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Original Article

Influence of Nanoclay on the Fire Resistance Properties of Epoxy-Based Intumescent Retardant Coatings for Steel Plate

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Abstract: The intumescent retardant coating was fabricated by a combination of epoxy binder and flame-retardant ingredients for the steel plate. This paper investigates the influence of nanoclay content on improving the fire properties of intumescent fire-retardant coatings. The fire performances of the coatings were determined by a fire test at 950 ºC for one hour. The coating degradation was characterized by Thermal gravimetric analysis (TGA). The morphology, and composition of char were studied by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). The results revealed that the intumescent coating containing 3 wt.% of nanoclay showed the best reduction in substrate temperature compared to the intumescent coating without nanoclay. The results also concluded that nanoclay increased fire protective performances of the intumescent coating.

Keywords: Nanoclay, intumescent coating, epoxy, steel plate.

1. Introduction

Steel has been widely used in many different aspects of life such as construction, industries, marine, and military applications. However, steel material can collapse when the temperature is above 500 ºC [1]. Hence, the protection of steel structures against fire is one of the important problems. Passive fire protection is a method that is usually used for structural steel. It includes some solutions such as i) Fire-retardant chemicals; ii) Modified fire-rated fabricated structures; and iii) Intumescent retardant coatings [2].

Clay was added to intumescent coatings to improve fire protection performances [3-6]. Y. Lee et al., [7] studied the influence of halloysite clay and zirconium phosphate on the thermal property of intumescent retardant coating. J. Kaur et al., [8] reported the effect of bentonite clay on the enhancement in adhesion of char with the substrate. The results showed an increase in residual weight to 33.45 wt.%, and the plate temperature decreased to 170 ºC. R. Puri et al., [9] investigated the role of cenospheres on the char and fire protection properties of water-based intumescent coating.

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The results revealed that cenospheres enhanced the char's ability to anti-oxidation. Ullah et al., [3] revealed that intumescent coating reinforced with 5% kaolin clay has the temperature of the backplate reduced to 257 °C after 60 minutes fire test. Chuang et al., [10] studied the effect of nanoclay for styrene-acrylic resin on intumescent fire retardancy. Improvement in fire properties of the coating containing some different types of clay for steel substrate is widely reported [2-8] but adding nanoclay on epoxy-based intumescent retardant coating is not popular.

In this study, the effect of nanoclay content on the fire resistance performances of intumescent coatings using ammonium polyphosphate (APP), pentaerythritol (PER), and melamine (MEL) is investigated. The epoxy and nanoclay-based intumescent coatings were developed to serve as coatings for steel substrates. The formulations' thermal protective behavior, residual weight, char composition, and char morphology were characterized by Thermal gravimetric analysis (TGA), X-ray spectroscopy (EDS), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) techniques.

2. Experimental

2.1. Materials

Nanoclay (hydrophilic bentonite) was supplied by Sigma-Aldrich and TiO_2 was provided from China. Ammonium Polyphosphate (APP, $(NH_4PO_3)_n$ with n > 1000, acid source) was provided by Shifang Changfeng Chemical Co., LTD., China. Melamine 99% (MEL, $C_5H_{12}O_4$, MW = 136.15 g/mol, blowing agent) and Pentaerythritol 98% (PER, $C_3H_6N_6$, MW = 126.12 g/mol, charring agent) were purchased from Sigma-Aldrich. The binder is used as epoxy resin supplied by Dow Chemical. The hardener was provided by Evonik from Singapore.

2.2. Methods

The coatings ingredients in their respective weight percentages are given in Table 1. The synthesis procedure of the intumescent coatings has three main stages. In the first stage, APP-PER-MEL, TiO_2, and nanoclay with a ratio as listed in Table 1 were dispersed on a high-speed stirrer for 1 hour. Then, the binder was added and stirred for 30 minutes in the next stage. Finally, the hardener was mixed to avoid the curing of epoxy during mixing. The as-synthesized coatings were diluted with purified water to obtain a suitable operating viscosity.

