Effects of hybrid flame-retardant fillers on fire-resistive and mechanical properties of solvent-borne intumescent coatings

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Abstract. The aim of this research project was to investigate the effects of hybrid flame-retardant fillers on the fire protection and mechanical properties of solvent-borne intumescent coatings. Formulations of intumescent coatings with different combinations of flame-retardant fillers were developed and investigated through Bunsen burner test, adhesion strength test and Scanning Electron Microscopy (SEM). It was found that the formulation of intumescent coating was optimized with four combinations of flame-retardant fillers in proper compositions and had improved the fire protection performance and mechanical properties of the coating. In overall, filler compositions of coating sample D (1 wt.% nano CES/ 2 wt.% expandable graphite/ 1 wt.% zinc borate/ 4 wt.% calcium silicate) had contributed to positive fire protection performance (equilibrium temperature of 190 °C) and adhesion strength (2.62 MPa). Significantly, the incorporation of an appropriate combination of hybrid nano CES bio-filler, expandable graphite, zinc borate and calcium silicate had led to a better fire protection performance and mechanical properties of the solvent-borne intumescent coating.

1. Introduction

Fire protection has become one of the most important key considerations especially in building designs around the world due to the risks of fire. Fire can bring the risks of taking human’s life and loss of property, at the same time will cause the environmental effects, which are the air pollution problems resulting from the emission of toxic gases and smokes during the combustion process. Generally, the fire protection system is divided into two main types, which are active and passive systems. The examples of passive systems mainly consist of fire doors and fire protective coatings [1].

Intumescent coatings which act as passive fire protection (PFP) have been widely used in steel structures, offshore oil rigs, air crafts and building components to slow down the spread of fire to ensure the fire safety by following the building regulations practice in many countries [2]. It is considered as one of the most economical, easiest, and effective methods to prevent the rapid spread of flame during the event of fire to protect the substrates and building structures [3]. In addition, intumescent fire protective coatings consist of the flame-retardant materials which have obtained broad acceptance for fire protection application in worldwide [4]. Application of intumescent fire protective coatings have been highly recommended as passive fire protection (PFP) in buildings or infrastructure projects.
especially commercial buildings as they can reduce the destructing cost of fire in terms of both human life risks and damage of property.

The advantages of intumescent coatings are light in weight, easily to be coated, have a good decorative effect and do not change the intrinsic properties of steel [5]. Normally, intumescent coatings are composed of three flame-retardant additives, which are an acid source namely ammonium polyphosphate phase II (APP), a carbon source namely pentaerythritol (PER) and melamine (MEL) which acts as blowing agent combined with various flame-retardant fillers and a polymer binder. The coating will expand once exposed to adequately high temperature by releasing non-combustible gases to form a protection barrier against oxygen, thereby protecting the substrate from heat or flame. Moreover, incorporation of any flame-retardant filler has a significant effect on the end use properties of intumescent coatings, especially the fire-retardant performance [6]. This research project highlights a beneficial bio-filler extracted from the chicken eggshells (CES) bio-waste and its potential role in the fire protection coatings industry. Recently, CES has accumulated attention due to its reclamation potential. The chemical composition and availability of CES has made it to become a potential source of compatible bio-filler to improve the thermal and mechanical properties to the intumescent coatings [7,8].

2. Experimental program
2.1. Materials and sample preparation
In this research project, different formulations of intumescent fire protective coatings were prepared with various combinations of flame-retardant fillers with fixed ingredient of flame-retardant additives and polymer binder. Table 1 shows the compositions of solvent-based intumescent coatings.

| Table 1. Compositions of Intumescent Coatings |
|---------------------------------------------|
| **Materials**                  | **Coatings (grams)** |
|                               | A     | B     | C     | D     |
| Flame-retardant additives     |       |       |       |       |
| APP                           | 20    | 20    | 20    | 20    |
| MEL                           | 10    | 10    | 10    | 10    |
| PER                           | 10    | 10    | 10    | 10    |
| Binder                        |       |       |       |       |
| Acrylic Resin                 | 50    | 50    | 50    | 50    |
| Pigment                       |       |       |       |       |
| TiO₂                          | 2     | 2     | 2     | 2     |
| Flame-retardant fillers       |       |       |       |       |
| Nano CES                      | -     | -     | -     | 1     |
| Expandable graphite           | -     | 4     | 2     | 2     |
| Zinc borate                   | 8     | 4     | 2     | 1     |
| Calcium silicate              | -     | -     | 4     | 4     |

