



## EFFECT OF ALUMINUM PHOSPHATE ON STRUCTURAL AND FLAME RETARDANT PROPERTIES OF COMPOSITES FIBREGLASS

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### ABSTRACT

Composite fiberglass boats are basically constructed with three broad groups of resin, reinforcement and core material. The combination of these material forms high strength, low density, economic and easy to manufacture structure for boat construction. In the composite system, resin is one of components that has high flammability properties. Phosphate types of fire retardants are well known can increase the fire retardance properties by the higher retention due to the char formation. This study was conducted to analyse the interaction of modified polyester resin and composites fiberglass with aluminum phosphate as new fire retardance. The interaction mechanism of aluminum phosphate ( $AlPO_4$ ) was investigated in seven layers composite fiberglass system. The Fourier Transform Infrared (FTIR) spectroscopy of modified polyester resin and composite fiberglass showed an improved of reaction bonding stability at 5wt% of  $AlPO_4$  respectively. Flammability properties of composite obtained using vertical burning (UL 94) test method produced a similar finding.

**Keywords:** composite, fiberglass, phosphate,  $AlPO_4$ , FTIR.

### INTRODUCTION

Flame retardants are chemical materials used to diminish the spread or intensity of fire. The function of this fire retardant is to decrease the potential of ignition and delay the spread of flame. Polyester resin contributes to give effect on the combustibility of the underlying fiberglass laminate system. Polyester is usually modified chemically and physically through attachment with halogen atom to improve its flame retardant properties. However, the combustion of halogenate resin produce corrosive and toxic gaseous that detrimental to environment. The phosphorus type fire retardant materials are another option in solving the halogenated typed fire retardant additive. The most common phosphorus types fire retardant additive for polyester polymer are red phosphorus [1], ammonium polyphosphate (APP) [2,3] and aluminum phosphinate (AlPi) [4]. The char layer or intumescent in phosphorus additive is an important factor that can inhibit the fire ignition and fire propagation in polyester polymer. Oxidation and pyrolysis of polymer containing phosphorus fire retardant produce both char and gaseous that gives phosphorus its inhibition mechanism. Pyrolysis decreases the concentration of hydrocarbon gaseous due to char formation. This char and gaseous formation depends on the types of flame retardant additive, interaction with polymer matrix and interaction with other additive such as nano size flame additive, metal salts, melamine and many more. Moreover, the concentration of flame retardant additive is also an important factor that needs to be considered due to large amount of phosphorus may risk the mechanical properties and production process of composite. Other commercial fire retardants used in combination with polyester system were found to have disadvantages such as high concentration or high loading that affect the mechanical

performance such as in aluminum trihydroxide (ATH) additive [2], high smoke formation in uncontrolled ventilation involved in APP usage and non-homogenous mixture (nanosize additive) [5]. Meanwhile aluminum phosphate was reported in various types of coating, such as carbon coating film [6], metal coating [7], oxide coating [8] and intumescent coating [9]. Other than coating, aluminum phosphate also discussed as fire retardant additive system in polymer nanocomposites [9]. Furthermore, recent research found that the combination of nano-alumina and phosphinate in unsaturated polyester system showed significant improve in fire retardant properties [5]. There is no research found of the usage of Aluminum phosphate as a fire retardant additive in the polyester polymer formulation. This paper focused to analyse the possibility of interaction between aluminum phosphate with polyester resin and composite fiberglass as new fire retardant materials. Later, the evaluation of appropriate ratio of aluminum phosphate to enhance the fire retardant properties the composite fiberglass was also investigated.

