Development of an epoxy-based intumescent retardant coatings comprising of different fillers for steel structure

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ABSTRACT

Intumescent coating is one of the useful methods to protect steel structures under fire conditions. In this study, the influence of single and hybrid two or three flame-retardant fillers among TiO_2*,* $Al(OH)_3$*, and* $Mg(OH)_2$ *on paints containing ammonium polyphosphate (APP), melamine (MEL), pentaerythritol (PER) based on the epoxy resin was investigated to improve the fire protection performance of the intumescent coatings. The performances of the intumescent coatings were determined by a fire test at 950 °C for 1 hour. The coating degradation was characterized by Thermal gravimetric analysis (TGA). The morphology and composition of the char after the fire test were studied by Fourier transform infrared spectra (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray spectra (EDS). The results revealed that* $Al(OH)_3$ *or combination of* $Al(OH)_3$ *and* TiO_2 *are the effective solution to increase fire protective performances of the epoxy-based intumescent coatings.*

Keywords: Intumescent coating; Epoxy; Fire retardant filler; Steel structure.

1. INTRODUCTION

Steel structures has been widely used in many various fields of life such as construction, industries, marine, and military applications. However, steel materials can collapse when the temperature is above 500 °C [1]. Therefore, the thermal protection of steel structures against fire is a very important problem.

Intumescent flame-retardant coating has the following ingredients: carbon donor (char former), acid donor (catalyst), blowing agent, binder, and flame-retardant fillers [2]. Some researchers on intumescent flame-retardant coatings which based on APP-PER-MEL in combination with different fillers have been published in the past time [3-8]. Evtushenko et al. reported the effect of $Al(OH)_3$ on the fire protection performances of intumescent coating using polyvinyl acetate as a binder [3]. Puri et al. revealed that intumescent coating containing 10% of cenospheres improved residual weight by 39.3% and enhanced the anti-oxidation ability of the char [4]. Ullah et al. reported that the formulation added 5% of kaolin clay enhanced the fire resistance of the coating [5]. The incorporation of flame-retardant fillers to improve the thermal insulation of intumescent coatings has gained research attention. The synergistic effects of halloysite clay and zirconium phosphate on the thermal insulation performance of intumescent coatings were studied by Lee et al. [6]. Zoleta et al. investigated the effects of CeO_2 and dolomite additives on the pyrolysis behavior and fire protection performance of intumescent coating [7]. Yew et al. stated the effects of individual and combinations of TiO_2, $Al(OH)_3$, and $Mg(OH)_2$ on the fire resistance property of intumescent coating using acrylic resin as a binder [8]. Besides, epoxy-based intumescent retardant coating has earned a lot of attention in the past years. M. Yasir et al. investigated the effects of basalt fibers on thermal degradation and fire performance of epoxy-based coating [9]. J. Kaur et al. studied the role of Bentonite clay on improving in char adhesion of intumescent coating using epoxy resin [10]. The results revealed that the combination of retardant fillers strongly influenced the properties of fire protection, water resistance, flammability, and adhesion strength of the intumescent coatings.

This study presents the effects of the individual and various combinations of TiO_2, $Al(OH)_3$, and $Mg(OH)_2$ on the fire protection performance of the epoxy-based intumescent coating. The formulations' thermal protective behaviour, residual weight, char composition, and char morphology were characterized by TGA, EDS, SEM, and FTIR techniques.

2. EXPERIMENTAL

2.1. Materials

Ammonium polyphosphate (APP, $(NH_4PO_3)_n$ with n > 1000, act as acid source) was provided by Shifang Changfeng Chemical Co., LTD., China. Melamine 99% (MEL, $C_5H_{12}O_4$, MW = 136.15 g/mol, act as blowing agent) and Pentaerythritol 98% (PER, $C_3H_6N_6$, MW = 126.12 g/mol, act as charring agent) were supplied by Sigma-Aldrich. TiO_2, $Al(OH)_3$, and $Mg(OH)_2$ were purchased from China. Epoxy resin was used as a binder and provided by Dow Chemical. The hardener was supplied by Evonik, Singapore. All chemicals were used as received without any further purification.

