materials. This phenomenon significantly contributes to the fire-retarding behavior of mATH. Our findings open a new method for developing effective eco-friendly FRs.

Keywords: Charred layer, Fire-retardant, Fireproof, Flame-retardant, Green Fire-Retardant

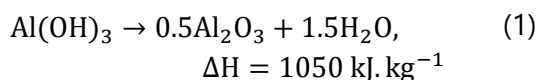
INTRODUCTION

Polymer materials have a wide range of applications. They have outstanding advantages, such as high strength, lightweight, and molding ease (Rothon 1995). However, flammability is their inherent drawback. Using additives, called fire-retardants (FRs), is a key measure to enhance polymers' fire-resistance. FRs delay the ignition and propagation of the

flame when the materials are exposed to an ignition source (Weil et al. 2015). FRs are categorized into halogenated, organophosphorus, nitrogenous, and inorganic groups (Pearce et al. 1975, Alaei et al. 2003, Haile et al. 2016). These substances retard fires through several working mechanisms (or modes of action), including heat sink due to endothermic decomposition, dilution of flammable elements by non-flammable gases (e.g.,

water vapor), the capture of free radicals, or formation of an charred insulating membrane (Pearce et al. 1975, Levan 1984). A given FR may act through a single or combined mode(s) of action depending on its chemistry (Holder et al. 2017). For example, halogenated FRs effectively capture free radicals. They work through the radicals-capturing mechanism (Levan 1984, Rakotomalala et al. 2010). In contrast, inorganic FRs such as metal hydroxides operate through a combination of heat sink and dilution of oxidant gases, thanks to their endothermic dehydration and the resulting water vapor, respectively.

Aluminum trihydroxide (ATH) is an inorganic FR of particular interest. It is the largest-consumed FR today (Weil et al. 2009, Elbasuney 2017). The prominent advantage of ATH is that it is eco-friendly and cost-effective. However, ATH has limited capability of fire-retardancy since its performance relies solely on the dehydration process. Under the heat of fires, ATH starts to decompose at temperatures from 180 to 220°C following Reaction (1) (Elbasuney 2017).



When every kilogram of ATH decomposes, it adsorbs 1050 kJ heat and releases 0.346 kg of water vapor. The absorption of heat cools down the burning surfaces. The release of water vapor dilutes combustible elements. These effects are responsible for the fire-retarding behavior of ATH as well as other metal hydroxides. The quantities of heat sink and water vapor emissions are limited due to the

stoichiometry of dehydration reaction(s), which set upper limits for the functionality of inorganic FRs. Hence, improving the performance of inorganic FRs is highly demanded (Nine et al. 2005, Weil et al. 2009, Oualha et al. 2017, Cheng et al. 2019, Fredi et al. 2019).

To improve the performance of inorganic FRs, one must alter their working mechanisms. New generations of inorganic FRs must work via new mechanisms in addition to dehydration reactions. It was found that forming a charred insulating layer offers a feasible approach to better fire-retarding behaviors. Such a layer acts as a barrier of heat and mass transfer that stops the fire's development (Zhang et al. 2005, Chen et al. 2017, Laoutid et al. 2017, Chen et al. 2018, Phan et al. 2019). However, to have such functionality, the charred layer has to be dense and insulating, to shield the interior combustible matters from contacting atmospheric oxygen. Such properties of charred layers are not attained naturally since charred layers, in reality, are porous and fragile (Zhang et al. 2005).

Here, we report an innovative way to improve the resistance of the charred layers. We synthesized a new type of inorganic FRs, called mATH. By tuning the compositions into the soda-silicate glass, the FRs could be produced that could be melted into the molten glass under the fire's heat. Not only does the fusion of FRs cause a heat sink, but also the molten glass forms a dense charred layer that plays an essential role in retarding the fire. The mATH showed a much better performance compared to traditional ATH. Our findings open a new route for developing effective

eco-friendly inorganic FRs based on the formation of dense charred layers.

