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Effect of Inorganic Fillers on Thermal Performance and Char Morphology of Intumescent Fire Retardant Coating

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ABSTRACT
An intumescent fire retardant coating is a substance when exposed to fire, it expands many time of its thickness forming as insulating layer of char which is strong enough to protect steel structure from fire and retain the structural integrity. Intumescent fire retardant coating has been developed by using Ammonium Polyphosphate (APP), Expandable Graphite (EG), Melamine (MEL), Boric Acid, Bisphenol A (BPA) and polyamide amine as a curing agent. Thus, local inorganic fillers which are alumina (Al_2O_3), aluminum trihydrate-ATH ($Al(OH)_3$) and fumed silica added in the fire retardant materials. The main objective of this paper is to investigate the effect of local inorganic fillers on residual weight and char morphology of intumescent fire retardant coating. Intumescent fire retardant coating with addition of alumina fillers show greater residual weight and better char morphology.

Key words: Intumescent fire retardant coating, local inorganic fillers, thermal performance, char morphology

INTRODUCTION
Steel has been used widely in construction of mega buildings, offshore structures, bridges, ships, railways and airports. It starts to lose its properties when exposed to high temperature between 470-500°C (Jimenez *et al*., 2006). Intumescent fire retardant coating is a type of passive fire protection which acts as an insulation to the steel substrate from direct fire to maintain its structural integrity. Under the exposure of heat, the coating will expand and form char layer to protect the substrate. Intumescent fire retardant coatings are composed of three components: (1) an inorganic acid (dehydrating agent); (2) a carbonaceous char-forming material and (3) a blow agent (Wang and Yang, 2011). The performance of the intumescent system depends on the choice of the ingredients and their appropriate combinations. Currently, this traditional method of intumescent fire retardant system which is APP-PER-MEL system is not satisfactory due to its poor performance of anti oxidation and fire retardancy (Li *et al*., 2007).

Recently, research has been done to modify and improve the performance of intumescent fire retardant coating. Locally inorganic fillers are added in APP-PER-MEL system to have the improvement in char morphology, thermal insulation, mechanical properties and excellent chemical resistance. Research conducted by University of Pretoria shown that the incorporation of fillers in intumescent coating has made the char became harder and more solid even though it was lesser in volume (Labuschagne, 2003). Some authors have shown that effect of various inorganic fillers such as alumina (α-Al_2O_3), calcium carbonate ($CaCO_3$), silica (SiO_2) and feldspar ($KAlSi_3O_8$) on the flammability behavior of Polypropylene (PP) composites. Alumina-filled PP shows greater flame-retardant behavior and decreasing rate of burning at both the 40 and 60% filler loadings (Razak *et al*., 2007). The addition of ammonium polyphosphate and aluminium trihydroxide (ATH) in the coating had improved thermal stability between 200-600°C. Hapuarachchi and Pejis (2009) found that the use of ATH in combination with APP was expected to impart an improved flame retardant effect in the UP system. According to Ye *et al*. (2010), a suitable amount of fumed silica can promote the formation of compact intumescent charred layers and prevent the charred layers from cracking which effectively protects the underlying polymer from burning. Boric acid was used as additives in intumescent fire retardant coating system to improve the char strength and the adhesion of char to the steel substrates (Ullah *et al*., 2011b).

In this research work, expandable graphite in the coating acts as a carbon source in replacement of PER which is used in the APP-PER-MEL coating system (Ullah *et al*., 2011a). EG can be a carbon source and a synergistic agent to improve the performance of the IFR coating. However, EG cannot help in enhancing the residue weight of the coating because it can easily oxidize at high temperature in contact with air (Wang *et al*., 2007). By incorporating inorganic filler in the coating, it is expected to improve the coating performance by improving the residue weight and eventually enhancing the fire resistant performances. Various inorganic filler such as alumina, ATH and fumed silica are used to study their effect towards the performances of intumescent fire retardant coating. Moreover, epoxy resin is used as binder with addition of inorganic fillers into the fire retardants materials which consisting ammonium polyphosphate, expandable graphite, melamine and boric acid.

