Thermal performance of alumina filler reinforced intumescent fire retardant coating for structural application

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Abstract. In the modern construction, fire safety has significant consideration for the protection of people and assets. Several intumescent fire protection systems are in practice and have constrain of releasing toxic gases on degradation forms an insulating char layer protecting underlying substrate. An intumescent coating expands many times of its thickness on exposure to fire and protect the underlying substrate from fire. This study presents the results of thermal performance of an intumescent fire retardant coating (IFRC) developed for structural application. IFRC was developed using expandable graphite (EG), ammonium polyphosphate (APP) and melamine (MEL), epoxy resin Bisphenol-A (BPA) and hardener triethylenetetramine (TETA) were used as a binder as a curing agent. Char expansion of IFRC was measured by furnace fire test at 450°C, thermal performance was measured using a Bunsen burner at 950°C and temperature of substrate was recorded for 60 min at an interval of two min. Results showed that IFRC containing 3wt% alumina showed char expansion X19. After one hour exposure of coating to heat, substrate temperature recorded was 154°C. X-ray Diffraction (XRD) results showed the presence of high temperature compounds present in the char of coating, considered responsible to reduce the penetration of heat to the substrate.

1. Introduction

Steel is a commonly used material in the construction of our regular infrastructures almost existing in all construction of buildings, vehicles, airplanes and oil platforms. Steel acquire good strengths and ductility while also being incombustible, however steel loses its physical properties when subjected to heat at high temperature such as in the case of fire. Heat treated carbon steel begins to lose its mechanical properties at temperatures above 400°C and continues to reduce in strength at steady rate up to temperature of 800°C [1].

Intumescent coating is a type of passive fire protection system which commonly used to protect steel against fire. The coating comprises of three active ingredients, usually ammonium polyphosphate-APP, expandable graphite and melamine-MEL [2]. The three main ingredients are linked together with a binder which then reacts together at higher temperatures. The result of the reaction is the expansion of the coating and the formation of a foamed char. The resulting foamed char acts as a thermal barrier and help reduces heat transfer to the coated material.

The binders for intumescent coatings mainly based from organic binders which have good expanding effect and char structure. Although having a good expanding effect and char structure, organic binders release solvent, toxic gas and smoke in a fire [3]. Comparing with inorganic
intumescent coatings, the amount of toxic gas emission and smoke upon heating is relatively low. However, the inorganic intumescent coating only protects against fire at low temperature and are vulnerable to water and moisture [4, 5].

The objectives of this research work are to develop an intumescent coating formulation with added mineral based fillers of talc and alumina and to investigate the coating performance on the heat shielding effect, char expansion, structure, and water resistivity.

2. Materials and Methods

Ammonium polyphosphate (APP), expendable Graphite (EG), melamine (MEL), boric acid (BA), alumina, bisphenol A epoxy resin BE-188 (BPA) and Tetraethylene tetramine hardener and steel plate. The intumescent ingredients were mixed with their weight percentage composition homogeneously for 30min using Ultra Turrax mixer. The formulation NF (No filler) acts as a control with APP-EG-Boric acid-epoxy-hardener. The formulation was coated manually on the steel substrate. The coating was allowed to dry for 24 hours. Then, Bunsen burner and furnace oven was used for fire test. FEEM images of char formation were taken.

| Sample | BPA  | TETA | APP  | EG   | Mel  | ZB   | Filler |
|--------|------|------|------|------|------|------|--------|
| NF     | 44.44| 22.22| 11.11| 5.56 | 5.56 | 11.11|        |
| T1     | 43.94| 21.72| 11.11| 5.56 | 5.56 | 11.11| 1 (Talc)|
| T2     | 43.44| 21.22| 11.11| 5.56 | 5.56 | 11.11| 2 (Talc)|
| T3     | 42.94| 20.72| 11.11| 5.56 | 5.56 | 11.11| 3 (Talc)|
| T4     | 42.44| 20.22| 11.11| 5.56 | 5.56 | 11.11| 4 (Talc)|
| T5     | 41.94| 19.72| 11.11| 5.56 | 5.56 | 11.11| 5 (Talc)|
| A1     | 43.94| 22.22| 11.11| 5.56 | 5.56 | 11.11| 1 (Alumina)|
| A2     | 43.44| 21.72| 11.11| 5.56 | 5.56 | 11.11| 2 (Alumina)|
| A3     | 42.94| 21.22| 11.11| 5.56 | 5.56 | 11.11| 3 (Alumina)|
| A4     | 42.44| 20.72| 11.11| 5.56 | 5.56 | 11.11| 4 (Alumina)|
| A5     | 41.94| 19.72| 11.11| 5.56 | 5.56 | 11.11| 5 (Alumina)|

3. Analysis and Characterization

Heat shielding effect: Bunsen burner was used as a fire test source by using the standard UL94. K-type thermocouple connected to AMS-850 data logger was used to measure the temperature in front and the backside of the substrate. The flame temperature of Bunsen burner is 800°C.

