

Synthesis and Characterisation of Unsaturated Polyester Resin /Aluminium Hydroxide/Magnesium Hydroxide Fire Retardant Composite

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Aluminium hydroxide ($\text{Al}(\text{OH})_3$) and Magnesium hydroxide ($\text{Mg}(\text{OH})_2$) can be used as the alternative for fire retardant additive which can improve the fire retardancy without giving the bad effect on health. In this research, the synthesis of fire retardant UPR based composite has been conducted by varying the concentration of $\text{Al}(\text{OH})_3/\text{Mg}(\text{OH})_2$ additive. Fire retardancy was observed by using UL-94V standard. The thermal degradation behaviour of composite was studied by thermal gravimetric (TG) and differential scanning calorimetry (DSC) analysis while the mechanical properties were observed from tensile strength and hardness testing. The best fire retardancy was obtained from the composite with concentration of $\text{Al}(\text{OH})_3$ 40 %/ $\text{Mg}(\text{OH})_2$ 10 % and resulted V-0 flammability rating. Combination of $\text{Al}(\text{OH})_3$ 40 %/ $\text{Mg}(\text{OH})_2$ 10 % could improve the thermal stability of composite by reducing the mass loss rate (MLR) to 4.9 %/min and total mass loss to 77 %, while the tensile strength decreased to 64 % and the hardness improved to 64.5 %. The morphology and mapping of composite showed that $\text{Al}(\text{OH})_3$ additive was well-dispersed, while $\text{Mg}(\text{OH})_2$ had the tendency to agglomerate.

1. Introduction

Unsaturated polyester resin (UPR) has a wide variety of application in the transportation sector (Deli and Kandola, 2013), manufacturing of water pipe, chemical container, offshore application, construction, and the paint industry (Pereira et al., 2009). UPR, like the other polymer material, has limitation in fire retardancy. UPR releases volatile gas that trigger the fire ignition when it is thermally degraded (Isao and Shinichi, 2003). Halogen additive can improve the composite's fire retardancy but nowadays, the use of halogen additive has been minimised due to the release of halogen radical and halide acid which are harmful to the human health during burning (Gerard et al., 2010).

Alternative materials which are more environmental friendly and can be used as replacement for halogen additive are magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and aluminium trihydroxide ($\text{Al}(\text{OH})_3$). Both materials are known to be able to improve the fire retardancy of the composite material through decomposition mechanism that produce water vapour, absorb the heat, and form protective layer in the material surface (Rakotomalala et al., 2010). $\text{Mg}(\text{OH})_2$ in composite is used as filler, fire retardant, and is able to minimise the production of smoke (Liang and Zhang, 2010). $\text{Al}(\text{OH})_3$ basically has the same decomposition mechanism with $\text{Mg}(\text{OH})_2$ but occurs in lower temperature and more water vapour is produced (Rakotomalala et al., 2010).

In this study, the synthesis of fire retardant is conducted by using $\text{Al}(\text{OH})_3/\text{Mg}(\text{OH})_2$ additive. The combination of both additives will enable the composite to have double protection. $\text{Al}(\text{OH})_3$ will start to decompose first at 200 °C, while $\text{Mg}(\text{OH})_2$ will begin to decompose at higher temperature (Nikolaeva and Karki, 2011). $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ concentration are varied in order to discover the effect of the combination of additive concentration to the fire retardancy of the composite. The effect of various concentration of additive are compared for the thermal stability, mechanical properties, morphology, and mapping of composite to obtain the concentration of $\text{Al}(\text{OH})_3/\text{Mg}(\text{OH})_2$ additive that gives a good fire retardancy, thermal stability, and mechanical properties to the composite.

2. Experimental

2.1 Materials

Materials used in this study were unsaturated polyester resin with Everpol 323 AR brand containing 0.3 wt% cobalt accelerator from PT. Arindo Pacific Chemicals, methyl ethyl keton peroxide (MEKP) from PT. Arindo Pacific Chemicals as catalyst, aluminium hydroxide (Merck) and magnesium hydroxide (Sigma Aldrich) as additive.

2.2 Synthesis of Neat Resin

As a reference for comparison, neat resin was made by mixing the resin and 1 wt% MEKP catalyst which was then stirred. After that, this mixture was kept for a while to allow the trapped air to be removed from the mixture before pouring into the mould and left for curing for 12 h under room temperature.