The products were coated on a 100 x 100 x 1 mm steel substrate using a brush. The process was repeated 4 - 5 times to gain an average thickness of 600 µm (measured by a coating thickness gauge, GM 200A-Benetech). The applied coatings were dried in air at room temperature for 7 days and the fire properties were then characterized by different techniques.

Table 1. Compositions of intumescent formulations (wt.%)

Components	**M1**	**M2**	**M3**	**M4**	**M5**
APP	11.76	11.76	11.76	11.76	11.76
PER	5.76	5.76	5.76	5.76	5.76
MEL	11.76	11.76	11.76	11.76	11.76
TiO_2	5.80	5.80	5.80	5.80	5.80
Epoxy	43.42	42.76	41.42	40.16	38.90
Hardener	21.71	21.38	20.71	20.08	19.45
Nanoclay	0	1	3	5	7

2.3. Characterization

The Char's Fourier Transform Infrared spectroscopy (FTIR) was measured by the KBr pellet method (JACOS 4700).

Heat insulation test: The intumescent coatings were carried out by the Bunsen burner test [8]. The coated steel panels were exposed to a direct flame from a liquified petroleum gas (LPG) torch. The distance between the torch and the coated substrate is about 7-8 cm and the consumption rate of gas was kept at 170-180 g/h. The backplate temperature of the coated substrate was measured by using a J-type thermocouple for 60 minutes. The image of the burner test system is shown in Figure 1.

Figure 1. Experimental setup for testing fire performance of intumescent coatings

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

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

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

The thermal degradation of the samples was tested by thermogravimetric analysis (TGA) using Labsys 1600, Setaram model (France) at 10 °C/min in an air atmosphere from ambient temperature to 900 °C. The mass of each sample was about 4-10 milligrams.

To examine the morphology of intumescent char after the fire test, scanning electron microscopy (SEM) was studied using JEOL JSM 6500F equipment. The char's Energy Dispersive X-ray spectroscopy (EDS) spectra were analyzed using the JEOL JED-2300 spectrometer.

3. Results and Discussion

3.1. Fire Resistance of Intumescent Coatings

The change in backside plate temperature of the formulations is depicted in Figure 2. After one hour of the fire test, the back panel temperature of the coating without nanoclay (sample M1) was 383 °C. The samples containing nanoclay M2, M3, M4, and M5 show a back substrate temperature of 306, 291, 353, and 367 °C, respectively. As a result, sample M3 showed the highest reduction in substrate temperature of 92 °C compared to sample M1.

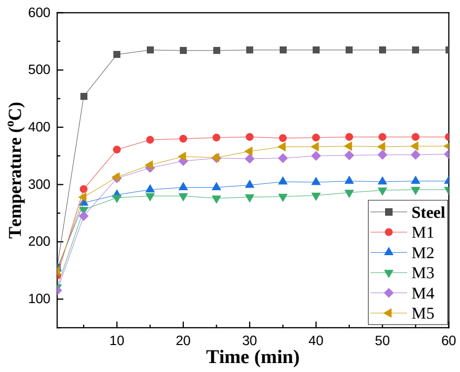

Figure 2. The backside plate temperature of coatings after the fire test.

It is known that intumescent coating without nanoclay forms a relatively fluffy fire-retardant barrier, which is readily penetrated by fire [11]. The significant improvement in the intumescent formulations adding nanoclay with various amounts was shown in Figure 2. This phenomenon suggests that there is a synergistic effect between fire additives and nanoclay leading to the formation of a ceramic-like coating. Therefore, it would be favorable to fire protection. Thus, it is apparent from the results that adding nanoclay improved the coatings' thermal insulating properties compared to the pristine sample.