The objective of this work is to develop formulations of Intumescent Fire Retardant (IFR) coating by using local inorganic fillers and to analyze the effect of inorganic filler addition to the thermal performance and char morphology for protection of steel substrate.

MATERIALS AND METHODS

Experimental materials and formulations: Acid source (Ammonium Polyphosphate-APP), Carbon source (Expandable graphite-EG), Blowing agent (Melamine-MEL), Additive (Boric acid-BA), Epoxy resin (Bisphenol-A-BPA), hardener (Tetraethylene Tetramine- TETA), Inorganic Fillers (Alumina, Aluminum Trihydrate-ATH and Fumed Silica) were selected for developing formulations. The formulation prepared is shown in Table 1. The weight ratio of the binder and IFR was 2:1. IFR

Table 1: Intumescent fire retardant formulations

Components (wt. %)	IFR 1	IFR 2	IFR 3	IFR 4
BPA	42.94	42.94	42.94	42.94
TETA	20.72	20.72	20.72	20.72
APP	11.11	11.11	11.11	11.11
EG	5.56	5.56	5.56	5.56
MEL	5.56	5.56	5.56	5.56
BA	11.11	11.11	11.11	11.11
Inorganic fillers				
Alumina	-	3	-	-
ATH	-	-	3	-
Fumed silica	-	-	-	3

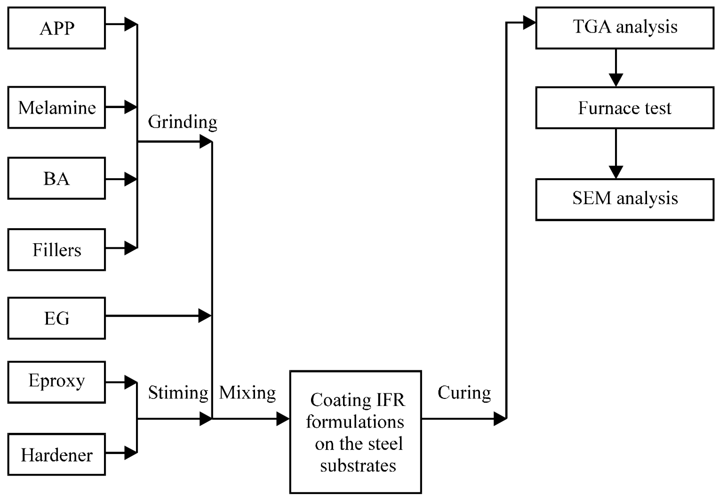

Fig. 1: Experimental procedure flowchart

consisted of APP, EG, MEL and BA. The weight ratio of APP, EG, MEL, BA was 2: 1: 1: 2. 3% of inorganic filler was added to the main ingredients. IFR1 is the controlled formulation while IFR 2, IFR 3 and IFR 4 are added with alumina, ATH and fumed silica, respectively.

Experimental procedure: For all IFR coating formulations, selected weight percentage of the APP, MEL, BA and filler were grounded by using grinder for 60 sec. This was followed by mixing of epoxy binder (BPA) and hardener (TETA) homogeneously by using high Shear mixer. The grinded APP, EG, MEL, BA and filler were added to the mixture of epoxy and hardener. The ingredients were mixed and stirred in Shear mixer for 20 min at 50 rpm. The coatings were applied on one side of structural steel coupon with dimension of 5×5 cm^2. The coated test coupons were cured at the ambient temperature for 1 week. Ensuring fully cured, the coating samples were considered ready for characterizations analysis. Before fire test, the coatings were examined on the residual weight by using Thermogravimetry Analysis (TGA). Then, all the coatings were tested for char formation by using carbolite furnace at 500°C for 1 h. Char expansion were measured and recorded. The char morphology was observed and analyzed by using Scanning Electron Microscope (SEM). The flow chart of the experimental procedure is shown in the Fig. 1.

RESULTS AND DISCUSSION

Residual weight of intumescent fire retardant coating: TGA curves of the IFR coating with different inorganic fillers are presented in Fig. 2.