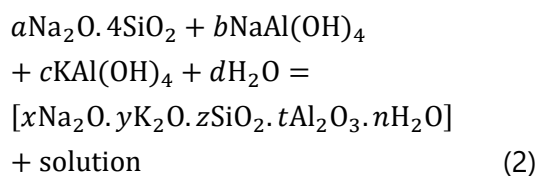
MATERIALS AND METHODS

Materials

Materials used in this work include sodium metasilicate ($\text{Na}_2\text{SiO}_3 \geq 98\%$, Merck), hydrochloric acid (37%, Merck), aluminum trihydroxide ($\geq 98\%$, Merck), sulphuric acid (97%, Merck), sodium aluminate (Merck), potassium hydroxide ($\geq 85\%$, Merck), sodium hydroxide (99%, Merck), and unsaturated polyester resin (industrial grade).

Synthesis of Fire-Retardants

A solution of $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$, called liquid glass, was prepared through the treatment of commercial sodium metasilicate (see Supporting Information). FRs were synthesized as follows. Firstly, the desired amount of liquid glass was added to a solution containing $\text{KAl}(\text{OH})_4$ and $\text{NaAl}(\text{OH})_4$. The mixing was undertaken under the desired temperature and stirring conditions by using a hot plate magnetic stirrer. A white precipitate was formed in the solution, following Equation (2).



Reaction (2) is proposed in reference to the literature (Matar et al. 1989). The mixed oxides in the square bracket are a precipitate. Exceeded amounts of reactants remained in the solution. The mole ratios of reactants, expressed in a , b , c , and d , are

shown in Table 1. These sets of a , b , c and d were selected based on screening experiments, then varied the compositions of reactants and tested the fire-retarding behaviors of the respective additives.

Table 1. Conditions of synthesis of mATH

Samples	T, °C	Mole ratios			
		Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃
ATH	-	-	-	-	-
mATH1	60	2	0	4	1
mATH2	60	1.75	0	3	1
mATH3	60	1.5	0	2	1
mATH4	25	2	0	4	1
mATH5	25	1.75	0	3	1
mATH6	25	1.5	0	2	1
mATH7	60	3.5	1	2	4
mATH8	60	1	1	4	1
mATH9	25	1	1	4	1
mATH10	25	3.5	1	2	4

For each set of a , b , c and d , the precipitate was filtered and washed with deionized water until neutral pH was achieved in the filtrate (tested using pH paper). The obtained solid was dried at 70°C for 10 hours in an electric dryer in an air environment. Finally, the dried solid was ground and sieved into a fine powder (sized at around 80µm) and was stored in sealed plastic bags for subsequent uses. This fire-retardant was called mATH. Traditional aluminum trihydroxide (ATH) was also dried and ground similarly and used as a referencing sample.

Characterization of Fire-Retardants

Thermal properties of mATH and ATH were analyzed by using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) carried out on Labsys Evo S60/58988 instrument (Setaram, France) at

a heating rate of 10°C/min in an air environment. Chemical compositions of mATH were evaluated by using energy-dispersive X-ray spectroscopy (EDS). Morphology of the charred layer after combustion was studied using scanning electron microscopy (SEM). Both EDS and SEM were recorded on the S4800 instrument (Hitachi, Japan).

Fire-Retardant Test

Each sample in Table 1 was mixed with unsaturated polyester (PE) resin at the desired dosages. The resulting material was molded into a bar shape, dimensions 100×20×1.2 (mm³).