*Bunsen burner test*

The purpose of Bunsen burner test is to investigate the performance in fire protection of intumescent coating during fire and to determine the thickness of the protective char layer formed after exposed to fire. Each coating sample prepared had applied by painting method onto a steel plate, each with a dimension of 100 mm × 100 mm × 3 mm. This coating process was repeated for several times until the coating thickness of 2 mm ± 0.2 mm was achieved. In this research project, the critical temperature of 400 ºC was chosen and set for the steel plate to ensure a higher level of safety. Basically, the critical temperature of 400 ºC was chosen due to the reason that steel will lose its properties at around 550 ºC. During the burning process (about 1000 ºC), the temperature profile of the coated steel plate was mounted vertically and recorded using a digital handheld thermometer, which connected to a
thermocouple plate located behind the coated steel plate for 60 minutes as shown in Figure 1. The gas consumption of the Bunsen burner was set at about 160 g/h. The distance between the coated steel plate and fire source was fixed at about 8 cm. The response of intumescent coating during the burning process was observed. The temperature changes of the steel plate were recorded for the first 6 minutes (at 1-minute time interval) and every increment of 3 minutes after the first 6 minutes onwards. The thickness of the char layer formed by each sample after the test was measured and recorded using the steel ruler.

2.2. Adhesion strength test
The purpose of adhesion strength test is to determine the bonding strength of the intumescent coatings prepared. The adhesion strength of each coating sample was investigated with the aid of the Instron Micro Tester. The two attached cylindrical steels coated with sample coating and epoxy resin were fixed on the Instron Micro Tester machine and then drawn apart vertically and continuously in tensile mode at constant rate of 1 mm per minute, as shown in Figure 2, until the intumescent coating on the cylindrical steel cracks. Meanwhile, the adhesion strength, $f_b$ (N/m²) for each coating sample was calculated using the equation below:

$$ f_b = \frac{F}{A} \quad (\text{equation 1}) $$

where

- $f_b$ = the adhesion strength (N/m²);
- $F$ = the crack charge (N);
- $A$ = sticking area of the intumescent coating on the cylindrical steel surface (m²).

2.3. Scanning Electron Microscopy (SEM)
Scanning electron microscopy, which is commonly known as SEM, was carried out to investigate the surface morphology of the char layers formed by intumescent coating. The cracking parts and porosity of the char layers formed by different intumescent coating samples can be observed and analysed by using SEM. In this research project, SEM was operated at low beam energy of 1 kV for observation, in order to minimize the thermal damage’s possibility to the char layer. In addition, SEM was operated under two levels of magnification, which are 1000 and 8000 magnification.

3. Results and discussion
3.1. Bunsen burner test
There were four kinds of coating samples (marked A, B, C and D) that were conducted through Bunsen burner test. The evolution of temperatures at the back of each coated steel plate and the thickness of char layer formed were recorded and compared. The temperature profiles for coating samples were shown in Figure 3, while the thickness of char layer formed after the 60 minutes burning process was presented in Figure 4.
The fire protection results showed that the equilibrium temperature and thickness of char layer formed after 60 minutes burning process of coatings A, B, C and D were about 237 °C (9 mm), 201 °C (24 mm), 198 °C (25 mm) and 190 °C (28 mm), respectively. All coatings showed a similar rise in temperature at the first five minutes resulting from thermal degradation of the coatings and the formation of the char layer due to the physical and chemical reactions from the coating ingredients [9]. Coating A showed the worst fire protection performance with the highest equilibrium temperature of about 237 °C due to the char layer hard to expand with the addition of 8 wt.% zinc borate. A high dosage of zinc borate promotes the formation of a strong char layer, but it did not show a strong synergic effect with flame-retardant additives and polymer binder on the formation of multicellular char layer in protecting the steel. Coating D showed the best fire protection performance with a lower equilibrium temperature of about 190 °C, while coatings B and C had a slightly higher equilibrium temperature of about 200 °C. The difference in equilibrium temperatures of these two coatings was about 10 °C. Both coating formulations were added with same flame-retardant fillers (expandable graphite and zinc borate), but only differ in the amount of calcium silicate. The results showed that coating D which incorporated an with additional 1 wt.% of nano has promoted a better fire protection performance by having a lower equilibrium temperature. Since both coatings B and C had the almost same thickness of multi-cellular char layer formed (about 25 mm). The reason is that denser, uniform and less porous multi-cellular char layers promote a better efficiency in inhibiting the heat transfer to the underlying steel plate, thus resulting in lower equilibrium temperature. As a conclusion, the coating D (thickest char layer of 28 mm) shows a positive effect on fire protection performance to the underlying steel plate, with optimized formulation by adding proper combinations of flame-retardant fillers (nano CES, expandable graphite, zinc borate and calcium silicate). This indicates that there is a significant improvement in fire protection performance by incorporating hybrid flame-retardant fillers into the coating formulation.

