Effect of basalt fibres reinforcement and aluminum trihydrate on the thermal properties of intumescent fire retardant coatings

Muhammad Yasir[1], Norlaili Binti Amir[1], Faiz Ahmad[1], N. Syahirah Rodzhan[1]

Mechanical Engineering Department, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak, Malaysia

Abstract. This research is carried out in order to study the synergistic effect of aluminium trihydrate and basalt fibres on the properties of fire resistant intumescent coatings. Intumescent fire retardant coatings were developed using different flame retardants such as ammonium polyphosphate, expandable graphite, melamine and boric acid. These flame retardants were bound together with the help of epoxy binder along with curing agent. Furthermore, individual and combinations of aluminium trihydrate and basalt fibres was incorporated in the formulations to analyse mechanical and chemical properties of the coatings. Char expansion was observed using furnace test, thermogravimetric analysis was used to determine residual weight, X-Ray Diffraction was performed to investigate compounds present in the char, shear test was conducted to determine char strength and scanning electron microscopy analysis was performed to observe morphology of the burnt char. From the microscopic investigation it was concluded that the dense structure of the char increased the char integrity by adding basalt and aluminium trihydrate as fillers. X-Ray Diffraction results shows the presence boron phosphate, and boric acid which enhanced the thermal performance of the coating up to 800°C. From the Thermogravimetric analysis it was concluded that the residual weight of the char was increased up to 34.9 % for IC-B2A4 which enhanced thermal performance of intumescent coating.

1. INTRODUCTION

Structural steel is the main and critical part of every building due its high mechanical strength, high ductility and toughness with less construction time, etc. [1], which made it the worthy component of the construction industry. But nowadays, the catastrophes caused by fire which damage the steel structure have made people wary of the risk of fire under the structure. In case of fire, the temperature of the unprotected steel rises sharply and it starts losing its load bearing capability when the temperature reaches to 500°C. The structure collapse in less than 45 minutes, as witnessed in the Edgewater fire accident of 2015 which demolished almost 240 luxury apartments and displaced almost 1000 people [2]. There are passive fire protection systems available such as intumescent coating which is the most efficient technique to protect the steel structures from fire. Intumescent coating is the one of the oldest and efficient mechanism to protect the substrate against fire. In the event of fire it swells up forming a protective layer or char that gets permanently attached to the material [3, 4]. The char limits the rapid increase of temperature of the substrate as it acts as an insulating barrier [5-9].

Intumescent protective layer is valuable for enhancing the collapse time required for structural steel under fire or to promote the resistance against fire wall or the ceiling of several materials, protecting fire diffusion and temperature of the wall's opposite surface. To enhance the anti-oxidation properties or fire resistance of the intumescent coating, various reinforcement materials used and their synergistic effect is of great attention in the current research trend in this field [10-14]. Many researchers have worked on fillers in order to reinforce the intumescent coatings. However, the adhesion of the char with the substrate at high temperature is a great challenge and these coating are not satisfactory to protect the substrate [15-18]. In order to enhance the adhesion of the intumescent coating, various coating formulations have been developed to study the effect of fillers on the mechanical strength and thermal performance of the intumescent coating. Amir et al. [12] who used Rockwool and single glass wool fibres showed some improved mechanical and thermal performance. Ullah et al. [19] included boric acid with kaolin clay in the formulation which resulted in good thermal performance of the intumescent coatings. Similarly, synergistic effects of nano-clay and multi-walled carbon nanotubes of organ phosphorus fillers in the intumescent coating have improved the thermal performance to a great extent [20].

Basalt fibres have become as an important reinforcement in the field of composite materials. Basalt is basically a volcanic rock that can be processed in order to get the basalt fibres. The chemical composition of the basalt fibres consist of SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3 and FeO [21-23]. The presence of Fe content in basalt fibres make them higher heat resistant materials, which is best suited to be used as reinforcement in intumescent coatings. Apart from that, basalt fibres have a very good mechanical strength that makes them as a good alternative of glass fibres. Aluminium trihydrate (ATH) is a non-halogen based material that can find use in flame retardation as well as smoke suppression.
This research is carried out in order to study the behaviour of basalt fibres and ATH on the thermal performance and mechanical strength of the intumescent coating.

2. MATERIAL AND METHODS

Basalt fibres and aluminium trihydrate were purchased from MY EAST Sdn. Bhd. Expandable graphite (EG), Hardener (H 2310) and ammonium polyphosphate (APP) were supplied by McGrowth Chemicals Sdn. Bhd. Malaysia. Whereas, Melamine (MEL) and Boric acid (BA) were bought from Sigma-Aldrich (M) Sdn. Bhd. Seven pieces of mild steel S355 (50mm x 50mm x 1.5mm) supplied by TSA Industries (Ipoh) Sdn. Bhd. The structures of aluminium trihydrate (ATH) and basalt fibres were being analysed from the image produced by the Scanning Electron Microscope (SEM) as illustrated in Figure 1(a,b). The average size of ATH particle was 16.51 μm meanwhile the average diameter of the basalt fibres was 12.17 μm respectively.