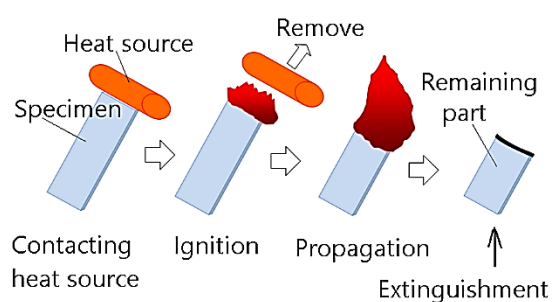


Fig. 1: The illustration of fire-retardant test

Each specimen was placed into a combustion chamber of COD 000-945 equipment. One end of the bar was fixed to a sample holder. The other end was brought into contact with an ignition source, i.e., an electrically heating rod having a temperature of around 1500°C (Fig. 1). When the flame occurred, the ignition source was removed. The fire propagated laterally along the bar. We measured the ignition delay and the lateral spreading rate (or lateral burning rate) of the flame along the bar. The ignition delay was defined as a period between the point

of time when the specimen contacted the ignition source and the point of time when a flame occurred.

RESULTS AND DISCUSSIONS

Properties of mATH and ATH

Figure 2 shows an EDS result for mATH10, for an example. It is shown that the sample contained oxygen, sodium, aluminum, silicon, and potassium. This observed composition is consistent with the precipitate's desired formula ($x\text{Na}_2\text{O}\cdot y\text{K}_2\text{O}\cdot z\text{SiO}_2\cdot t\text{Al}_2\text{O}_3\cdot n\text{H}_2\text{O}$) in Reaction (2).

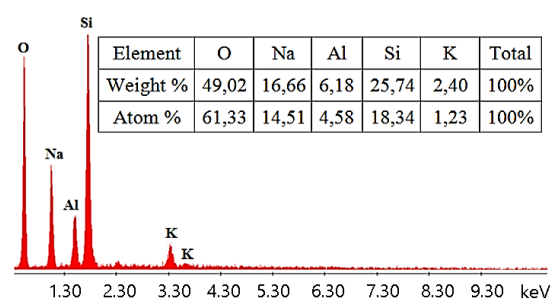


Fig. 2: EDS result of mATH10. It confirms that mATH has a composition of $x\text{Na}_2\text{O}\cdot y\text{K}_2\text{O}\cdot z\text{SiO}_2\cdot t\text{Al}_2\text{O}_3\cdot n\text{H}_2\text{O}$.

Fire-retarding behaviors of mATH and ATH were evaluated through TGA-DSC. As a reference, a TG-DSC diagram of ATH is shown in Figure 3. A total mass loss of 34.52% associated with three endothermic events respectively at 237.2, 313.7, and 523.4°C is assigned to the decomposition of $\text{Al}(\text{OH})_3$. The mass loss (34.52%) indicates the net content of bound water in ATH. This value agrees with a stoichiometric value of 34.61% as calculated from Reaction (1). No further thermogravimetric effect is observed for ATH at temperatures between 700 and 1000°C. This observation is

expected since the product of decomposition (i.e., Al_2O_3) has a melting point at 2072°C (Patnaik 2003). The heat sink due to endothermic decomposition, and the released water vapor give rise to the fire-retarding behavior of ATH.

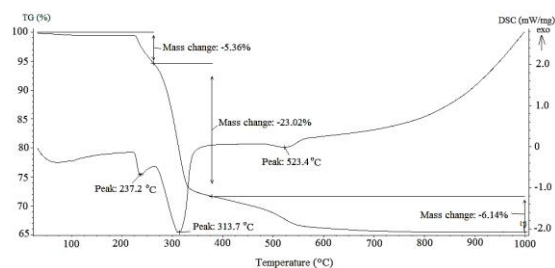


Fig. 3: TG-DSC diagram of ATH. The dehydration of ATH upon heating occurs at temperatures between ambient and 700°C . No further thermal effect is observed at temperatures between 700 and 1000°C .