2.3 Synthesis of Resin/Additive Composite

The composite was prepared using the procedure described by Tang et al. (2013). Resin/additive composite was made by mixing the additive and resin which was then stirred for an hour. After that, 1 % MEKP catalyst was added and stirred until homogenous. This mixture is then poured into the mould and let it cured for 12 h in room temperature. After 12 h, the composite was put into the oven in 60 °C for 12 h for post curing. The variation of additive used in wt% for Al(OH)₃/Mg(OH)₂ respectively was 0 : 50, 10 : 40, 20 : 30, 30 : 20, 40 : 10, and 50 : 0.

Table 1: Composition of Composite Resin/Additive

No.	Code	Resin (wt%)	Al(OH) ₃ (wt%)	Mg(OH) ₂ (wt%)
1	A1	50	-	50
2	A2	50	10	40
3	A3	50	20	30
4	A4	50	30	20
5	A5	50	40	10
6	A6	50	50	-

2.4 Flammability Test

Flammability test was performed based on the UL-94V standard procedure which resulted in three levels of flammability rating: V-0, V-1, V-2 and NR (non-rated) for the specimen that was completely burned. From this test, some parameters could be obtained, such as time to ignition (t_i), time taken to retard the fire (t_r), and burning time (t_b).

2.5 Thermal Stability Test

Thermal stability test was performed by using Thermal Gravimetry Analysis (TGA). The result of TGA was a graph that showed the temperature when the mass of material started to decrease (T_{onset}), the mass loss rate (%/min), and the maximum temperature (T_{max}) when the mass loss rate reached its highest point. In this study, TGA was performed with a heating rate of 10 °C /min until the temperature reached 800 °C in the inert gas atmospheric condition.

2.6 Mechanical Strength Test

In this study, the mechanical strength was observed by characterising the tensile strength and hardness of the composite. In the tensile strength test, the composite was characterised based on ASTM D638. The hardness test was conducted by using Barcol Hardness Impressor type GYZJ 934-1 based on ASTM D2582.

2.7 Composite Morphology and Mapping

Scanning Electron Microscope-Energy Dispersion X-ray (SEM-EDX) was used to observe the composite morphology and mapping. The morphology of composite was needed to discover the distribution of additive in the composite while the mapping of composite was used to study the formation of protective layer after the composite was burned.

3. Results and Discussion

3.1 Effect of Additive Al(OH)₃/Mg(OH)₂ to The Fire Retardancy of Composite

The measured parameters as fire retardancy in this study were time to ignition (t_i), burning time (t_b), time to retard the fire (t_r), and flammability rating. The result was shown in Table 2.

Table 2. Flammability Test Based on UL-94V for Resin/Additive Composite

No.	Code	Time to ignition, t_i (s)	Burning time, t_b (s)	Time taken to retard the fire, t_r (s)	Rating
1.	A0	10.0	125.4	-	NR
2.	A1	14.0	161.8	-	NR
3.	A2	20.0	182.4	-	NR
4.	A3	24.0	41.6	6.8	V-1
5.	A4	27.5	191.0	31.5	NR
6.	A5	22.5	7.8	6.2	V-0
7.	A6	25.0	112.0	34.5	V-1

The flammability data for neat resin was set as a standard that would be compared with other compositions. It could be seen that the addition of additive increased the time to ignition of material. Hapuarachchi and Peijs (2009) observed that the endothermic decomposition reaction caused by the increase in temperature of hydroxide fire retardant additive could release water vapour and absorb heat so that the decomposition process becomes slower. It was observed that t_i increased as the concentration of $\text{Al}(\text{OH})_3$ increased and $\text{Mg}(\text{OH})_2$ decreased. The lowest t_r was obtained from the composite with an additive concentration of $\text{Al}(\text{OH})_3$ 40 % and $\text{Mg}(\text{OH})_2$ 10 % (code A5) where the fire could be retarded in 6.2 s. The high loading of $\text{Mg}(\text{OH})_2$ tend to increase the viscosity of mixture that caused the dispersion of additive particles became not homogenous, which influenced the fire retardancy. For the specimen that was burned (NR rating), the parameter compared was the burning time (t_b) because the increase in t_b could be used as an indicator of the increasing in the fire resistance of material. The burning time increased due to the increase in $\text{Al}(\text{OH})_3$ and the decrease in $\text{Mg}(\text{OH})_2$ concentration. The result showed that additive $\text{Al}(\text{OH})_3$ gave a better effect to the material than the additive $\text{Mg}(\text{OH})_2$ due to the difference in dispersion effect caused by those additives.