Field Emission Scanning Electron Microscope (FESEM): The charring layer and the morphological structures of the char formation were observed and analyzed using SUPRA Instrument FESEM.

X-Ray Diffraction: The composition of residual char of the intumescent coating after the fire test was analysed by XRD and measurements were performed on a Diffractometer Bruker AXS D8 Advance using Cu Kα radiation and a nickel filter (k = 0.150595 nm) in the range (10 < 2θ < 90).

Static immersion test: Static immersion test is considered as a standard method to evaluate water
resistivity of coating using gravimetric method. Coating formulations were immersed in distilled water at 25°C and weighed every 24 h. The samples then were dried at 40°C for 1 h in furnace oven. Weight change percentage was calculated using Eq. (1), and the result was plotted against time.

\[ \Delta W = \frac{W_2 - W_1}{W_1} \times 100\% \]  

(1) \[ \Delta W \] weight loss, %; \[ W_1 \] sample weight before water immersion, g; \[ W_2 \] sample weight after water immersion, g.

4. Results and Discussion
4.1. Heat shielding effect
In this study, 11 samples with different compositions of intumescent ingredients were tested. The result after testing shows that formulation A5 which contains 5% of alumina fillers gives the best intumescent effect.

![Figure 1: Thermal behaviour of coating APP-EG-BA-Alumina-Epoxy and hardener.](image)

The temperature time curves for heat shielding of fire retardant coating with added alumina fillers are illustrated in Figure 1. The coating with no added filler has the backside substrate temperature of 290°C after 60 min. Fig 2, after 60 min, formulation A1 has the backside substrate temperature of 312.2°C, formulation A2 has the backside substrate temperature 332.0°C, formulation A3 has the backside substrate temperature of 196.0°C, formulation A4 has the backside substrate temperature of 282.8°C and formulation A5 has the backside substrate temperature of 154.6°C. From the alumina filled result, formulation A5 has the lowest backside substrate temperature followed by A3, A4, A1 and A2.

From the result, formulation A5 gives the best intumescent effect as it contains the highest percentage of alumina. Higher percentage of alumina gives better strength to the char formation thus giving the better intumescent effect. Alumina have outstanding physical ability such as high mechanical strength at room temperature and high melting point of 2050°C [6] hence higher percentage of alumina presence would enhance the heat shielding capability of the coating.
Figure 2: Thermal Behaviour of Coating APP-EG-BA-Talc-Epoxy and hardener.

The temperature time curves for heat shielding of fire retardant coating with added talc fillers are illustrated in Figure 2. The coating with no added filler has the backside substrate temperature of 290°C after 60 min. Fig 3, after 60 min, formulation T1 has the backside substrate temperature of 293.9°C, formulation T2 has the backside substrate temperature 270.1°C, formulation T3 has the backside substrate temperature of 132.4°C, formulation T4 has the backside substrate temperature of 254.2°C and formulation T5 has the backside substrate temperature of 237.7°C. From the heat shielding result of talc filled coating, formulation T3 has the lowest backside substrate temperature followed by T5, T4, T2 and T1. 3% filled talc formulation, T3, produces the best intumescent effect after A5 formulation. This is because presence of talc reinforces the mechanical stability of the intumescent protective shield [4]. A study conducted by Almeras et al. [7] on the effect of talc fillers suggested a chemical reactivity between talc and intumescent ingredients that may affect the performance of the formulation. The study demonstrates that the ratio percentage of talc and intumescent ingredients must be optimized to produce the best intumescent effect. This explains why 3% filled talc performed better than the higher filled talc formulation.

This proved that the addition of talc and alumina as fillers enhanced the fire retardant effect. The presence of alumina and talc provide better strength to the char structure and better mechanical stability thus maintaining the thermal barrier longer before rupturing.

