Investigation on solvent-borne intumescent flame-retardant coatings for steel

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This paper presents an investigation on solvent-borne intumescent flame-retardant coatings that can provide good bonding strength, water resistance and fire protection to the steel substrate. The fire protection performance and characterisations of the coatings were investigated by using the Bunsen burner test, thermogravimetry analysis, field emission scanning electron microscope, static immersion test and Instron Micro Tester. It was found that the fire protection and foam structure of the coating significantly improved by adding the combination of Mg(OH)2 and TiO2 flame-retardant fillers to the flame-retardant additives and acrylic binder. The formation of uniform foam structure and reaction of the coating which decompose into voluminous and multi-cellular char layers with thermal insulation properties contribute an important fire protection to the steel substrate from reaching its critical temperature. However, the combination of [Al(OH)3 and Mg(OH)2] flame-retardant fillers to the flame-retardant additives and epoxy binder led to maximum adhesion strength. The improvement in the bonding properties of the coating to the metal surface was attributed to the effective [Mg(OH)2 and TiO2] fillers/epoxy binder interface adhesion. Hence, the findings of this study reveal that the selection of appropriate combination of binders and flame-retardant fillers strongly influenced the fire protection, water resistance and mechanical properties of intumescent coatings.

Keywords: Acrylic resin, Epoxy resin, Flame-retardant additives, Intumescent coating, Steel

Introduction

Intumescent flame-retardant coatings act as passive fire protection (PFP), have played a significant role for containing the fires or slowing the spread of flame to the substrate. Intumescent coatings have typically applied to a steel structure to maintain the structure element properties below the critical temperature of 550°C. Usage of intumescent flame-retardant coating has highly recommended as PFP in infrastructure projects as it can protect precious human lives and properties against fire.1 Passive fire protection of steel members has typically achieved by using intumescent coatings, cement-based sprays and gypsum boards.2 The binder became important during the intumescent process because of the contribution of the protective char layer expansion and the formation of uniform foam structure.3–5 However, hydrophilic flame-retardant additives [ammonium polyphosphate (APP), pentaerythritol (PER) and melamine (MEL)] in the coatings were very sensitive to acid, alkali and water.6 The corrosive substances could be easily corroded the coatings in corrosive environment.7 The binder acting as a film-forming component could extremely reduce migration of flame-retardant additives and access of the corrosive substances.8,9 Moreover, polymer binders such as acrylic resin were not efficient enough to provide good water and corrosion resistance.10 Recently, many researchers have intensively studied the performances of intumescent coatings in terms of fire protection, water resistance and mechanical properties.11–17 There are several methods to produce intumescent fire protective coating. Currently, intumescent fire protective coatings have fabricated from three fire retardant additives comprising an acid source (APP), a carbon source (PER) and a blowing agent (MEL) mixed together with a binder. In addition, incorporation of any inorganic flame-retardant filler [such as aluminium hydroxide (Al(OH)3) or magnesium hydroxide (Mg(OH)2)] has significant influence on the final use properties of intumescent coatings, especially for the fire retardant performance. Incorporation of inorganic fillers resulted to the prevention of the melt dripping of intumescent coating in the event of a fire.9 To form an effective protective char layer, the flame-retardant ingredients and binder have to be optimised in terms of physical and chemical properties.18 This protective char layer creates heat shield in the surface and impedes the heat transfer to
steel, resulting in the protection of the underlying material.19

This work presents an experimental study to assess the performance of solvent-borne intumescent coatings as a PFP material. The influences of flame-retardant fillers on thermal degradation, fire resistant and adhesion strength of intumescent coatings have evaluated. Besides that, water resistance of intumescent coatings has also analysed.

**Experimental work**

**Materials**

In this research, acrylic resin and epoxy resin were used as a binder. Acrylic resin is a 100% solid thermoplastic substance derived from acrylic acid, methacrylic acid, esters of these acids or acrylonitrile and is a general purpose polymer with good hardness, broad compatibility and weather resistance. Furthermore, epoxy resin is derived from bisphenol A and epichlorohydrin. This epoxy resin has excellent properties on water resistance, mechanical strength and corrosion protection.