The optical images of char are indicated in Figure 3. In which, Figure 3A showed that the char of sample M1 was fragile and had many big cracks. As a result, the adhesive between the char and the substrate was not good, leading to heat from the burner easily being transferred to the steel substrate. Hence, the steel backside temperature of the coating was the highest among all the formulations.

With the samples added nanoclay, it was observed that the coatings form a uniform, porous char layer which restrains the heat transfer from the burner to the steel plate. Nanoclay has enhanced the thermal performance of fire-retardant coatings.

Figure 3. Appearance of coatings after fire test: M1(A), M2(B), M3(C), M4(D), and M5(E).

3.2. Char Expansion

The char expansion is one of the factors that affect the thermal resistance behavior of the intumescent retardant coating. This factor can be calculated by the ratio of the thickness of the char after the fire test and the thickness of the coated film. Figure 4 shows the char expansion of various formulations. The results in Figure 4 indicated that the char expansion of sample M1 was 10 times while the nanoclay-reinforced samples showed the char expansion of 18 (M2), 25 (M3), 24 (M4), and 15 times (M5) compared to their original thickness.

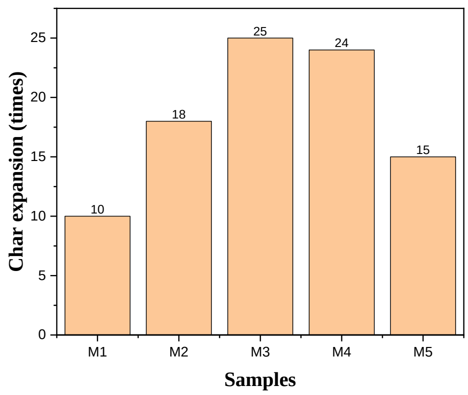

Figure 4. Char expansion of various formulations after 1 h fire test.

The addition of nanoclay in the intumescent coatings results in better heat insulation, restricting the released gases into the matrix and resulting in even char expansion. The decrease in the expansion of char at the sample M5 is due to crowding, hindering the expansion process.

3.3. FTIR Analysis

FTIR analysis was applied to evaluate the decomposition of the phosphocarbonaceous structure and the flame performance. Figure 5 shows the FTIR spectroscopy of char samples of M1, M2, M3, M4, and M5 after the fire test.

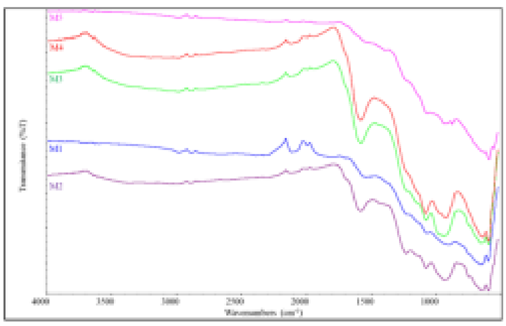

Figure 5. FTIR spectroscopy of char formulations after 1 h fire test.

The M1 sample observed typical absorption peaks at 2388, 2114, 662, and 598 cm^{-1}. A band at 2388 cm^{-1} indicates the bending vibration of (-CH-CH_2-) bonds of cured epoxy resin and the O-P-O occurred at 598 cm^{-1} due to APP [12]. With regard to samples added nanoclay, similar peaks appeared at around 1580, 1076, 930, 644, and 595 cm^{-1}. The symmetrical deformation of CH_2 and CH_3 was observed at around 1580 cm^{-1} due to the decomposition of melamine. The band at 1076 cm^{-1} belongs to the P-O stretching vibration in the P-O-C structure [13, 14]. The band at 938 cm^{-1} corresponds to the Si-O bond. The alcoholysis process of the polyphosphate chain formed the P-O-C bond [15].