4.2. Field Emission Scanning Electron Microscope (FESEM)
The FESEM micrograph images of char showing surface microstructure for sample A5 and T5 were obtained. Sample A5 and T5 were selected for testing as A5 gives the best intumescent effect and T5 as a direct comparison. The char obtained are from fire testing conducted earlier.
Figure 3 and figure 4 showed the holes and voids in FESEM image of formulation A5 and T5 respectively. The amount voids observed from formulation T5 is slightly lower compared to formulation A5. From Figure 5, no voids were observed due to the absence of filler which subsequently reduce the strength of the char. The holes were formed from evolution of trapped gas by blowing agent when the coating is subjected to fire. The voids act as a thermal barrier which prevent heat transmission to the substrate [7]. Voids also prevent diffusion of gaseous degradation products to the combustion zone and prevent oxygen diffusion to the surface polymer [8]. Fillers were believed to improve the efficiency of intumescent coating. This is down to the plate like microstructure of the fillers which consequently provide stabilizing effect on the cell structure of char foam [9]. This proved that the addition of talc and alumina fillers produced more voids compared to the no filled intumescent coating. Higher amount of voids produced means higher strength of char structure. This subsequently contributes to better intumescent effect.

Figure 3: FESEM micrograph A5 450°C char at 1000X.

Figure 4: FESEM micrograph T5 450°C char at 100X.
4.3. X-Ray Diffraction Analysis

After the residue char of the intumescent coating was gradually oxidized at high temperature, only some amorphous carbon and inorganic materials remained. The inorganic materials might be the main protecting layer at later stages of burning via XRD analysis [2]. Figure 6 and 7 shows the X-Ray diffraction peak of T5 formulation (5% talc) and A5 formulation (5% Alumina) with d-spacing value. Figure 6, it shows that after the addition of 5% talc, the d-spacing value obtained at 9.21968 and 2.98847 which is assigned to be Mg_2P_4O_{12} and Si_5O(PO_4)_6. Previous study performed by Levchik and co-workers [10] found that in XRD analysis, the residue of the reaction of talc and APP was ammonium Si(NH_4)_2P_4O_{13} at 300°C. At higher temperature, all the nitrogen group loss and the residue of magnesium cyclotetrapolyphosphate Mg_2P_4O_{12}, and silicon oxomonophosphate, Si_5O(PO_4)_6 was obtained. The overlapping peak at 3.8896, 3.51456 and 3.17264 is assigned to be titanium dioxide (TiO_2) and titanium pyrophosphate (TiP_2O_7). This residue can enhance char structure and protect the underlying substrate at higher temperature [11].

From Figure 7, the XRD analysis showed the existence of graphite, boron oxide (B_2O_3) and borophosphate (BPO_4). The dehydration of boric acid resulted in boron oxide which is a very hard glass. Besides, the formation of borophosphate was due to the reaction between ammonium polyphosphate and boric acid. When combining APP and boric acid, a good mechanical resistance is observed because borophosphate is a hard material. That resulted in providing the good structural properties of the char whereas phosphorous allows a good adhesion of the char to the steel plate [12].
4.4. Static immersion test

Weight change – time curves of all formulations are shown in Figure 8 and 9. Looking at the graph of alumina filled coating, weight change percentage of all the coating has increased dramatically from the first day until the fourth day of immersion where the percentage declined slightly. Equilibrium is not achieved in the initial stage of immersion therefore coatings continue to gain weight [13]. The increased weight change percentage is due to the absorption of water by the coating and the slight declination is due to the weight loss of the coating from formation of pores and damages to the surface [14]. The formation of pores allowed more water to be absorbed and the trend continue to increase until it reached physical and chemical equilibrium. Formulation A2 shows the highest water absorption rate of 0.167% and formulation NF has the lowest rate of absorption of 0.032%.
Based on the weight change time curves of talc filled intumescent coating, the trend of the curves are almost similar with alumina filled coating but with more settled curves. Formulation T1 has the highest water absorption of 0.170%. The talc filled intumescent coating does not produce pores and surface defects as alumina filled coating thus reaching physical and chemical equilibrium after 48 hours of testing.

5. Conclusion
The fire retardant time of EG-APP-Mel-B.A coating with 5% wt alumina showed the best intumescent effect and the temperature of the substrate was 154.6°C after 60 min. FESEM result showed improved formation of voids by addition of talc and alumina. Thus, the rate of heat transfer to the steel substrate can be reduced therefore giving better intumescent effect. Static immersion test show that alumina does not improve the water resistivity of the coating while talc improved the water resistivity by achieving equilibrium faster after just one day of immersion. Talc filled coating also does not produce pores and surface defects compared to alumina. Thus, the water resistivity is improved by the addition of talc.
6. References

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