Three main flame-retardant agents, two fillers and pigment have been selected:

1. APP phase II (n > 1000)
2. MEL (Melamine)
3. PER (Phenolic resin)
4. magnesium hydroxide [Mg(OH)\textsubscript{2}] and aluminium hydroxide [Al(OH)\textsubscript{3}] act as flame-retardant filler
5. titanium dioxide (TiO\textsubscript{2}) acts as a pigment and non-combustible filler.

The compositions of intumescent coatings are listed in Table 1. The formulations were prepared by mixing the components using a high-speed disperse mixer (3000 rev min\textsuperscript{-1}). The prepared coating was coated on a steel plate using a gun sprayer.

**Fire protection performance test**

The Bunsen burner test has carried out to examine the fire protection performance of the intumescent coating during burning. The intumescent paint has sprayed onto the grit-blasted steel plates (dimensions: 100×100×2.6 mm). This process has repeated five to seven times until 1.5 ± 0.2 mm dry film thickness has achieved. The gas consumption of the Bunsen burner was about 160 g h\textsuperscript{-1}, and the coated plate mounted vertically has exposed to fire (about 1000°C) for 60 minutes. In this study, the critical temperature of 400°C has chosen for steel.12 The temperature profile during exposure to fire has recorded using a digital hand-held thermometer. Moreover, the thickness of the char layer after burning has measured in order to check the fire resistive performance of the intumescent coating.

**Thermogravimetric analysis**

Thermogravimetric analysis (TGA) has carried out at 20°C min\textsuperscript{-1} under air flow (100 mL min\textsuperscript{-1}) using a TGA/SDTA851e model to study the thermal stability and determine the residual weight of the coatings.

**Field emission scanning electron microscopy**

Field emission scanning electron microscopy (FESEM) has used to examine the surface morphology of the intumescent char layers. For FESEM observation, low beam energy of 1 kV has operated to reduce the possibility of any thermal damage to the char layers.

**Static immersion test**

The static immersion test is considered as a standard method that evaluates water resistance of films using the gravimetric method. Samples of films were immersed in distilled water at 25°C. At a specific time intervals, the samples were removed and were blotted to absorb excess water on surfaces with a piece of paper towel. Weight change was calculated by equation (1) and expressed as a function of time:

\[
E_w = (W_o - W_o)/W_o \times 100\% \tag{1}
\]

where \(E_w\) is the water uptake ratio of film, \(W_o\) denotes the weight of the film at different times and \(W_o\) is the dry weight of sample.

**Adhesion strength**

The adhesion strength of the coated sample was determined by using the Instron Micro Tester equipment. The coatings were each sprayed on one side of 50×50×2.6 mm steel plates with a film thickness of 0.2 ± 0.05 mm. The steel plate with a dry film was attached to a bare steel plate (dimensions: 50×50×2.6 mm) using epoxy glue (thickness of 0.5 ± 0.05 mm). Then the two steel plates were then continually drawn apart in tensile mode at a constant rate of 1 mm min\textsuperscript{-1} along the plate face using the testing device until the coating on the steel plate cracked. Adhesion strength (\(f_b\)) in megapascal was calculated based on the following equation (2):

\[
f_b = F/A, \tag{2}
\]

where \(f_b\) is the adhesion strength, MPa; \(F\) is the crack charge, N; and \(A\) is the sticking area, mm\textsuperscript{2}.

| Table 1 | The compositions of the solvent-borne intumescent coatings |
|---|---|---|---|
| Composition (wt-%) | Polymer binder | Flame-retardant additives | Flame-retardant fillers |
| A | Acrylic resin | APP/MEL/PER | TiO\textsubscript{2} | Mg(OH)\textsubscript{2} | Al(OH)\textsubscript{3} |
| B | 55-60 | 18.5/9.25/9.25 | 3.7 | 3.7 | ... |
| C | 55-60 | 18.5/9.25/9.25 | ... | 3.7 | 3.7 |
| X | Epoxy resin: hardener | APP/MEL/PER | TiO\textsubscript{2} | Mg(OH)\textsubscript{2} | Al(OH)\textsubscript{3} |
| Y | 44-50:11.10 | 18.5/9.25/9.25 | 3.7 | 3.7 | ... |
| Z | 44-50:11.10 | 18.5/9.25/9.25 | ... | 3.7 | 3.7 |