2.2. Methods

The compositions of intumescent coatings were shown in table 1. The fabrication process has three main stages. Firstly, the components were dispersed on a high-speed stirrer for 1 hour. Secondly, the binder was poured and stirred for 30 minutes to obtain a homogenous solution. Finally, the hardener was added to avoid the curing of epoxy resin during mixing. The operating viscosity of intumescent coatings was covered by diluting them with purified water.

Table 1. *The compositions of intumescent formualations.*

Samples	APP	PER	MEL	TiO_2	$Mg(OH)_2$	$Al(OH)_3$	Epoxy
M1	18.5	9.25	9.25	7.4	0	0	55.6
M2	18.5	9.25	9.25	0	7.4	0	55.6
M3	18.5	9.25	9.25	0	0	7.4	55.6
M4	18.5	9.25	9.25	0	3.7	3.7	55.6
M5	18.5	9.25	9.25	3.7	0	3.7	55.6
M6	18.5	9.25	9.25	3.7	3.7	0	55.6
M7	18.5	9.25	9.25	2.46	2.46	2.46	55.6

The products were then coated on a 100x100x1 mm steel substrate by using a brush. The process was repeated 4 - 5 times to obtain an average thickness of 1 mm, measured by a coating thickness gauge (GM 200A-Benetech). The samples were dried in air at room temperature for one week and were characterized by fire resistance properties.

2.3. Characterization

The fire resistance test of intumescent coatings was conducted by the Bunsen burner test which was determined following the ASTM E119 standard. The coated steel plates were exposed to a direct flame from liquified petroleum gas (LPG) torch. The distance between the burner and substrate is about 7 - 8 cm. The gas consumption rate was kept at

170 - 180 g/h. The coating substrate's backside temperature was measured using J type thermocouple for 60 minutes. The image of the fire test system is shown in figure 1.

Figure 1. *The diagram of the fire test system.*

After the test, the intumescent factor (IF) of the char layer was calculated using the following equation [4]:

$$IF = (d_2 - d_o)/(d_1 - d_o) \qquad (1)$$

Where d_o was the thickness of the steel substrate, d_1 was the thickness of the coating before fire test, and d_2 was the thickness of the intumescent char after fire test.

The morphology of the intumescent coating's char after the fire test was characterized by using scanning electron microscopy (SEM, JEOL JSM 6500F). The char's Energy dispersive X-ray spectroscopy (EDS) spectra were analyzed by JEOL JED-2300 spectrometer. Fourier transforms infrared spectroscopy (FTIR, JACOS 4700) was measured by the KBr pellet method.

A thermogravimetric analysis (TGA) instrument (LABSYS TG/DSC1600 from Setaram, France) was applied to characterize the thermal degradation of the intumescent coatings at a heating rate of 10 °C/min in air atmosphere from a temperature range of ambient to 900 °C. Ground 4 - 10 mg specimens were used.

3. RESULTS AND DISCUSTION

3.1. Fire protection performance

The dependence of temperature on the time of the steel's plate backside with different intumescent coatings for a 1-hour fire test was exhibited in figure 2a.