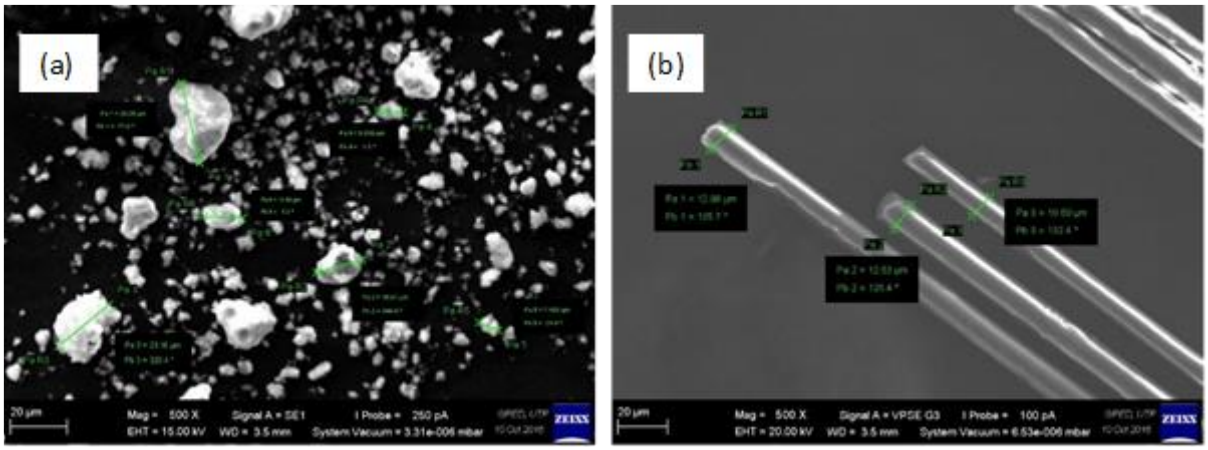

Figure 1. Microstructure of (a) ATH (b) BF

Seven intumescent coating formulations were synthesized which are shown in Table 1. Aluminium trihydrate and basalt fibres were used to reinforce the coating. The weight percentage of ATH was 3 wt.% and 4 wt.% while basalt fibres were used as 1 and 2 wt.% respectively.

Table 1. Weight percentage intumescent coating formulation based on basalt fibres and ATH

No.	APP	EG	MEL	BA	ATH	BF	BPA	PAA
CF	11.1	5.5	11.1	5.5	0	0	44.4	22.2
IC-B1A3	11.1	5.5	11.1	5.5	3	1	41.7	20.8
IC-B2A4	11.1	5.5	11.1	5.5	4	2	40.4	20.2
IC-A3	11.1	5.5	11.1	5.5	3	0	42.4	21.2
IC-A4	11.1	5.5	11.1	5.5	4	0	41.7	20.8
IC-B1	11.1	5.5	11.1	5.5	0	1	43.7	21.8
IC-B2	11.1	5.5	11.1	5.5	0	2	43.1	21.5

2.1. Sample preparation

Firstly, APP, MEL and boric acid were grinded for three minutes using mortar grinder (RM200) according to their respective weight as stated in Table 1. The basalt fibres mats were cut to form fibres with 12 mm in length. The weights of EG, basalt fibres and ATH were measured and they were manually mixed by using a spatula until they were uniformly dispersed. That mixture was added to BPA using a shear mixer at 40 rpm for 20 minutes. Then, hardener was added into the mixture in order to avoid curing of the epoxy and the mixing was continued for 20 minutes. The coating was applied onto 5 cm x 5 cm S355 steel substrate manually using a spatula. Lastly, the coated substrates were cured at ambient temperature for a week.

3. METHODOLOGY

3.1. Thermogravimetric Analysis (TGA)

The thermal stability of intumescent coating was analysed using Thermogravimetric Analysis (TGA). The test was conducted according to the standard ASTM E1131 using Perkin-Elmer TGA Q50 with 20°C/min heating rate in the presence of nitrogen (N_2) environment until 800°C.

3.2. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDS)

The material and char morphology structures condition were analysed using SEM technique. 15-20 kv electron high tension range with 3.5-13.5mm working distance and 22-10000X magnification were used using Zeiss supra SEM model. The elemental composition in the fillers and char was examined by using Energy Dispersive X-Ray Spectroscopy analysis.