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

3.4. Char Morphology

The char morphology of intumescent coatings after the fire test was carried out by SEM and shown in Figure 6. Sample M1 showed that the chars have a loose structure, and it was broken into small pieces while the char structure of sample M5 appeared many holes and cracks. Therefore, it provided convenience for flame and heat to reach the substrate, leading to poor fire protection. The charred structure of the samples containing nanoclay showed a compact char layer without cracks, a porous, and uniform foam structure. That was the reason why adding nanoclay to the formulations displayed better fire protection than the sample without nanoclay (sample M1).

3.5. Char Composition

To determine the ingredients of the char after the fire test, the EDS analysis of the coatings was used. The result is exhibited in Table 2. EDS spectroscopy of M1 and M3 samples is shown in Figure 7.

The char's carbon composition showed the level of carbonized and oxygen composition presented the oxidation level of the sample after combustion. The char layer having a lower C/O ratio has less antioxidant characteristics than the char layer with a higher C/O ratio [16].

The C/O ratio of sample M3 was 2.92 while this ratio of sample M1 was 2.1. The C/O ratio of the samples surged when adding nanoclay, which revealed the better anti-oxidation performance of the char structure under exposure to the fire.

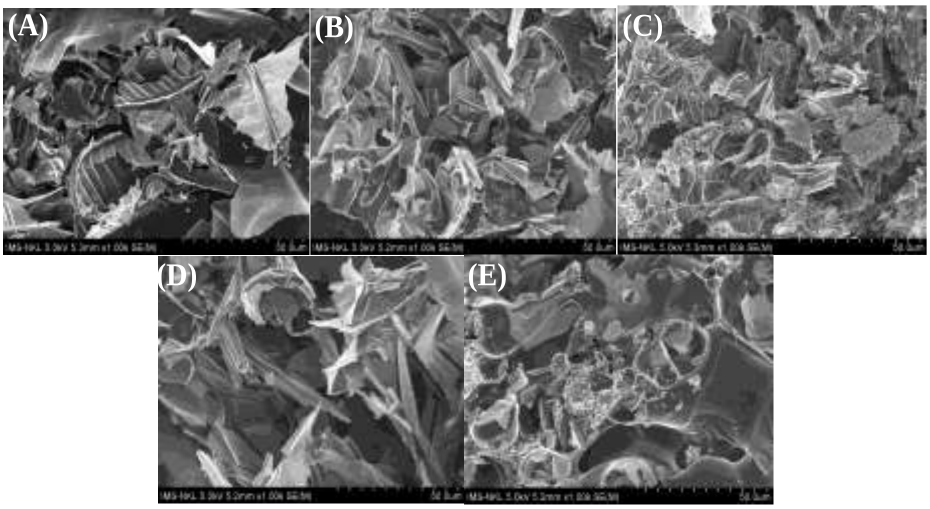

Figure 6. SEM images of char layer: M1(A), M2(B), M3(C), M4(D), and M5(E).

Table 2. Percentage of elements in the char layer

Samples	**Element percentage (wt.%)**						
	C	**O**	**P**	**Ca**	**Si**	**Ti**	**C/O**
M1	63.01	29.89	4.75	1.26	0	1.09	2.10
M2	60.16	21.92	8.56	3.94	0.82	4.60	2.74
M3	47.32	16.19	14.32	7.52	3.67	8.63	2.92
M4	58.36	27.13	8.37	2.35	1.16	2.13	2.15
M5	57.06	26.83	7.79	4.16	1.83	1.47	2.12