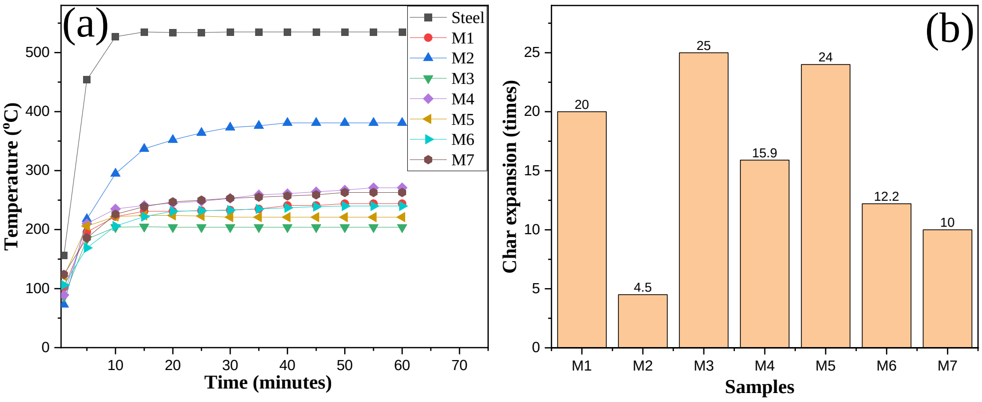

Figure 2. *The temperature curve of the steel's plate backside (a) and char expansion (b) of the intumescent coatings after a 1-hour fire test.*

After 1-hour fire test, the temperature of uncoated steel is 535 °C, while the temperature of the steel's backside substrate of the coatings adding individual TiO_2, $Mg(OH)_2$, and $Al(OH)_3$ (samples M1, M2, and M3) are 244, 381, and 204 °C, respectively. The samples containing a combination of TiO_2, $Mg(OH)_2$, and $Al(OH)_3$ indicate a back plate temperature of 271, 221, 240, and 263 °C corresponding to samples M4, M5, M6, and M7, respectively. The results showed that the steel coated intumescent coating has a significant decline in backplate temperature compared to the bare steel. Samples M3 and M5 have good thermal-insulating behavior among the coatings. This result could be explained by the synergistic effect of fillers and the interaction between fillers with flame-retardant compositions to improve the intumescence and adhesion of the coatings to the steel plate [8]. In addition, the sample M2 adding $Mg(OH)_2$ was the highest steel temperature due to the loss of adhesion of the char layer to the plate during the fire test.

Char expansion of the intumescent formulations was presented in figure 2b. The samples have char expansion of 20 (M1), 4.5 (M2), 25 (M3), 15.9 (M4), 24 (M5), 12.2 (M6), and 10 (M7) times compared to their original thickness. The results indicated that the coatings adding $Al(OH)_3$ (sample M3) and a hybrid of TiO_2 and $Al(OH)_3$ (sample M5) have char expansion higher than the other samples. This phenomenon was caused by constraining the evolved gases into the matrix and resulting in even char expansion. It can be concluded that intumescent coatings containing $Al(OH)_3$ and a combination of TiO_2 and $Al(OH)_3$ led to the best thermal protective ability with significantly lower steel substrate temperature and higher char expansion compared to the other samples.

3.2. Char morphology

Char's optical images of the intumescent coatings after the fire test were observed in figure 3. A thick carbonaceous layer of char form on exposure to fire which can act as heat insulation between fire and substrate. Sample M2 form a thin char with some cracks and the char was not bonded to the substrate, therefore, could not control the heat transfer to the plate. Otherwise, samples M3 and M5 have a thick, porous and multicellular structure which plays a critical role in deciding the fire protective of the coatings.