The TG-DSC diagram of mATH10 is shown in Figure 4 for an example. Several endothermic events associated with a total mass loss of 23.74% are observed in the temperature range between ambient and 600°C . These effects can be assigned to the dehydration of mATH10. However, the TG-DSC diagram of mATH10 differs largely from that of ATH by the following features. First, the total mass loss (23.74%) in this case is smaller than that (34.52%) of ATH. Therefore, mATH10 has a lower content of bound water. Second, the dehydration of mATH10 occurred mostly at temperatures below 200°C . Thus, mATH10 mainly contains physical water. Only a small portion (6.14%) of mass loss occurred at temperatures beyond 200°C , reflecting the fraction of chemical water (i.e., hydroxides). An outstanding behavior of mATH10 is a significant endothermic effect at 788.7°C that does not associate with any mass

changes. We attribute this effect to the fusion of the dehydration product of mATH10, i.e., soda-silicate glass. To confirm the fusion of mATH10, we placed ATH and mATH10 concurrently in a furnace and heated them at 900°C for 30 minutes. For ATH, we observed discrete white particles as a residual, i.e., Al_2O_3 . For mATH10, we observed a glass-like solid (Fig. 5). The glass-like solid has a smooth and dense surface. Combinations of TG-DSC and heating experiments confirm the fusion of mATH10 into the molten glass at 788.7°C .

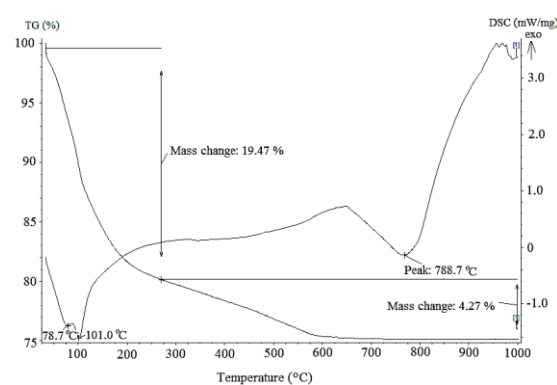


Fig. 4: TG-DSC diagram of mATH10. The dehydration occurs under 600°C . The fusion of the residual occurs at 788.7°C .

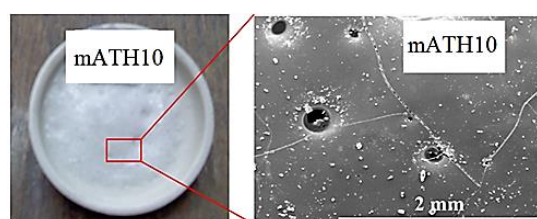


Fig. 5: The glass-like residual of mATH10 after being heated at 900°C for 30 minutes. This result together with the TG-DSC diagram, confirms the fusion of mATH10 at 788.7°C .

Using a similar procedure, we determined the mass loss and the fusion temperature of other mATH samples (Table

2). For all mATH samples, the mass loss is smaller than that of ATH. Therefore, the decomposition of mATH produces less amount of water vapor. In addition, mATH samples that contain two alkaline oxides (i.e., mATH7 – mATH10) have greater water contents than mATH samples that contain only Na₂O. Importantly, all of the mATH samples were melted at temperatures below 900°C. The melting temperature decreases further in the samples that had both Na₂O and K₂O. These measured melting temperatures agree with the low melting points of soda-silicate glasses (Martienssen et al. 2005, Ashby 2013, Karazi et al. 2017).

Table 2. Mass loss and melting against heating the sample to 900°C

Samples	Mass loss (%)	Melting upon heating to 900°C	Melting point (°C)
ATH	34.52	No	-
mATH1	16.03	Yes	893
mATH2	17.07	Yes	867
mATH3	17.37	Yes	866
mATH4	17.43	Yes	854
mATH5	18.47	Yes	853
mATH6	19.76	Yes	823
mATH7	23.04	Yes	780
mATH8	22.73	Yes	767
mATH9	20.58	Yes	766
mATH10	23.74	Yes	789

Fire-Retarding Performance of mATH

Fire-retarding behaviors of the samples in Table 2 were screened by evaluation experiments. Test specimens were prepared through the procedure described in the Method section. Each specimen contained

30 wt.% of mATH and 70 wt.% of PE resin. Figure 6a shows the ignition delay recorded for different FRs used. Pure PE resin started to burn after about 0.5 (s) contacting the ignition source. When ATH was added at 30 wt.%, the ignition was delayed to 2.1 (s). All specimens added with mATH delayed the ignition to more extended periods, ranging from 2.9 to 5.0 (s). Mainly, mATH10 showed the most extended ignition delay, namely, 5.0 (s).