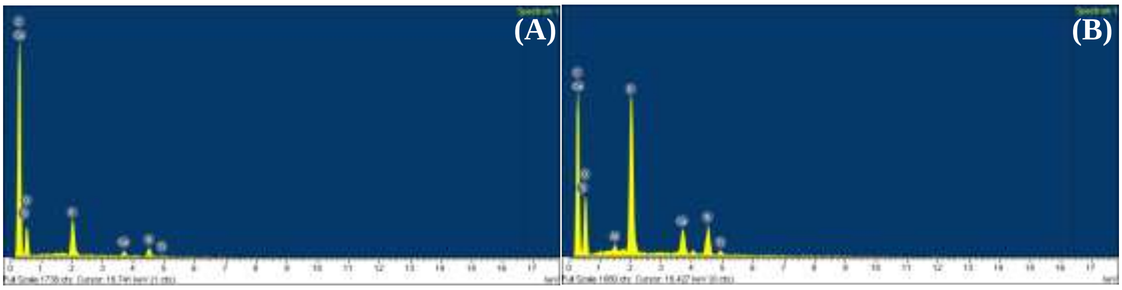

Figure 7. EDS spectroscopy of the char coatings: M1 (A) and M3 (B).

3.6. Thermal Degradation

The influence of nanoclay on the thermal stability of the coating was characterized by the TGA spectroscopy at 10 ^oC/min in an air atmosphere from room temperature to 900 ^oC. Weight loss diagrams are presented in Figure 8.

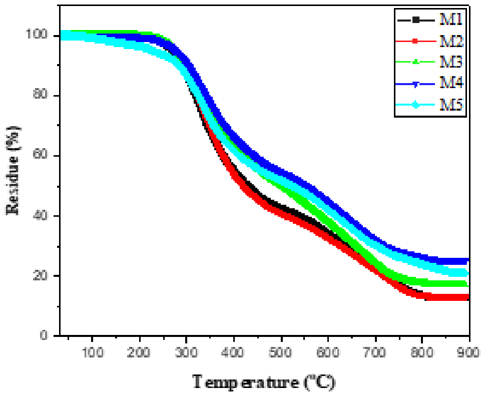

Figure 8. TGA curves of the coatings.

The results showed that the M1, M2, M3, M4, and M5 formulations have weight residue values of 12.61, 13.11, 16.92, 25.19, and 21.09 (wt.%) at 900 ^oC, respectively. The higher residual weight of the coatings with the addition of nanoclay compared to the coating sample without nanoclay, indicated that the addition of nanoclay could improve the fire resistance performance. DTG curve of the intumescent coatings is presented in Figure 9.

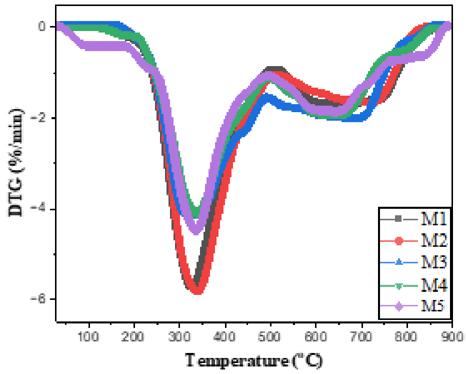

Figure 9. DTG curves of the coatings.

As we can see from the DTG diagram, the thermal degradation of the intumescent coatings includes five steps. The first stage is below 200 ^oC, which is attributed to residue water and partial decomposition of the samples. The stage between 200 and 300 ^oC is due to the degradation of PER which releases NH_3 gas. The weight loss of about 48% from 300 to 400 ^oC is caused by the decomposition of APP and melamine was 330-410 ºC [10]. 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 the carbonaceous char decomposes and the residue is inorganic phosphates [9].

4. Conclusion

We have successfully synthesized the intumescent retardant coating based on APP, PER, MEL, TiO_2, nanoclay, and epoxy resin. The influence of nanoclay content on the fire performances of the intumescent coating has been investigated. The presence of nanoclay can significantly enhance the thermal properties of the intumescent coating by increasing the quantity of residual weight left after thermal degradation. This research indicated that the sample added 3% of nanoclay can decrease the backside steel plate temperature to 92 °C after a 1-hour test compared to the coating without nanoclay. After the fire test, the char expansion and residue char have also improved compared to the reference sample. Therefore, nanoclay can be used as a potential candidate for enhancing the fire performance of the intumescent retardant coating which is applied for the protection of steel structures.

Acknowledgements

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