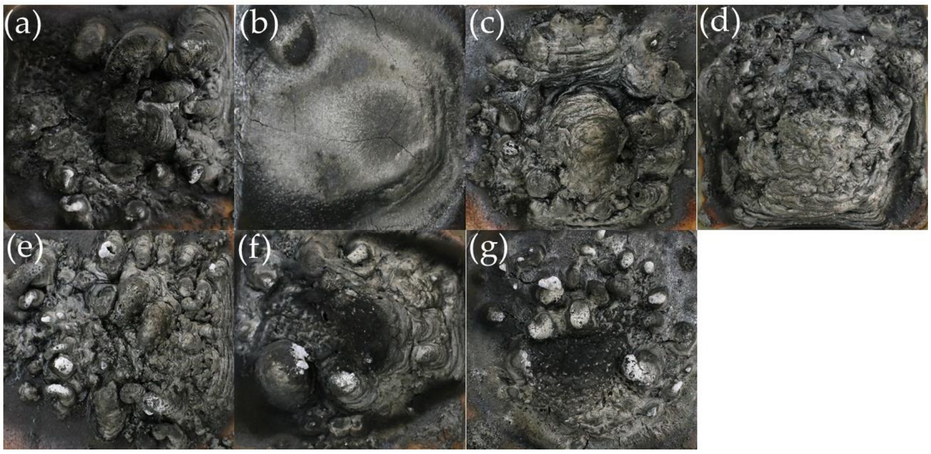

Figure 3. *Optical images of intumescent coatings after the fire test: M1(a), M2(b), M3(c), M4(d), M5(e), M6(f), and M7(g).*

The SEM images of internal char layers are showed in figure 4. The SEM images of the coatings after fire test showed that samples M3 and M5 have a compact structure, uniform foam char without cracks which leads to a better fire protection performance. Besides, the char layer of the other samples has a tiny form structure with some cracks. Therefore, heat might be transferred via cracks in the char layer, which lead to a decrease in the steel's backplate temperature as observed in figure 2a.

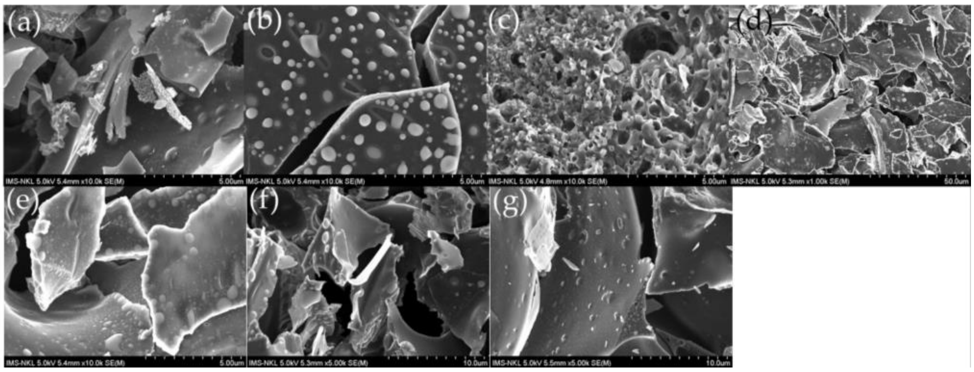

Figure 4. *SEM images of char's intumescent coatings after the fire test: M1(a), M2(b), M3(c), M4(d), M5(e), M6(f), and M7(g).*

3.3. Char composition

The EDS analysis was used to determine the chemical composition of coating's char after the fire test. The element composition of intumescent coatings is given in table 2. It is observed that the samples M3, M4 and M5 have more carbon and less oxygen in the char compared to the other samples. Therefore, the presence of more carbon and fewer oxygen elements in the char layer increases its resistance to thermal oxidation. The char layer with a higher C/O ratio has better antioxidant characteristics than one with a lower C/O ratio [11-12]. The C/O ratio of the samples M3, M4 and M5 are 2.09, 2.26 and 2.0, respectively. While this ratio in the other samples is lower. It is concluded that the addition of $Al(OH)_3$ and combination of TiO_2 and $Al(OH)_3$ leads to an increase in the C/O ratio, which results in an improvement in fire protection.

