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CeO_2-dolomite as fire retardant additives on the conventional intumescent coating in steel substrate for improved performance

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Abstract. Multiple combinations of CeO_2-Dolomite as fillers and Intumescent Flame Retardant (IFR) ingredients were used to optimize the intumescent coatings designed for I-beam steel substrates. The influenced of fillers and various combinations of flame-retardants on the fire protective performance of the coatings were evaluated using vertical Bunsen burner fire test and various characterization techniques. Formula C and Formula F having 1:1 and 2:2 CeO_2- Dolomite ratio, obtained the lowest substrate temperature around 150^{o}C and 150.4^{o}C, respectively after 90 minutes fire exposure. Also, the morphological structures of intumescent char observed by SEM-EDX, demonstrated that Formula C and Formula F stimulated the formation of homogeneous and more compacted surface structure. X-ray photoelectron spectroscopy (XPS) provide the binding energies of C and O constituents, it was observed that [-(C_2H_4)n-] was the most important free radical as it could promote the formation of aromatic carbon chain in the char surface. Finally, the findings of this study revealed that the selection of appropriate fillers and combinations of flame-retardant ingredients significantly influenced the morphological structure of the char layer, of which, Formula C and Formula F produced a char with higher thermal stability, resulting to a more fire resistive IFR coating during fire exposure.

1 Introduction

Intumescent coating used in steel-based infrastructures has become one of the essential requirements of fire safety construction legislation in many countries **[1,2]**. However, as reflected in Presidential Decree No.1096 also known as the National Building Code of the Philippines (1977), Chapter VI, Section 604 (Fire-resistive Requirements in Construction Materials), by no means, has no provisions relating to the application of fire retardant coatings **[2,3]**.

Steel undergo one major disadvantage during the event of fire, of which, when the temperature reaches 500^{o}C, the steel loses its structural integrity. Thus, this material needs to be protected from this incidence **[3-5,8]**. To resort solutions, chemical species so-called flame retardants have been developed in order to reduce the risk of fire. Compared to other fire retardants such as fire extinguisher, intumescent coatings are far different because these are passive coatings that decompose to produce a char, and this char provides us the protective barrier to prolong heat penetration prior to the failure of material.

On the current development of Intumescent Fire Retardant (IFR) coatings, researchers concluded that the performance of intumescent coating depends on the choice of ingredients and their appropriate combinations. Conventional IFR coating system having Ammonium polyphosphate as the acid source, melamine as the blowing agent and expandable graphite as the carbon source (APP-MEL-EG IFR system) , had shown to have poor thermal and char stability, owing to its poor morphological configuration which thus further destroy the flame retardant efficiency **[6]**.

Previous research conducted by Gillani et.al (2016), they integrated dolomite as an additive in the APP-MEL-EG coating system, as a result, dolomite significantly improve the thermal performance of the coating based on the resulting microstructure, wherein the resulting char formed a homogenous compacted layer after 500 ˚C. On the other hand, Feng et. al, (2016) used CeO_2 as an additive, wherein CeO2 significantly presents excellent catalytic effect that improves the thermal performance of the char structure owing to the formation of homogeneous compacted char layer as early as 250 ˚C **[7,8]**.

However, there are no reports regarding synergistic char formation regarding the combination of two (2) additives integrated in the conventional IFR system. Thus, this study will make a novel approach to

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investigate the effect of CeO_2 and dolomite on the char-forming behavior and fire performance of conventional IFR Coatings.

2 Materials and methods

2.1 Materials and reagents

Table 1 shows the experimental composition for each sample designed for this experiment. APP-EG-MEL IFR system consisting of Ammonium polyphosphate (APP, average polymerization degree n > 1000, Sigma Aldrich) as the acid source, Expandable Graphite (Sigma Aldrich) as the carbon source and Melamine (Sigma Aldrich) as the blowing agent were provided by Merteflor Enterprises.

Dolomite (99.99%) and Cerium oxide (99.99%) was purchased from Sigma Aldrich Singapore having CDS000645 and 1306-38-3 CAS no., respectively.

Table 1. IFR coating sample composition

SAMPLE I.D	IFR SYSTEM	Additives	
		Dolomite	CeO_2
BLANK	APP-MEL-EG	0	0
FORMULA A	APP-MEL-EG	1	0
FORMULA B	APP-MEL-EG	0	1
FORMULA C	APP-MEL-EG	1	1
FORMULA D	APP-MEL-EG	2	1
FORMULA E	APP-MEL-EG	1	2
FORMULA F	APP-MEL-EG	2	2
FORMULA G	APP-MEL-EG	3	3

The preparation of APP-EG-MEL intumescent flame retardant with the addition of CeO_2 and Dolomite was derived from the research conducted by Gillani et. al (2016). CeO_2 and Dolomite were mixed together in advance for 20mins to obtain a homogeneous mixture, and then the curing agent was added to the mixture and was mixed for another 10 min. The composites were prepared via Imarflex shear blending mixer with a rotor speed of 250 rpm. The mixing temperature and time was set at 170 ˚C for 8 min for each sample.