Every IFR coating shows the same trend of curve. There are three significant changes in the slopes which proved that its degradation process had at least 3 main steps. The difference in the curves where IFR 1 started to degrade earlier at 250°C compared to IFR 2, IFR 3 and IFR 4 at 350°C. It is proved that the addition of inorganic fillers in IFR 2, IFR 3 and IFR 4 delay the process of degradation and having high residual weight. The weight loss of IFR 1 was less than 6% below 250°C compared to IFR 2, IFR 3 and IFR 4 which were in the range of 7-13% below 350°C. At this stage, the weight loss was due to the unvolatilized solvent and small molecules of polymer (Li *et al.*, 2008).

As the temperature increasing higher than 350°C, the coatings started to degrade gradually. This is where the coatings ingredients such as APP, EG, Mel and boric acid decomposed and

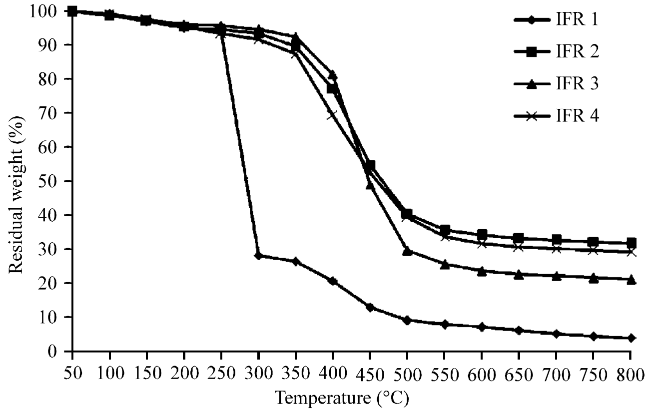

Fig. 2: Residual weight of IFR

Table 2: Residual weight (wt.%) of IFR coatings at different temperatures

	Temperature (°C)				
Fillers	400	500	600	700	800
IFR 1	20.82	9.20	7.17	5.27	4.01
IFR 2	77.19	40.46	34.16	32.70	31.69
IFR 3	81.41	29.66	23.69	22.13	21.17
IFR 4	69.46	39.38	31.76	30.23	29.16

produced inert gases such as ammonia and carbon dioxide to form insulating char layer (Gu *et al.*, 2007). The process of intumescence occurred at the same time as the coatings degrade at the temperature of 150 to 550°C. At the latter stage from 550 to 800°C, the non combusted residue char act as insulation layer and protecting the steel substrate. The residue weight of each coating from 400-800°C is shown in Table 2 below.

The highest residue weight was achieved by IFR 2 with 31.69% residue weight. Then, it was followed by IFR 4 (29.16%), IFR 3 (21.17%) and IFR 1 (4.01%). From the analysis, it is proven that the addition inorganic fillers improved the residual weight of the coatings. IFR 2 which contains alumina has the highest improvement of 87.35%. It is followed by IFR 4 which contains fumed silica with 86.52% improvement and IFR 3 which contains ATH with 81.06% improvement. At least 80% of the char residual weight can be enhanced by imparted inorganic filler in the coating compared to IFR coating without filler. The coating with the highest residue weight will exhibit good intumescent coating behavior where it could enhance the anti-oxidation of the coating at high temperature and eventually protect the substrate from losing its properties (Li *et al.*, 2007).

Char morphology of intumescent fire retardant coating: The coatings were burned at 500°C for 1 h in the carbolite furnace. On the outer surface of all char structure in Fig. 3-6, there are expanded graphites like worm. This worm like structure acts as a function of fiber which can enhance the resistance of char structure to deformation. These characteristics are favorable which help to get an efficient insulation layer and fire resistance of char structure (Wang *et al.*, 2007). The fiber like structure occurred when the expandable graphite was exposed to heat source. Upon heating, the intercalation compounds (sulphuric acid) in the crystal structure of graphite decomposed into gases product (carbon dioxide and water). The decomposition of the intercalation compound produced a strong push force between the graphite lattices, so the graphite basal planes