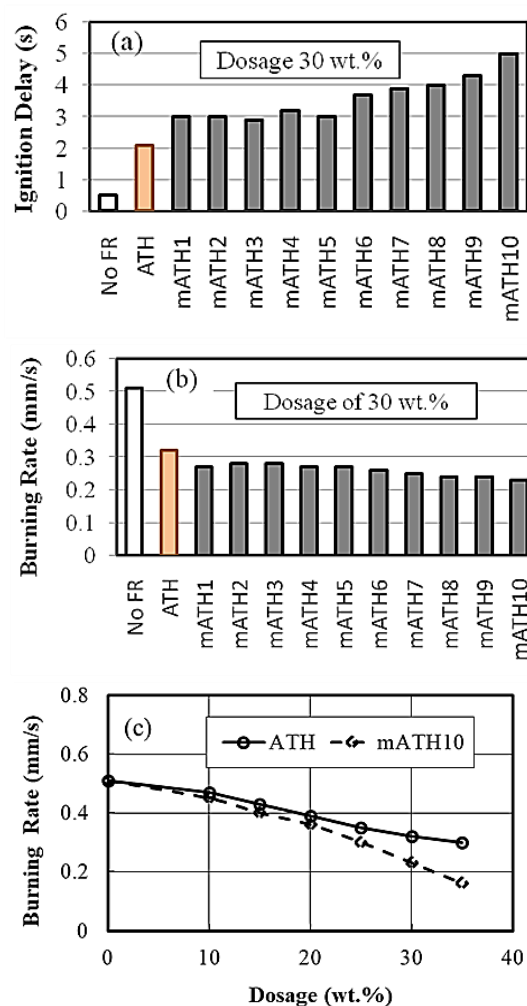


Fig. 6: Ignition delay (a) and lateral burning rate (b) for mATH samples compared to traditional ATH. (c): Lateral burning rate of mATH10 at different dosages compared to ATH. The mATH samples show much better fire-retardancy in comparison with ATH.

The lateral burning rate is presented in Figure 6b. The pure PE resin burnt steadily with a rate of 0.51 mm/s, and then the rate is reduced to 0.32 mm/s in the ATH-containing specimen. All mATH-containing specimens exhibit slower-burning rates, between 0.23 and 0.28 mm/s, demonstrating a better fire-retarding behavior of mATH in comparison with ATH. The lowest burning rate (0.23 mm/s) is especially attained for mATH10, showing a 28 percent reduction compared to the case of ATH. Therefore, mATH10 was chosen for further investigations.

Figure 6c shows the effects of the dosage on the fire-retarding behavior of mATH10 and ATH. Both mATH and ATH show enhanced performances with increasing dosages. However, mATH10 always exhibits a better performance than ATH. At 35 wt.%, the burning rate of the mATH-added specimen is as low as half of that of the ATH-added specimen. These results demonstrate that mATH additives, particularly mATH10, have much better fire-retarding behaviors over traditional ATH.

Working Mechanisms of mATH

Traditional inorganic FRs such as ATH and MH (magnesium hydroxide) retard fires through two main action modes (Hornsby et al. 1990). First, their endothermic dehydration causes heat-sink effects, lowering the temperature of the fire. Second, the dehydrations release water vapor that dilutes the oxygen and combustible elements (Hornsby et al. 1990). Certainly, these mechanisms also work for mATH since endothermic dehydration is clearly observed in TG-DSC measurements (Fig. 4 and Table 2).