2.2 Fire protection protective test

The UL-94 vertical tests (Bunsen Burner Fire Test) were performed on a Methane-Butane Bunsen Burner according to UL-94 standard with sample dimensions of 125 mm × 12.5 mm × 3.2 mm for 90 mins. Thermocouples were attached at the back of the steel substrate; all data were recorded manually as shown in **Fig. 1**.

Figure 1. Experimental set-up of horizontal Bunsen burner fire test.

2.3 Characterization and measurement

Scanning electron microscopy with energy dispersive x-ray (SEM-EDX) was performed to describe the morphology of the char residue obtained after fire test. X-ray photoelectron spectroscopy (XPS) was also conducted to characterize the atomic binding of char particles. Energy dispersive x-ray spectrometer (EDS) was also employed to validate the elemental component of the char residue.

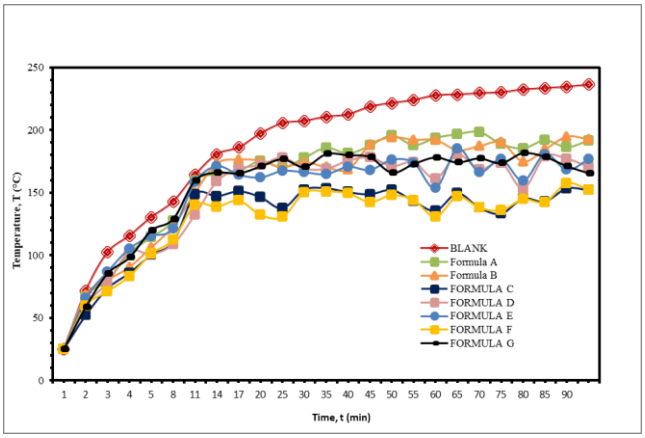

Figure 2. Time-temperature (T-T) curve of different formulations after 90 mins fire test.

3 Results and discussion

3.1. UL-94 vertical test (Bunsen burner fire test)

Fig. 2 shows the time-temperature curves of the different IFR compositions after 90 minutes fire exposure. It was observed that after 11 mins, all samples have experienced abrupt increased of substrate temperature, averaging to 18.05 ˚C/min. Also, Formula C and F have shown to have lowest substrate temperature around 150 ˚C compared to Blank sample having 236.3˚C after 90 mins. Formula C and F have an average rate of 0.18˚C/min after 11 mins compared to blank having 0.86˚C/min as shown in **Fig. 3**.

3.2. Scanning electron microscopy with energy dispersive X-ray (SEM-EDX)

Shimadzu superscan SSX-550 was used to analyze the morphological structure of the resulting char; it was calibrated to capture clear images at 15Kv accelerating voltage at 15 working distance (WD). It was observed in **Figs. 4(b) and 4(c)**, that Formula C and F have a homogenous compacted char structure compared to the Blank Sample. It was also noticed that the formation of bubble-like structure at the surface was predominantly composed of non-carbon radicals such as Phosphorus and Oxygen. Also, **Fig. 5(a)** shows that vanadium was present at the char surface of the Blank sample; it implies that the strengthening ingredient of steel was altered during fire exposure and attached at the surface of the resulting char. On the other hand, CeO_2, Ca and Mg were present at the char surface of Formula C and F as shown in **Figs. 5(b) and 5(c)**.

3.3. X-ray photoelectron spectroscopy (XPS)

XPS analysis of the char surfaces were conducted using JEOL JPS-9200 spectrometer (JEOL Ltd., Japan) equipped with a monochromatized Al Kα X-ray source operating at 100 W under ultrahigh vacuum (about 10^{-7} Pa). Narrow scan spectra of oxygen (O1S) and carbon (C1S) were obtained and corrected using C(1s) binding energy of adventitious carbon (285.0 EV). All XPS spectra were deconvoluted with XPSPEAK version 4.1using true Shirley background.

Fig. 6 shows the detailed XPS carbon scan at binding regions ranging from 280-300eV. It was observed that it consist of three (3) major peaks concentrated at 284.8, 288.1 and 286.1eV. XPS database from the National Institute of Standards and Technology (NIST) suggested that the formation of polymethylacrylate acid was formed abundantly at Formula C as shown in Table 2 having 32.11% at 286.1 eV, this implies that, this compound promotes the degradation process of ammonium polyphosphate, creating a more extensive avenue to produce the Polyethylene aromatic bond, which a double carbon bonding at 288.1 eV as shown in **Fig. 6** and **Table 2**.