The flammability rating obtained for each specimen could be seen in Figure 1. The highest flammability rating V-0 was obtained for composite with additive concentration of $\text{Al}(\text{OH})_3$ 40 %/ $\text{Mg}(\text{OH})_2$ 10 % (code A5) because the concentration of $\text{Mg}(\text{OH})_2$ was relatively low, which made the additive particle to be distributed more homogenously compared with other composition. When the material was burned, $\text{Al}(\text{OH})_3$ would be endothermically decomposed at temperature 200 °C by absorbing a heat of 298 kJ/mol, releasing around 1.5 time more water vapour than $\text{Mg}(\text{OH})_2$. $\text{Mg}(\text{OH})_2$ could absorb more heat when it was decomposed but its decomposition occurred in temperature 300 °C, which was higher than the decomposition temperature of $\text{Al}(\text{OH})_3$ (Tang et al., 2013). Due to this condition, the polymer resin might have been burned first before the material reached the decomposition temperature of $\text{Mg}(\text{OH})_2$. The uses of combination additives gave better result than the flammability rating of composite with single additive. Figure 1 showed that the composite with code A5 showed higher flammability rating compared with the report made by Devendra and Rangaswamy (2012) and local product, while it had similar flammability rating with the report by Vasanthakumari (2007), but it could be said that the composite code A5 had some advantages because it used less and is a safer material.

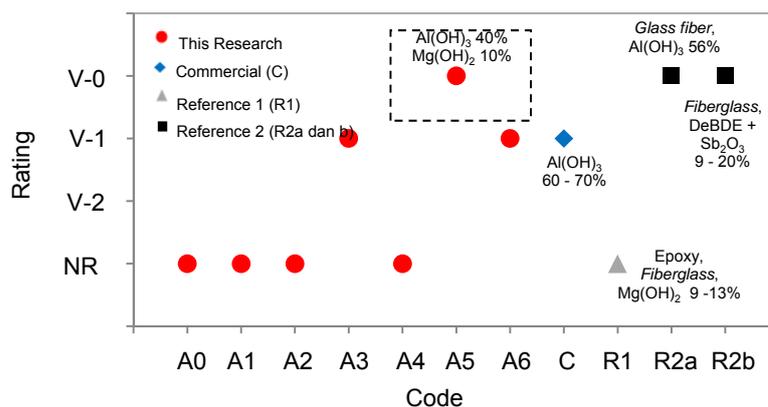


Figure 1: Flammability Rating for Composite Resin/Additive from This Study Compared to the Reference

3.2 Effect of Additive $\text{Al}(\text{OH})_3/\text{Mg}(\text{OH})_2$ to The Thermal Stability of Composite

The detail result for thermal stability test for all composition could be seen in Table 3. 5 wt% onset temperature was the temperature where the mass loss reached 5 % while the maximum temperature was the temperature where the mass loss rate reached its maximum point.

Table 3. Comparison of Thermal Stability Test Result

No.	Code	$T_{\text{onset 5 \% wt}} (\text{°C})$	$T_{\text{max}} (\text{°C})$	MLR (%/min)	Total Mass Loss (%)
1.	A0	285.1	389.4	11.6	100.0
2.	A1	238.6	419.5	7.9	71.9
3.	A2	287.6	409.4	6.0	65.5
4.	A3	289.8	410.6	5.9	66.5
5.	A4	288.8	405.8	6.1	71.1
6.	A5	268.8	394.0	4.9	77.0
7.	A6	269.0	409.2	5.4	71.7

Table 3 showed that the decomposition process of neat resin (A0) started on 285 °C with a maximum temperature of 389 °C where the MLR reached its maximum at 11.6 %/min. Total mass loss of neat resin was 100 %, showing that the resin was completely lost after the increase in temperature. The decomposition temperature for other compositions did not have linear trend and slightly increased for some compositions. The increasing of maximum temperature, MLR and decreasing of total mass loss for all compositions showed that the additive addition was able to increase the thermal stability of composite. The addition of additive had the positive effect on the decomposition of composite by the thermal dehydroxylation of $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ which reduced the MLR and total mass loss of composite. The best fire retardancy composite (code A5) was then thermally compared with the neat resin (code A0) and was presented in Figure 2.