However, mATH additives have outstanding performances over ATH, although the water content in mATH is smaller than that in ATH (Table 2). These observations indicate that another mechanism must govern the fire-retardancy of mATH.

Previous studies have indicated that dense charred layer formation contributes an important mode of action for fire-retardancy (Zhang et al. 2005, Chen et al. 2017, Laoutid et al. 2017, Chen et al. 2018). The dense charred layer acts as a barrier of heat and mass transfer. It hinders the contact between oxygen and the interior combustible materials, leading to the fire's self-extinguishment (Chen et al. 2018). However, such a shielding membrane is usually not attained in traditional inorganic FRs since charred layers are porous and fragile (Zhang et al. 2005). Consequently, significant efforts have been paid to seek synergists that can improve the charred layers' strength and denseness. Various synergists such as nano-clays, fumed silica, and graphene sheets have been used as nano-filters to enhance charred layers' resistance (Zhang et al. 2005, Chen et al. 2017, Laoutid et al. 2017, Chen et al. 2018).

The key feature of this present work is that by tuning the dry composition of mATH into a soda-silicate glass ($x\text{Na}_2\text{O}\cdot y\text{K}_2\text{O}\cdot z\text{SiO}_2\cdot t\text{Al}_2\text{O}_3$), which can lower down its melting temperature significantly. Under the heat of the fire, the residual oxide mixture is fused into molten glass. The fusion of mATH has two pronounced effects on its fire-retardancy. First, the fusion absorbs a noticeable amount of heat, indicated by an endothermic peak in the DSC diagram (Fig. 4). Second, the

molten glass acts as a glue that binds the chars into a non-combustible dense membrane that functions as a barrier of heat and mass transfer. Such a membrane is observed from the charred layer on the specimen (Fig. 7). Hence, we conclude that synthetic mATH additives have combined modes of action, those include (1) heat sink due to dehydration and fusion, (2) dilution of oxidant gases by water vapor, and (3) formation of dense charred layer thanks to the molten glass.

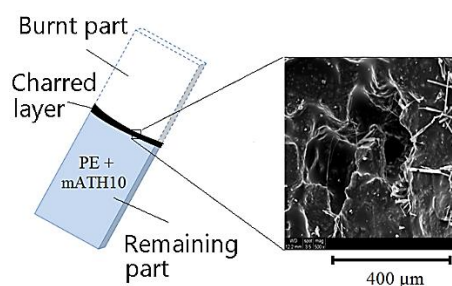


Fig. 7: SEM image of a charred layer on a specimen (PE resin added with 30wt.% mATH10). This is a dense layer covering the combustible material and preventing oxygen from penetrating into the combustion zone.

Economic Feasibility of mATH

At this beginning stage, the synthesis and characterizations of mATH were carried out based on laboratory-scale experiments. Therefore, we may not have sufficient data to make a thorough assessment of the economic feasibility of mATH. Even though, the mATH additives were prepared from common inorganic materials based on classical chemical routes. In addition, mATH is more efficient than traditional ATH (Fig. 6c). For example, a dosage of 25 wt.% of mATH10 has a fire-retarding performance equivalent to 35 wt.% ATH. Therefore,

mATH is potentially economically feasible. However, further studies would be needed for a more systematic assessment.

CONCLUSIONS

This present work is synthesized and characterized a new type of inorganic FRs based on soda-silicate glass. The synthetic FRs, mATH, showed a significantly improved fire-retarding behavior in comparison with traditional ATH. We indicated that the improved performance of mATH additives originated from their new working mechanisms. By tuning the composition of mATH into a soda-silicate glass, it can be lowering down their melting temperatures to below 900°C. Thus, the dehydrated mATH is melted under the fire's heat and forms a dense non-flammable layer. This layer acts as a barrier to mass and heat transfer, which retards the fire. Our work offers an innovative way to produce eco-friendly inorganic FRs. Further investigations are needed to gain insights into the precipitation reactions, i.e., Reaction (2) and assess the economic feasibility of mATH.

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