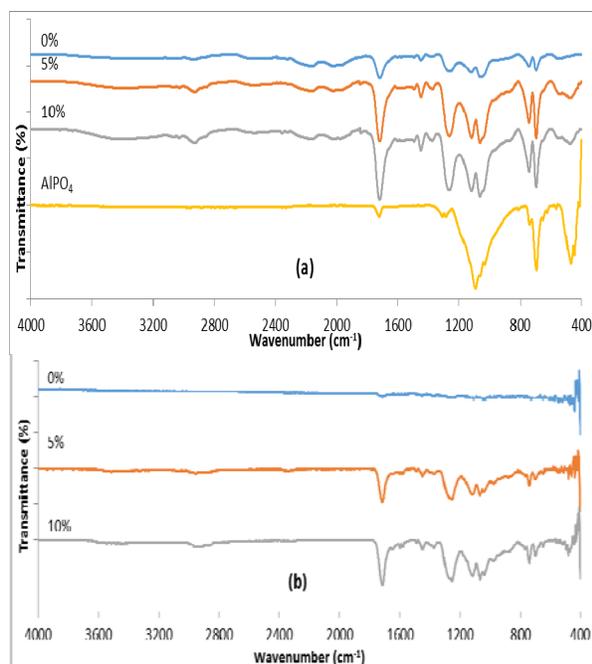
### METHODOLOGY

A commercially available unsaturated polyester resin, with 30 to 45% styrene monomer and trade name Norsodyne 3338W from Polynt Composites Malaysia Sdn. Bhd. was used as matrix. Methyl Ethyl ketone Peroxide (MEKP) from Mepoxe was supplied by Pt Kawaguchi Kimia Indonesia. Meanwhile aluminum phosphate was from Sigma Aldrich. Seven layers of composite fiberglass was prepared using hand lay-up method. Polyester resin, MEKP and various ratio of aluminum phosphate were mixed by continuous hand stirring for 5 minutes in a 1000 ml plastic beaker. The homogenous mixtures were applied for each design layer of fiberglass reinforcement



containing chopped strand mat and woven roving. Three types of laminate fiberglass chopped (300 and 450) strand mat and woven roving (600) were used in seven design layer. The fiber mats were allowed to cure for 12 hours before its removal from the mold at room temperature. The dried board was kept vertically at room temperature for 24 hours to prevent it from becoming curved. Three types of composites were prepared with 0, 5 and 10 weight percent of aluminum phosphate ratio. The chemical structures of powder and film for all samples were analyzed using FTIR spectroscopy were recorded in the range of 4000 to 400  $\text{cm}^{-1}$  with four scans on a Perkin Elmer System 2000 Fourier Transform Infrared (FTIR) with the resolution of  $4\text{cm}^{-1}$ . The UL94 vertical method was conducted with specimens dimension of  $125 \times 13 \times 5$  mm were hold vertically and a flame was applied to the bottom. The flame was applied for 10 seconds and then removed until flaming stops, at which time the flame was reapplied for another 10 seconds and then again removed.

## RESULTS DISCUSSION



**Figure-1.** FTIR spectra contained various ratio of aluminum phosphate (0wt%, 5wt% and 10wt %) of (a) modified polyester, (b) composite fiberglass.

Figure-1(a) and (b) show the effect of aluminum phosphate ratio (0wt%, 5wt%, 10wt%) weight percent on polyester polymer resin and composite fiberglass. The spectra for sample with 0wt% of  $\text{AlPO}_4$  ratio shows unsaturated polyester that contains peaks of C-H ( $2928\text{ cm}^{-1}$ ), C=O ( $1718\text{ cm}^{-1}$ ), C-H ( $1450\text{ cm}^{-1}$ ), C=C ( $1375\text{ cm}^{-1}$ ), C-O ( $1262, 1121, 1063\text{ cm}^{-1}$ ), C-H bending ( $743\text{ cm}^{-1}$ ) and C-H ( $696, 543\text{ cm}^{-1}$ ). Addition of aluminum phosphate observed several new peaks occur in modified polyester resin at  $3360\text{-}3436\text{ cm}^{-1}$ ,  $3027\text{-}3028\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$ ,

$1495\text{-}1496\text{ cm}^{-1}$  and  $476\text{-}475, 414\text{ cm}^{-1}$  assigned to band of OH, C=C,  $\text{CH}_2$  and O-P-O-Al respectively. Increasing ratio of aluminum phosphate observed a broadened of OH peak at  $3360\text{ cm}^{-1}$  and  $3027\text{ cm}^{-1}$ . There are shifted of OH peak at  $3360\text{ cm}^{-1}$  wave number towards lower wave number as aluminum phosphate ratio increase.

The  $1718\text{ cm}^{-1}$  peak confirms the present of ester group due to stretching vibrations of COO group [10]. The C=O bond in unsaturated polyester shows an increase in intensity with increase in aluminium phosphate ratio form a C-O-P- $\text{AlPO}_4$  bond. The similar bond also observed in the reaction between partially phosphorylated polyvinyl alcohols (PPVA) with aluminum phosphate. However due to low C=O bond in PPVA, the peak slowly vanished as aluminium phosphate increase. Meanwhile in unsaturated polyester high C=O bond observed intense at high concentration of aluminium phosphate [11]. Peak at  $1600\text{ cm}^{-1}$  and  $1495\text{ cm}^{-1}$  a slight intense peak observed with unchanged of peak position.