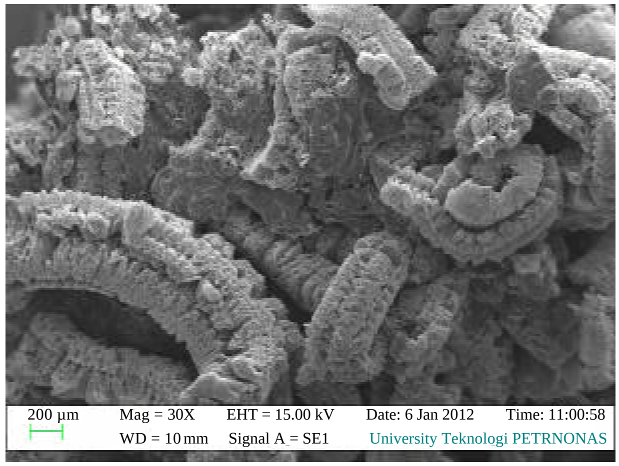

Fig. 3: SEM image of IFR 1 fibrous structure

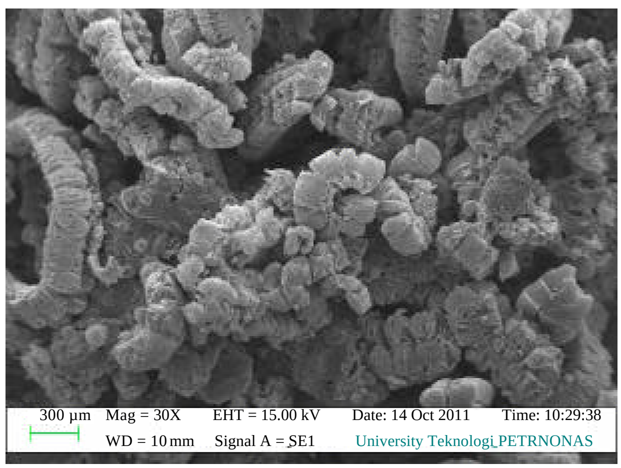

Fig. 4: SEM image of IFR 2 fibrous structure

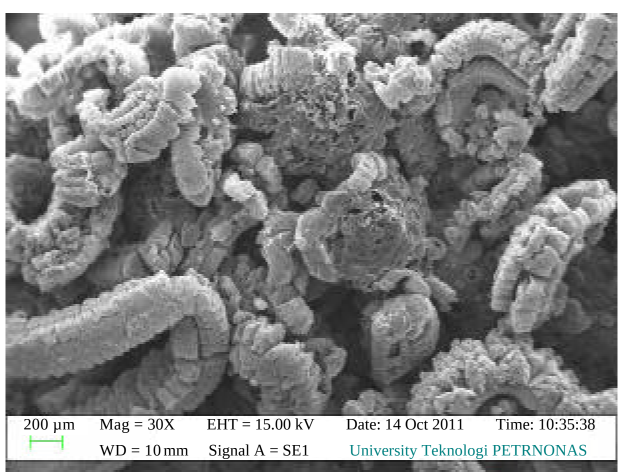

Fig. 5: SEM image of IFR 3 fibrous structure

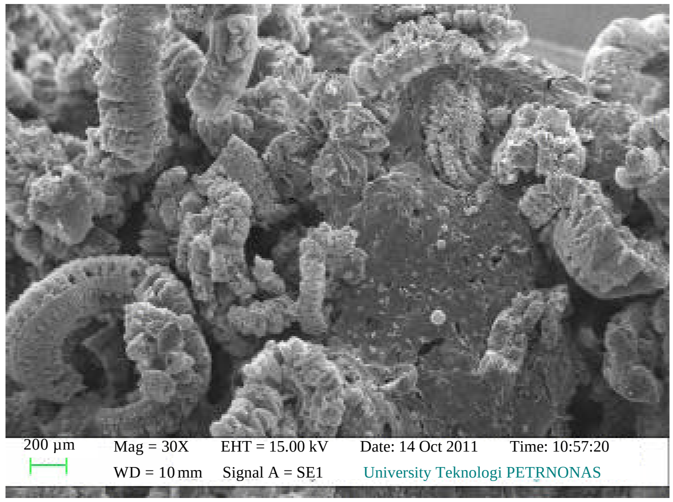

Fig. 6: SEM image of IFR 4 fibrous structure

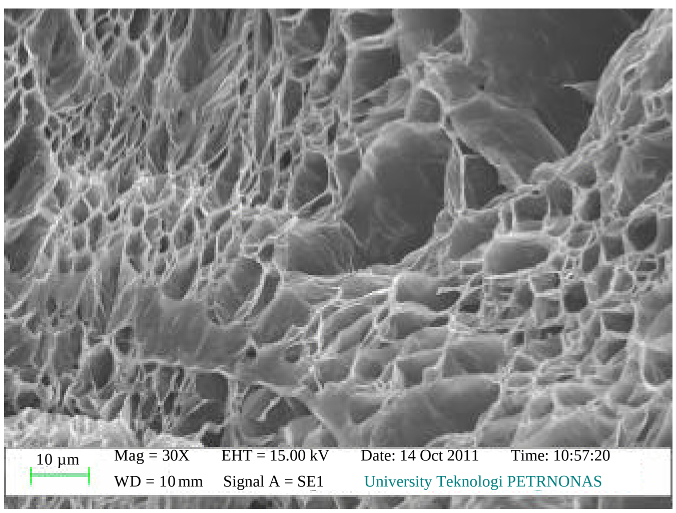

Fig. 7: SEM image of cellular structure of IFR 1

can be pushed apart. During the expansion, the fused resin can stick a large amount of expanded graphite. That is why the expandable graphite is embedded in the char structure in a fibered way (Han *et al.*, 2006).

With higher magnification in Fig. 7-10, the outer surface showed compact foam of char structure. This foam char structure provides a shield that insulates the steel substrate from radiant heat and direct contact with the flame (Wang and Yang, 2010). The multiporous char structure can block heat transferring to the steel substrate and protect the substrate from fire. The speed of heat transfer depends on the resistance of the substrate to fire. That is why the expansion effect and char structure are important to the fire resistant properties (Li *et al.*, 2007).

Besides that, image of regular open cellular structure are observed from the Fig. 7-10. It is due to the expansion of expandable graphite which expands several times greater to its original thickness (Wang *et al.*, 2007). The difference of average cell size distribution can be observed