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*Yew et al. Investigation on solvent-borne intumescent flame-retardant coatings for steel*
Results and discussion

Fire protection of coatings

The four kinds of coatings (marked as A, B, X and Y) were studied using the fire protection test. The evolution of temperature at the back of the steel plates coated with the four different coating formulations, respectively, was recorded and compared (as shown in Fig. 1). The influences of binder and flame-retardant filler on fire protection of coatings were evaluated.

The curves of the temperature profiles were similar for all the coatings. During the first 5 minutes, the temperature increased rapidly of each coating. Then after 30 minutes of the test, the temperatures of coatings A, B, X and Y reached an equilibrium value and almost remained constant. The experimental results showed that the thickness of the intumescent protective layer of A, B, X and Y is 25-7, 22-5, 18-7 and 14-6 mm, respectively, and their relative equilibrium temperature is 188, 201, 285 and 323°C, respectively. The intumescent char has formed by coatings X and Y with the content of epoxy that hinders the amine and carbon dioxide from swelling, resulting in producing a ‘lampwick’ influence on the fused compound. The ‘lampwick’ effect lowers flowing of the fused compound and hence severely damages the intumescence of the coatings. A significant decrease in the thickness of the protective layer adversely affects fire protection performance of coatings X and Y.20,21 The intumescent char made by coating A can provide excellent fire protection for metal substrate because of its significant increase in the thickness of the intumescent protective layer. It indicated that the equilibrium temperature of coatings (A and B) was decreased with the content of acrylic binder, and the equilibrium temperature of A was obviously lower than those of other coatings.

Morphology of intumescent char layers

High magnification surface micrographs enables the observation of the surface morphologies of form structures (marked as A, B, X and Y) are shown in Fig. 2.

The efficiency of the char layer depended strongly on its physical structure.22 The porosity of the surface structure (Samples B, X and Y) was clearly observed. The heat and fire may be transferred to the steel substrate through the foam structure that is porous, which could lead to a reduction of the fire protection of B, X and Y. The char layers of X and Y showed agglomeration and coalescence of the foam structure because of the content of epoxy, with Y having a greater level of agglomeration and coalescence.23 The results indicate that the agglomerations of the foam structure of Samples X and Y were not uniform and porous, which could increase the rate of heat transfer and reduce the efficiency of fire protection. Furthermore, the intumescent char layer of A had a uniform and dense foam structure with the content of acrylic. This foam structure could isolate the steel substrate from fire and provide better fire protection.

Thermal analysis of coatings

Thermal degradation of coatings A, B, X and Y was analysed using the TGA test as shown in Fig. 3. The curves of the coatings (A and B) were similar between 100 and 300°C, and weight loss of each coating was less than 35 wt-% at 300°C. When the temperature was higher than 300°C, the TGA curves of the coatings became slightly different from each other. The TGA curves showed that the residue weight of the coating A was higher than a coating B at 1000°C.

Furthermore, the curves of the coatings X and Y were similar between 100 and 420°C, and weight loss of each coating was less than 20 wt-% at 300°C. The TGA curves of the coatings X and Y became slightly different from each other at a temperature of 420°C. The residue weight of coatings A, B, X and Y at 750°C was 28-07 wt.%, 27-76 wt.%, 17-70 wt.% and 12-98 wt.%, respectively. When the temperature is higher than 850°C, there is no weight loss of the coatings. The weight loss at 250–300, 300–400 and 400–620°C initiates intumescence of coatings A and B with the content of acrylic. However, the weight loss of each coating was less than 20 wt-% at 300°C. The TGA curves of the coatings X and Y became slightly different from each other at a temperature of 420°C. The residue weight of coatings A, B, X and Y at 750°C was 28-07 wt.%, 27-76 wt.%, 17-70 wt.% and 12-98 wt.%, respectively. When the temperature is higher than 850°C, there is no weight loss of the coatings. The weight loss at 250–300, 300–400 and 400–620°C initiates intumescence of coatings A and B with the content of acrylic. However, the weight loss at 300–400 and 400–620°C initiates intumescence of coatings X and Y with the content of epoxy. Thermogravimetric analysis results demonstrated that coatings decompose, absorb heat, swell and form the protective char layers at the different temperature ranges, and, therefore, these cooperated reactions provide a good fire protection for the metallic substrate in a fire. The higher residue weight of the Sample A indicated that the appropriate combination of 3-7 wt-% TiO2 and 3-7 wt-% Mg(OH)2 with flame-retardant additives and acrylic binder, resulting in the enhancement of the anti-oxidation, thermal stability and fire protection performance of the coating.