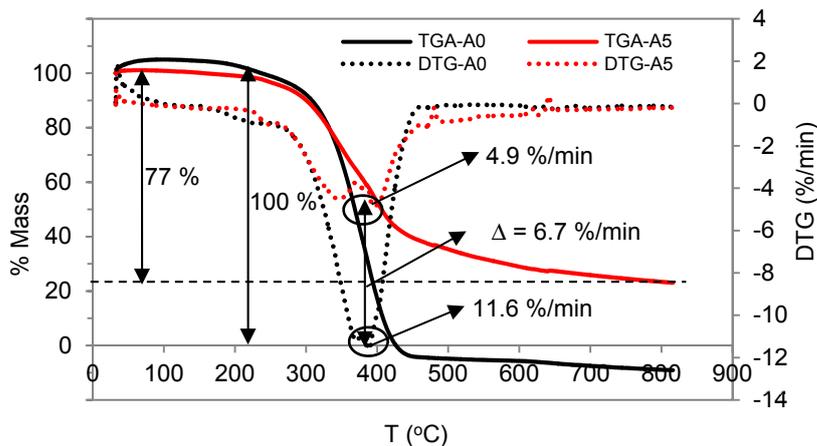


Figure 2. TGA and DTG Graph for Neat Resin (A0) and Resin/Additive Composite (A5)

Compared with neat resin, the addition of additive $\text{Al}(\text{OH})_3$ 40 %/ $\text{Mg}(\text{OH})_2$ 10 % could significantly reduced the total mass loss from 100 % to 77 %, and MLR from 11.6 %/min to 4.9 %/min. The endothermic decomposition of both additives released water vapour and absorbed the heat which led to the increasing of thermal stability of composite.

3.3 Effect of Additive $\text{Al}(\text{OH})_3/\text{Mg}(\text{OH})_2$ to The Mechanical Strength of Composite

The tensile strength and hardness test were performed for the neat resin and resin/additive composite with the best fire retardancy (code A5), shown in Figure 3. Compared with the neat resin, the addition of $\text{Al}(\text{OH})_3$ 40 % and $\text{Mg}(\text{OH})_2$ 10 % resulted in the decrease of tensile strength from 50 MPa to 18.2 MPa, decreasing about 64 %. Devendra and Rangaswamy (2013) observed that the increase of additive concentration could reduce the strength of interfacial bond between additive and matrix which resulted in the decrease of mechanical properties of material. The low interfacial bonding could cause the composite to have the tendency to break when the composite was drawn during the tensile test.

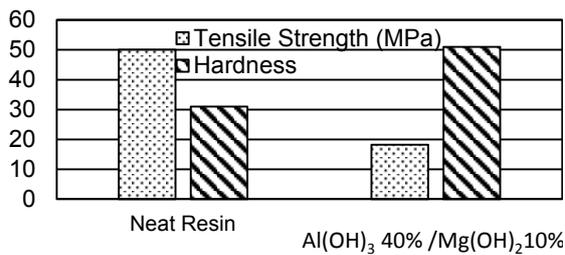


Figure 3. The effect of $Al(OH)_3$ and $Mg(OH)_2$ Additive to the Tensile Strength and Hardness of Composite

Table 4. The average result of tensile strength test of $Al(OH)_3$ 40%/ $Mg(OH)_2$ 10%

Specimen No.	Tensile Strength (MPa)	
	Neat Resin	$Al(OH)_3$ 40 %/ $Mg(OH)_2$ 10 %
1	52.3	17.8
2	49.0	13.2
3	44.7	17.0
4	50.0	22.5
5	54.0	20.4
Average	50.0	18.2
Std. Deviation	3.5	3.6

Figure 3 showed that the combination of $Al(OH)_3$ 40 % and $Mg(OH)_2$ 10 % could increase the hardness from 31 to 51, or increase for about 64.5 %. Flores et al. (2000) stated that the increase of composite hardness happened because the possible dispersion of the additive particles in the structure would increase the material hardness. In the hardness test, the density of particles in the region below the indentation was forced to increase, so as the indenter moved downward, it would encounter resistance from the material with an increase in concentration of particles which resulted the hardness value to increase (Shen and Chawla, 2001).