3.2. Surface morphologies of char layers
Surface morphologies of the char structure formed by intumescent fire protective coating can be observed under high magnification surface micrographs through SEM. The char layers formed by the coatings A-D were conducted through SEM to observe the surface morphologies of their char structures. Figure 5 shows the surface morphologies of coatings A-D under magnification of 8000.
From the observation, it was found that the foam structure of coating A had a porous and non-uniform which was unable the char layer to insulate the heat effectively from reaching the underlying steel plate. In addition, there are some holes in its foam structure which led to the poor performance in fire protection due to the heat might transfer through the holes easily. The foam structure of char layers B and C was significantly improved by incorporating expandable graphite (which produced a denser and more uniform foam structure) compared to coating A which incorporated with only zinc borate flame-retardant filler (which produced porous, non-uniform and tiny foam structure). One contributing factor is that char layers formed by coatings B and C had a uniform and dense foam structure, which was able to isolate the underlying steel plate from heat or fire by offering a better fire protection performance. From the observation, it was found that the foam structure of coating D was significantly improved with an additional of 1 wt.% nano CES bio-filler content (which produced a denser and more uniform tiny foam structure) compared to other coatings. One contributing factor is that the foam structure of coating D demonstrated more even expansion cells burst which led to heat reduction by lessening heat transfusion rate and thus enhancing its fire protection performance.

3.3. Adhesion strength

The values of adhesion strength of coating samples A, B, C and D were 1249.89, 1620.31, 1979.86 and 2066.50, respectively. Coating D had the highest adhesion strength (about 2.62 MPa), while coating A had the lowest adhesion strength (about 1.58 MPa). One contributing factor is that coating D formulation has extra 1 wt.% of nano CES as compared to coatings A, B and C. The results indicated that appropriate combination of amount of nano CES, zinc borate, expandable graphite and calcium silicate would enhance the adhesion strength of the coating due to metal–polymer composites adhesive interfaces. The difference between the adhesion strength of both coatings (A and D) were about 1.34 MPa (about 39.69 % difference). Figure 6 shows the appearance of the bonding surface area for the coatings A (lowest), B, C and D (highest) adhesion strength after undergoing the pull off test.

As comparing the adhesion strength test results obtained, the bonding strength of the coatings was improved with proper combination of flame-retardant fillers in the coating formulation. The improvement in adhesion strength was about 40 % increment, by comparing the coating samples with the lowest adhesion strength. This indicated that the coating formulation to achieve the best adhesion strength for the coating has been optimized, whereby an appropriate amount of the combination of nano CES, expandable graphite, zinc borate and calcium silicate flame-retardant fillers with polymer matrix has contributed to the best adhesion strength.

4. Conclusions

Influence of flame-retardant filler on the fire protection and mechanical properties of solvent-borne intumescent fire protective coatings were analysed and investigated. Based on the overall results obtained, Coating D showed the best formulation in terms of fire protection performance and mechanical properties. The fire protection performance of the Coating D formulation (1 wt.% nano CES/ 2 wt.% expandable graphite/ 1 wt.% zinc borate/ 4 wt.% calcium silicate) had significantly improved with an appropriate combination of nano CES, expandable graphite, zinc borate and calcium silicate fillers, which contributed to the lowest equilibrium temperature performance of 190 °C and the highest adhesion strength of 2.62 MPa. Another contribution is that the Coating D has promoted a good expansion of char layer by forming the greatest thickness of char layer, which is able to insulate the heat
effectively. Furthermore, the incorporation of nano CES bio-filler had reduced the ingredient cost of the coating, at the same time preserve the environment. Hence, the finding from this research project reveals that an appropriate combination of hybrid flame-retardant fillers is important to optimize the formulation in terms of fire protection and mechanical properties of solvent-borne intumescent coatings.

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