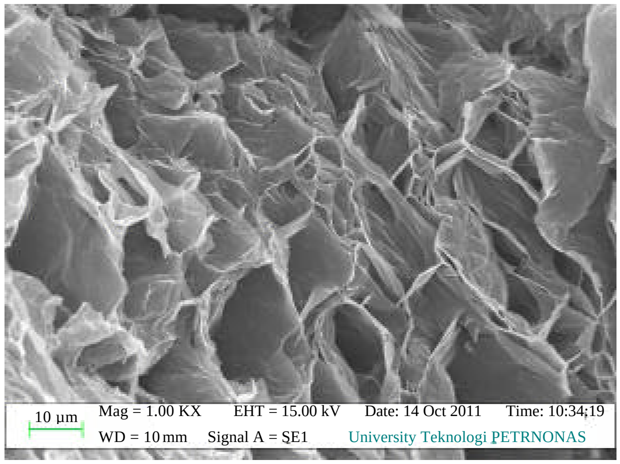

Fig. 8: SEM image of cellular structure of IFR 2

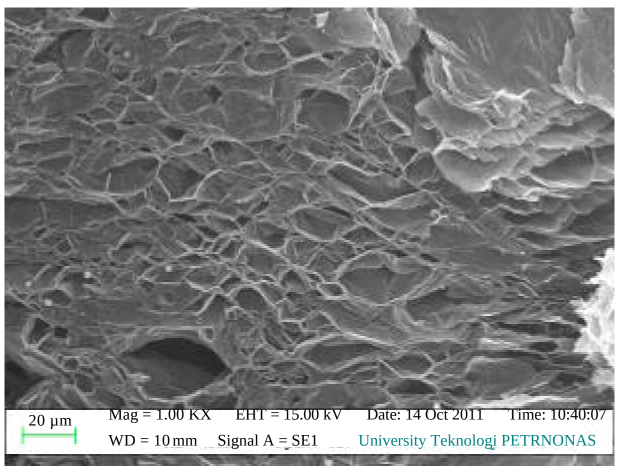

Fig. 9: SEM image of cellular structure of IFR 3

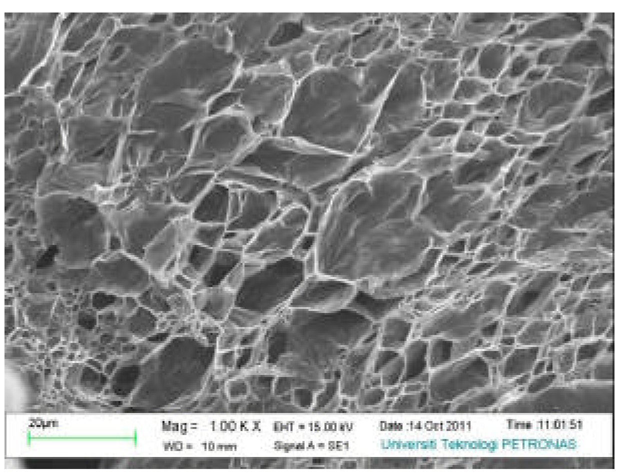

Fig. 10: SEM image of cellular structure of IFR 4

Table 3: Average cell size for each formulation with different inorganic fillers

Formulations	Cell size (μm)
IFR 1	2.19
IFR 2	12.08
IFR 3	6.83
IFR 4	8.08

measured as shown in Table 3. Addition of inorganic filler can modify the size of pores inside the char. IFR 1 which do not contain any filler was having the lowest cell size distribution which only 2.19 μm. By incorporating different inorganic fillers, the cell size distribution varies. The cell size distribution of IFR 2, IFR 3 and IFR 4 improve to 12.08, 6.83 and 8.08 μm, respectively.

Alumina shown a good effect in term of achieving bigger cell size distribution compared to fumed silica and ATH. Cell distribution and cell size are important in determining a good char microstructure. Uniform cell distribution and bigger cell size is needed to ensure an excellent char microstructure. However, if there is crack or hole, it may affect the cell structure where the heat transfer to the substrate will increase. Holes with diameter >40 μm can lead to increase the heat transfer by air convection. Thus, it will attack the underlying substrate and steel starts to lose its properties (Wang and Yang, 2011).

Bigger and uniform cell size is desired because it can decrease speed of the heat transfer to the steel substrate. During degradation of the coating, the inert gases such as ammonia (NH_3) and nitrogen (N_2) can blow up the char layer and at the same time entrap in the foam structure lower down the heat transfer efficiency (Wang and Yang, 2011). Thus, it can enhance the anti oxidation of the char layer and improved the thermal stability.

CONCLUSION

From the residual weight result, the highest residual weight for 3% of inorganic filler was achieved by IFR 2 with 31.69% followed by IFR 4 (29.16%) and IFR 3 (21.17%). The lowest residual weight was obtained by IFR 1 with only 4.01%. Thus, the addition of inorganic fillers improves the anti oxidation and thermal degradation of the coating.

Based on cell size distribution, the highest average cell was demonstrated by IFR 2 (12.08 μm), followed by IFR 4 (8.08 μm) and IFR 3 (6.83 μm). Average cell size for IFR 1 was only (2.19 μm). Multiporous char structure of IFR with alumina, ATH and fumed silica gave more expanding effect and prevent heat to the underlying materials.

Compared to other formulations, IFR 2 which is containing alumina as filler demonstrated the strongest influence because it achieved the highest residual weight percentage and bigger cell size distribution. Therefore, it is proven that by incorporating alumina as filler in intumescent fire retardant coating can develop and improve the thermal efficiency and char morphology of intumescent fire retardant coating.

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