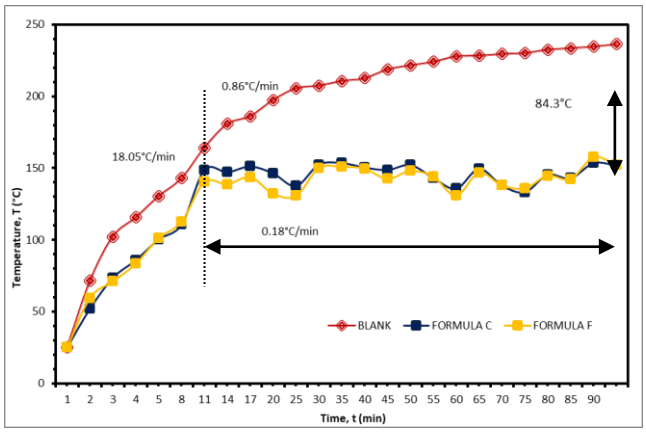

Figure 3. Time-temperature curve of selected IFR sample.

Table 2. XPS detailed carbon scan.

Sample I.D.	%Area Carbon		
	284.8 eV	286.1 eV	288.1 eV
BLANK	50.4365	27.8266	21.7369
Formula C	36.4994	32.1154	31.3851
Formula F	49.7321	28.4223	21.8455

4 Conclusion

Formula C and Formula F having the same ratio but different weight composition of CeO_2 and Dolomite have shown to have a better fire resistance during vertical Bunsen burner fire test. These samples obtained an average of 150˚C substrate temperature, having 0.18 ˚C/min heating rate after 11 mins fire exposure. It was observed that Formula C and F promoted the formation of a more compacted homogenous char structure, which suppressed heat penetration at the steel substrate during fire exposure. XPS revealed the formation of polymethylacrylate acid which helps the phosphoric acid to fasten the Votalization of epoxy and Triethylenetetraamine, which is responsible to form the aromatic radicals of polyethylene at the char surface, which promotes lesser surface porosity, thus, stabilizing char formation at higher temperatures.

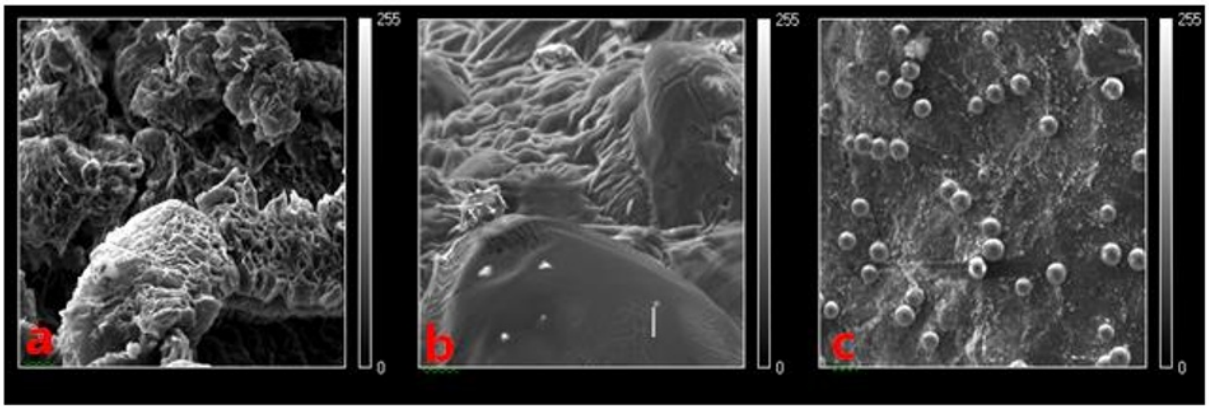

Figure 4. Scanning electron microscopy images of 4(a) blank; 4(b) Formula C and 4(c) Formula F.