The C-O bond at  $1121\text{ cm}^{-1}$  observed a shifted towards lower wavenumber and intense peak with increasing ratio of aluminum phosphate indicates a strong interaction between polyester and aluminium phosphate by the formation C-O-P- $\text{AlPO}_4$ . This peak has a tendency to merge with  $1063\text{ cm}^{-1}$  peak and form one single peak at high ratio of aluminum phosphate as observed earlier in the mixture of polyester with phosphate group. The C-O-P- $\text{AlPO}_4$  bond merge and exist together with O-P- $\text{AlPO}_4$  band at high concentration of phosphate group [11]. Meanwhile the vibration of C-H band at  $743\text{ cm}^{-1}$  is due to bending vibration of polyester benzene ring [12]. The C-H and C=O band shows a slightly shift in wavenumber but the intensity of these two peak increase with increasing ratio of aluminum phosphate also indicates a strong interaction between unsaturated polyester ad aluminium phosphate as observed in Figure-1(a).

The O-P-O band at  $476\text{ cm}^{-1}$  increases at increasing ratio of aluminum phosphate. Meanwhile peak at wavenumber  $414\text{ cm}^{-1}$  only observed in sample with 5wt% of aluminum phosphate ratio. Increased amount of aluminum phosphate ratio diminished the size of this peak, which indicates strong interaction of unsaturated polyester and aluminium phosphate with formation of O-P-O- $\text{AlPO}_4$  bond. Observation of effect phosphate group on polyvinyl alcohol shows similar observation as the phosphate group have a maximum reaction with polymer it tends to increase more O-P-O in fingerprint region [11].

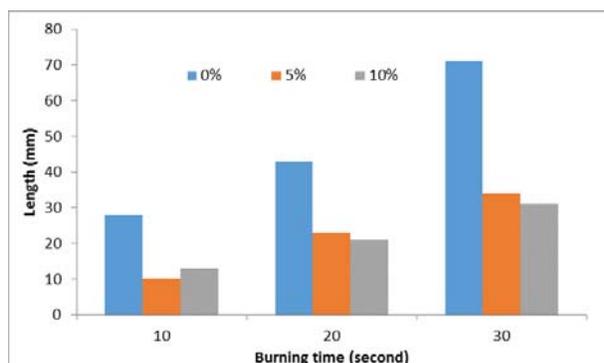
Figure 1(b) shows the FTIR spectra of composite fiberglass with aluminum phosphate ratio (0wt%, 5wt%, 10wt%). The first spectra are a composite fiberglass without addition of aluminum phosphate (0%) observed a massive peak at fingerprint region with wavenumber below  $500\text{ cm}^{-1}$ . Introduction of aluminum phosphate shows a significant improvement in the spectra with occurrence of  $1718, 1254, 1119, 1065, 743, 701, 521$  and  $453\text{ cm}^{-1}$  peak that represent various band assignments such as C-O-Al, O-P-O-Al and O-Al that contribute to phosphate-carbonaceous char formation [4]. FTIR spectra lower than  $500\text{ cm}^{-1}$  shows a shifted of wavenumber for



peak at 488, 437, 424 and 410  $\text{cm}^{-1}$  to lower and higher wavenumber due to interaction with various ratio of aluminum phosphate. There are only two bands (470  $\text{cm}^{-1}$  and 458  $\text{cm}^{-1}$ ) that remain unchanged in peak position although high ratio of aluminum phosphate involved. The band at 1119, 743, 701, 521 and all peak at lower than 500 have interaction with aluminum phosphate with formation of C-O-Al [13] and Si-O-Al linkage [14]. The interaction of aluminum phosphate with both polyester and composite fiberglass confirm by the occurrence, vanishing, broadening, shifted and intensity of peak in FTIR spectra. Sample with 5wt% aluminum ratio observed strong interaction of aluminum phosphate in both polymer and composite fiberglass with occurrence of extra aluminum phosphate peak at 414 and 453  $\text{cm}^{-1}$  respectively. Table 1 summarizes all peaks and band assignment for both modified polyester and composite fiberglass.