Static immersion test

The weight change rate curves of the thin film coatings are shown in Fig. 4. When Samples A, B, X and Y were immersed in water for 12 hours, two main processes (permeation and migration) took place. In this experimental work, the migration process occurred in Samples A and B. Moreover, the permeation process occurred for Samples X and Y.

A weight loss rate of Samples A and B is 18-7 and 12-1%, respectively. Sample B has better water resistance compared to Sample A because of its higher water resistance of Mg(OH)2 and Al(OH)3, flame-retardant fillers. Incorporation of Al(OH)3 to flame-retardant additives and acrylic binder could slow down permeation of water and migration of fire retardant additives of Sample B because of its poor solubility in water,24 which led to an improvement in the water resistance of coatings. However, Sample A had poor water resistance.
with the addition of TiO$_2$ and Mg(OH)$_2$ flame-retardant fillers. In the migration process, some hydrophilic fire retardant additives might migrate from coating and could be dissolved in water. It was observed that the water could destroy some components of hydrophilic flame-retardant additives and flame-retardant fillers as well as break some bonds of binders, so the water resistance of intumescent coatings decreased significantly.

Moreover, water could infiltrate into the pore structure of the coating, which led to the increase of weight of Samples X and Y. The experimental results show that the weight gain rate of Samples X and Y maintained relatively constantly (only 0-18%) at 12 hours because of their excellent performance in water resistance with the content of epoxy resin. After immersing in water for 12 hours, the cracking and blistering phenomena did not occur in all samples. The weight change rate of all samples maintained relatively constant after 10 hours of the test when the two processes of coatings reached equilibrium.
Adhesion strength of intumescent coating
The adhesion strength of Samples A, B, X and Y was 0.37, 0.26, 1.28 and 0.69 MPa, respectively. The adhesion strength of coatings A and B with the content of acrylic is lower than that of coatings X and Y with the content of epoxy. The adhesion strength of coatings X and Y is obviously enhanced by epoxy resin. The difference in the bonding strength of coatings X and Y is 0.59 MPa. This indicated that the coating X with the optimal combination of TiO₂ and Mg(OH)₂ to the components led to a significant improvement in bonding strength when compared to the coating Y [addition of Mg(OH)₂ and Al(OH)₃]. It can be concluded that coating X containing 3.7 wt-% TiO₂ and 3.7 wt-% Mg(OH)₂ is efficient enough to improve the adhesion strength of the coating without the expense of fire-resistant properties.

Conclusion
In this study, the solvent-borne intumescent coatings have investigated and evaluated. The fire protection performance and foam structure of the coating A has significantly improved by adding Mg(OH)₂ and TiO₂ to flame-retardant additives and acrylic, which produced the greatest thickness of the char layer. In addition, the thermogravimetric analysis results showed that the residue weights of the Sample A were higher than that of other samples. This indicates that the Sample A has better anti-oxidation because of its optimal combination of acrylic and flame-retardant ingredients. The results of Instron Micro Tester indicate that the adhesion strength of the coatings (X and Y) has improved with the epoxy content. Coating X showed the excellent water resistance and exhibited maximum bonding strength to the metal surface because of its effective coating/steel interface adhesion. Hence, this study reveals that the selection of the appropriate combination of flame-retardant ingredients and binders strongly influenced the physical and chemical properties of intumescent coatings.

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