3.4 Analysis Morphology and Mapping Composite

Dispersion of additive particles in matrix influenced the characteristic of composite (Wen et al., 2012). Morphology and mapping analysis was conducted for the best composite resin/additive before (Figure 4) and after the flammability test (Figure 5).

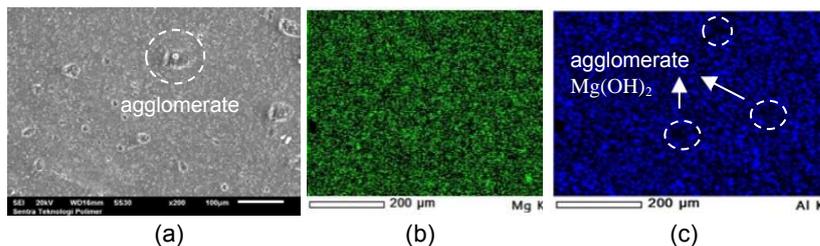


Figure 4: Morphology and Mapping of Composite with Additive $Al(OH)_3$ 40 % / $Mg(OH)_2$ 10 % (Before Flammability Test) (a) Surface Morphology (b) Mg Element , (c) Al Element

Figure 4(a) showed that the addition of additive could lead to the formation of agglomerate. This condition was due to higher additive concentration, resulting in the formation of material structure that was not fulfilled enough with the resin and influenced the bond between matrix and additive particles. The mapping analysis in composite surface before flammability test was presented in Figure 4(b) and (c) and performed in order to observe which additive have more tendencies to agglomerate. The black spots showed in Figure 4(c) was the agglomerate that was formed due to the presence of $Mg(OH)_2$. The mapping after flammability test was also conducted to identify the presence of protective layer for composite code A5 and shown in Figure 5(a) and (b).

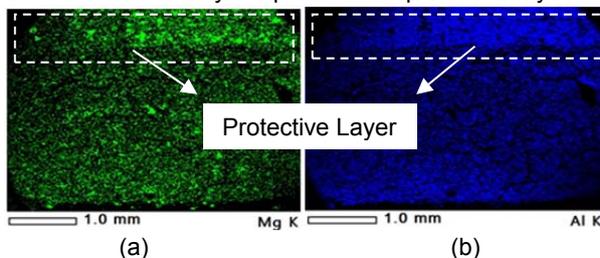


Figure 5: Mapping of Composite with Additive $Al(OH)_3$ 40 % / $Mg(OH)_2$ 10 % (After Flammability Test) (a) Mg Element, (b) Al Element

Figure 5 showed that there was a colour gradation in the top side which showed the possibilities of protective layer formation. Hull and Stec (2009) stated that $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$ when burned would be decomposed into Al_2O_3 and MgO which formed the protective layer in the surface of composite. This layer gave positive influence for the composite fire retardancy because it could avoid the heat and oxygen flowed into the composite and avoid the discharge of flammable gas that was produced during the thermal degradation. When the heat, oxygen, and flammable gas concentration were under the ignition level, the fire would be retarded.

4. Conclusions

This research showed that the best fire retardancy was obtained from the composite with concentration of $\text{Al}(\text{OH})_3$ 40 %/ $\text{Mg}(\text{OH})_2$ 10 %. Combination of $\text{Al}(\text{OH})_3$ 40 %/ $\text{Mg}(\text{OH})_2$ 10 % could also improve the thermal stability of composite by reducing mass loss rate to 4.9 %/min and total mass loss to 77 %. On the other hand, the tensile strength of composite decreased to 64 % but the hardness improved to 64.5 %. Overall, the addition of $\text{Al}(\text{OH})_3/\text{Mg}(\text{OH})_2$ additive to unsaturated polyester resin can increase the fire retardancy of composite and can be used as an alternative to synthesise fire retardant composite.

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