Table 2. *The char compositions of intumescent formulations.*

Samples	Element composition (wt.%)							
	C	O	P	Ti	Ca	Mg	Al	C/O
M1	51.04	35.17	6.95	3.54	3.30	0	0	1.45
M2	52.28	34.58	10.77	0	0	2.37	0	1.51
M3	58.51	27.91	10.86	0	0	0	2.72	2.09
M4	59.57	26.28	11.50	0	0	1.60	1.05	2.26
M5	55.26	27.62	12.37	1.93	1.52	0	1.30	2.00
M6	51.65	28.83	14.93	1.92	1.45	1.22	0	1.79
M7	55.20	29.34	10.89	1.99	0.89	1.69	0	1.88

3.4. FTIR analysis

The Fourier transform infrared spectroscopy (FTIR) of the intumescent coating was used to evaluate the decomposition of the phosphocarbonaceous structure and was depicted in figure 5. In the FTIR spectra of the char coatings, a band at 2359 cm^{-1} indicates the bending vibration of ($-CH-CH_2-$) bonds of cured epoxy and the O-P-O occurred at 595 cm^{-1} due to APP [13]. The symmetrical deformation of CH_2 and CH_3 was observed at around 1570 cm^{-1} due to the decomposition of melamine. In the P-O-P region

(1400 - 800 cm^{-1}) band at 973 cm^{-1} belongs to the P-O stretching vibration in the P-O-C structure [14]. The band at 1570 cm^{-1} correspond to carbonaceous hydrogen-deficient compounds (coke) [15].

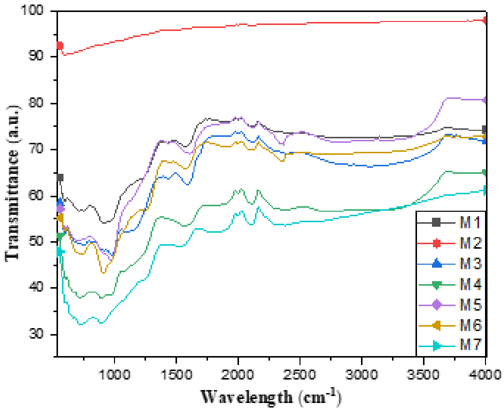

Figure 5. *FTIR diagram of char's intumescent coatings after fire test.*

The FTIR results confirm the presence of P-O and P-O-C bonds in the char layer after the fire test revealing the interaction between APP, PER, and epoxy with the samples added additives. This interaction leads to the formation of aromatic and phosphocarbonaceous char. The char structure is helpful in the fire protection of intumescent coatings.

3.5. Thermal degradation

The thermal gravimetric analysis (TGA) was applied to investigate the thermal stability of intumescent retardant coatings. figure 6 shows TGA and DTG curves of various samples.

Weight loss diagram of the coatings are depicted in figure 6a. The residue weight after fire test of the samples M1, M2, M3, M4, M5, M6 and M7 were 11.31, 9.37, 15.71, 14.91, 10.62, 15.51, and 13.75 (wt.%) at 900 °C, respectively. The result showed that M3 sample has the higher residual weight due to the formation of thermally stable char layer.