**Table-1.** FTIR absorption bands for modified polyester and composites fiberglass at three Aluminum phosphate ratio (0wt%,5wt% and 10wt%).

Modified polyester			Band Assignments	Composite fiberglass			Band Assignments
0wt%	5wt%	10wt%		0wt%	5wt%	10wt%	
-	3360	3436	OH in $\text{AlPO}_4$	-	-	-	-
-	3027	3028		OH	-	-	
2928	2926	2926	C-H stretching vibration	-	-	-	-
1718	1719	1719	C=O, C-O- $\text{AlPO}_4$	-	1718	1719	C-O-Al
-	1600	1600	C=C	-	-	-	-
-	1495	1496	$\text{CH}_2$	-	-	-	-
1450	1450	1450	C-H band	-	-	-	-
1375	1374	1374	C=C	-	-	-	-
1260	1262	1263	C-O	-	1254	1265	C-O- $\text{AlPO}_4$
1121	1119	1119	C-O, C-O- $\text{AlPO}_4$	-	1119	1114	C-O- $\text{AlPO}_4$ , @ Si-O-Al linkages
1063	1064	1065	C-O, C-O- $\text{AlPO}_4$	-	1065	1070	C-O- $\text{AlPO}_4$ , Si-O-Al linkages
743	743	743	C-H bending from benzene ring	-	743	744	C-O- $\text{AlPO}_4$ , Si-O-Al linkages
696	696	696	C-H out of plane	-	701	704	O-P-O-Al
543	-	-	C-H	-	-	521	O-P-O-Al
-	-	-	-	488	488	497	Si-O, Si-O-Al
-	476	475	O-P-O-Al	470	469	470	Si-O
-	-	-	-	458	459	459	Si-O
-	-	-	-	-	453	-	O-Al
-	-	-	-	442	437	441	Si-O, Si-O-Al
-	-	-	-	421	424	425	Al
-	414	-	O-P-O-Al	410	407	416,407	Si-O, Si-O-Al



**Figure-2.** UL94 vertical burning samples length measurement of 10, 20 and 30 seconds of aluminum phosphate ratio (0wt%, 5wt% and 10wt %).

Figure-2 shows the UL94 vertical burning samples length measurement of 10, 20 and 30 seconds for all samples. Sample with 0wt% of aluminum phosphate shows highest propagation of burning length for all burning time. Meanwhile, sample with 5wt% of aluminum ratio shows the lowest length of fire propagations at  $t_1$ . At this ratio the ignition and propagation of fire was delayed by good interaction between aluminum phosphate and composite fiberglass. Similar finding reported in the interaction between polyester with combination of two fire retardant materials ATH and APP concluded more Al-P-O bonding occur and delay the time of ignition in the system [2]. However, once the ignition of fire started, increase ratio of aluminum phosphate observed decrease in fire propagation as observed in sample with 10wt% ratio at 30 seconds. Penczek earlier summarized that excessive amount of phosphorus type fire retardant will have an adverse effect to the composite [3]. Furthermore recent research also observed that optimum formulation of phosphate (10-15wt%) ratio and nano-alumina (0-5wt%) ratio lead significant improvement in fire retardant properties which in the similar range to what we have observed [5]. This observation supported the FTIR finding that at 5wt% aluminum ratio produce the optimum interaction between aluminum phosphate and composite fiberglass. All samples observed no cotton ignition by flaming drips and no glowing or flaming combustion for all three burning time.

## CONCLUSIONS

The interaction of aluminum phosphate and composite fiberglass reveal that the optimum bonding between aluminum phosphate and composite fiberglass occurs in the aluminum phosphate ratio at 5wt% with the occurrence of C-O-Al, O-P-O-Al and O-Al as discussed earlier. The vertical burning supported the FTIR result observed low ignition time at 5wt% ratio. It is concluded from this research that aluminium phosphate is suitable as flame-retardants for the composites additives of material. Thus, the research aims to make a valuable contribution towards a better understanding of phosphorus that containing flame retardants has been achieved. In general, the findings of this study are beneficial as it enhance understanding on the modified composite polyester fiberglass properties, which will assist researchers in developing a new fire retardant composite fiberglass additive for marine applications.

## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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