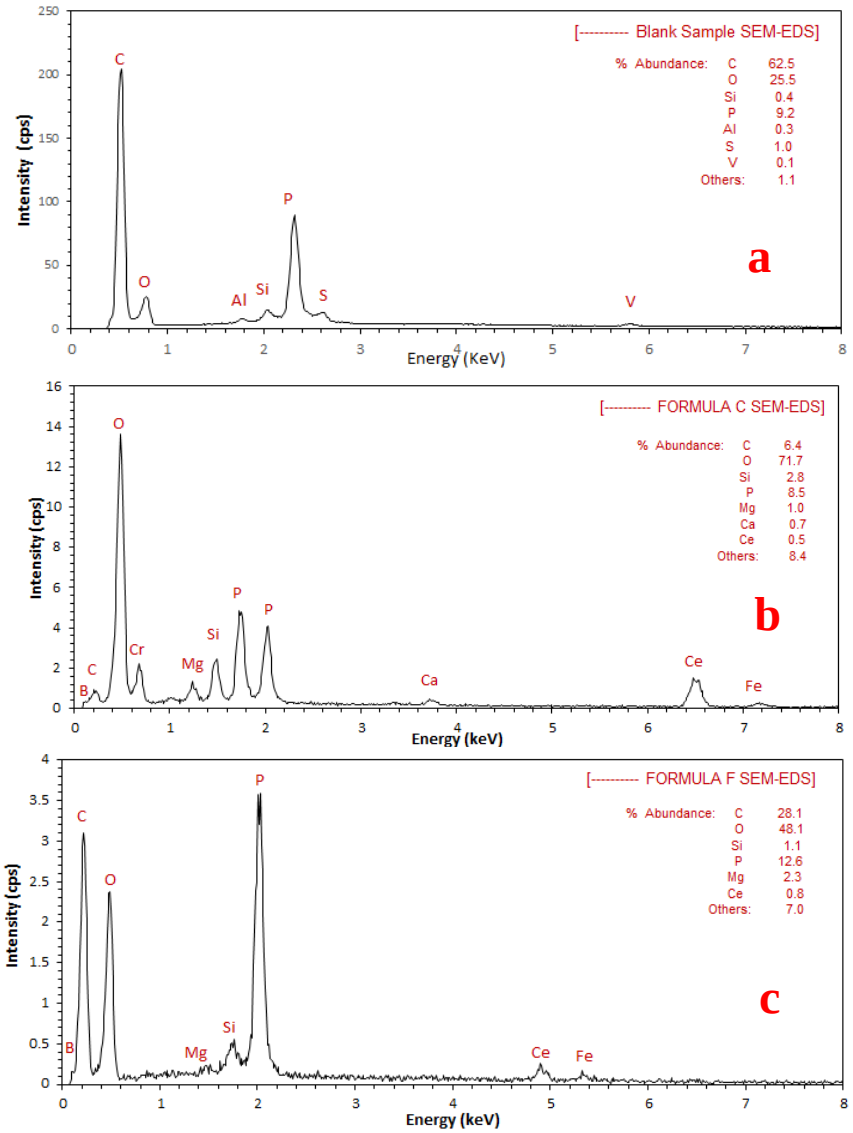

Figure 5. Energy dispersive x-ray of 5(a) blank; 5(b) Formula C and 5(c) Formula F.

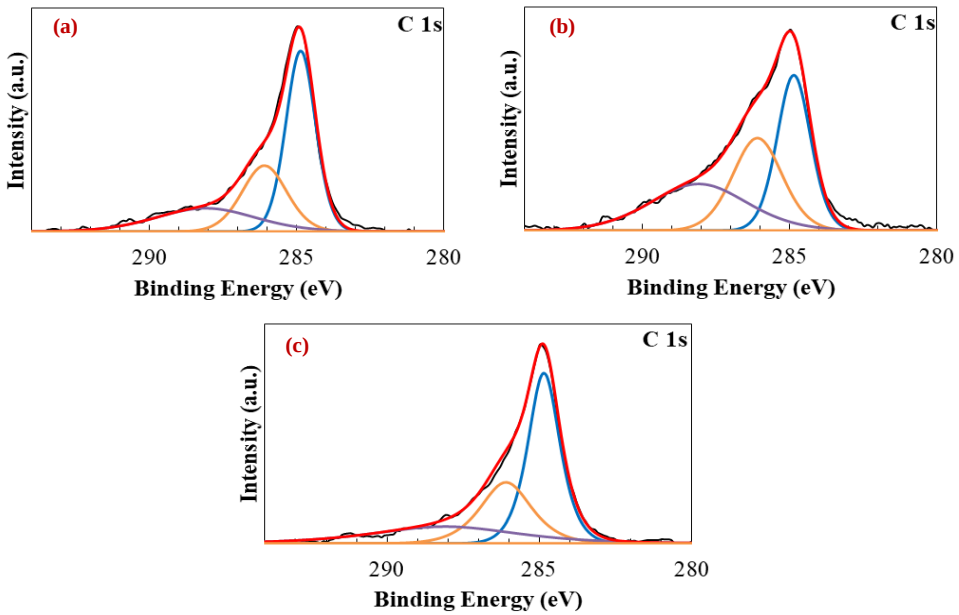

Figure 6. Detailed x-ray photoelectron carbon (C) scan at different binding energies of (a)blank; 5(b) Formula C and 5(c) Formula F.

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