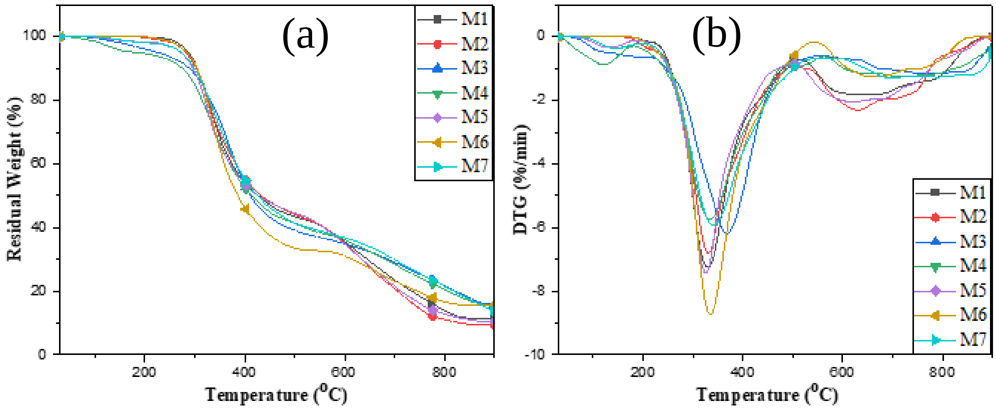

Figure 6. *TGA (a) and DTG (b) diagram of the intumescent coatings.*

As we can see from the DTG diagram, the thermal degradation of the intumescent coatings includes five steps. The first stage is below 200 °C, which is attributed to residue water and partial decomposition of the samples. The stage between 200 and 300 °C is due to degradation of PER which releases NH_3 gas. The weight loss from 300 to 400 ^oC is caused by the decomposition of APP and melamine was 330 - 410 ^oC [16]. Ammonia, phosphoric acid, and water were produced. The next step is the decomposition of APP at 450 ^oC. The last stage is higher than 500 ^oC, part of carbonaceous char decompose and the residue is inorganic phosphates [4]. The intumescence process and reactions are explained as: when flame heated, the binder was melted and a acids is released by breaking the acid source which results in dehydration and carbonization of char formers. Then, the blowing agent decomposes to form gases which get constrained in the matrix making it swell and creating a shielding multi-cellular protective char layer. This char layer help to prevent heat transfer from the flame to the substrate [2].

4. CONCLUSIONS

We have successfully synthesized the intumescent retardant coating based on APP, PER, MEL, epoxy resin and some different fillers. The influence of single and combination of fillers (TiO_2, $Mg(OH)_2$ and $Al(OH)_3$) on the fire performances of the intumescent coating have also investigated. The results indicated that the steel's backplate temperature of the samples using $Al(OH)_3$ and combination of $Al(OH)_3$ and TiO_2 are 204 and 221 °C, respectively. After the fire test, the char expansion of the samples adding single $Al(OH)_3$ and hybrid of $Al(OH)_3$ and TiO_2 are higher than the other samples. Therefore, intumescent retardant coatings based on epoxy resin using $Al(OH)_3$ or combination of $Al(OH)_3$ and TiO_2 can be a helpful solution for enhancing the fire performance application for steel structures.

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TÓM TẮT

Nghiên cứu chế tạo sơn chống cháy kiểu trương nở trên cơ sở nhựa epoxy và các loại phụ gia chậm cháy nhằm ứng dụng cho vật liệu thép

Sử dụng sơn chống cháy kiểu trương nở là một trong những biện pháp hiệu quả để bảo vệ cấu kiện thép trong điều kiện cháy. Trong bài báo này, chúng tôi tiến hành nghiên cứu ảnh hưởng của các phụ gia chậm cháy TiO_2*,* $Al(OH)_3$ *và* $Mg(OH)_2$ *lên tính chất chống cháy của sơn chống cháy kiểu trương nở trên cơ sở ammonium polyphosphate (APP), melamine (MEL), pentaerythritol (PER) và nhựa epoxy. Tính chất chống cháy của sơn được khảo sát bằng thiết bị đốt ở nhiệt độ* 950^oC *trong thời gian 1 giờ. Sự phân hủy nhiệt của màng sơn được khảo sát bằng thiết bị phân tích nhiệt trọng lượng TGA. Hình thái, cấu trúc và thành phần nguyên tố của lớp than sau khi đốt trong 1 giờ được xác định lần lượt bằng kính hiển vi điện tử quét (SEM), phổ hồng ngoại biến đổi Fourier (FTIR) và phổ tán xạ năng lượng tia X (EDS). Các kết quả nghiên cứu chỉ ra rằng, sử dụng* $Al(OH)_3$ *hoặc kết hợp giữa* $Al(OH)_3$ *và* TiO_2 *là những giải pháp hiệu quả để cải thiện tính chất chống cháy của sơn chống cháy trên cơ sở nhựa epoxy.*

Từ khoá: Sơn chống cháy; Nhựa epoxy; Vật liệu thép; Phụ gia chống cháy.