3.3. Furnace Test

Furnace test was conducted to evaluate the char expansion by heating the samples using Carbolite electric furnace from ambient temperature to up to 500°C for 60 minutes. The temperature was maintained for 60 minutes in order to let the samples burn completely and then allowed to cool down back to room the temperature for about 20 minutes in order to prevent any crack occurrence on the samples.

3.4. Char strength test

Char strength test was used to test the char strength by determining the capability of the char, to resist the deformation when a specific load was applied. This simple quantitative test was done by continuously and progressively adding load on top of the char with a uniform increment of 100g. Seven discs of known different weights; 0.981N (1 piece), 1.962N (2 pieces), 4.905N (1 piece), 5.886N (1 piece) and 9.81N (2 pieces) were used in this test. At each load, the height reduction of the char after one minute was recorded [11].

3.5. X-ray Diffraction (XRD)

XRD was used to determine the char elements after fire test. XRD model number AXS D8 Advance manufactured by Bruker using Cu Kα radiation with nickel filter (k = 0.150595 nm) in the range ($10^o < 2\theta < 90^o$).

4. RESULTS AND DISCUSSIONS

Figure 2 shows the thermal degradation of all the seven intumescent coating formulations. In degradation process, there were four steps involved which were independent of the composition of the fire retardant intumescent coating (FRIC). Melting occurred at temperature range 0-200°C followed by intumescence at 200-350°C, char formation (350-550°C) and finally the degradation of char at 500-800°C. Boric acid is used in the formulation because its sub-oxides are thermally stable. Boric acid decomposes in temperature range of 100-300°C. It dehydrated upon heating from 100-140°C to metaboric acid (HBO_2), which further break down to form boron oxide (B_2O_3). Boron oxide is a stable compound like hard glass against high temperature. It produced high weight residue of the char and more the residual weight means more it can protect the substrate from rise in temperature along with the mechanical strength of the char. Similarly, boron oxide when heated above 300°C, forms suboxides which are a source of insulation for the char. The thermal degradation of pure APP involves in two steps. In first step it begins to degrade at temperature above 200°C forming polyphosphoric acid. In second step it reacts with boric acid at temperature of 250°C to form borophosphate [3, 13]. EG starts to decompose at temperature above 200°C to form CO_2 and SO_2. The intumescence of the coating starts at temperature range 260-460°C in which Melamine decomposes to form NH_3 and CO_2 which are non-combustible compounds. At this stage maximum quantity of the coating is reduced [4]. Finally, the degradation of the char occurred at temperature range of 460-800°C.

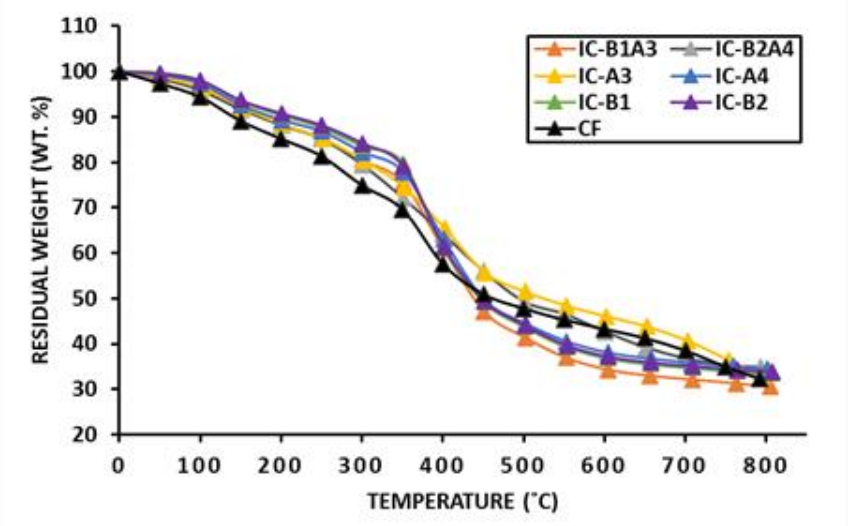

Figure 2. TGA analysis of formulations

The overall weight loss of the coating occurred as follows: At First stage; 10-15% weight is reduced, second stage 10-15% weight loss occurred, third stage 20-25% weight loss occurred and the weight loss was 22% at the final stage of degradation. The control formulation was reinforced with basalt fibres and aluminium trihydrate in order to enhance the residual weight and anti-oxidation degree at higher temperature. The residual weight of the char with reinforcement was higher than the control formulation. The final residual weight percentage of the char at 800ºC for IC-B1A3, IC-B2A4, IC-A3, IC-A4, IC-B1 and IC-B2 was 32.01, 34.9, 33.21, 34.5, 33.4 and 33.9% respectively. Low weight loss occurred during final degradation stage i.e. 15.62%. Residual weight of coating was enhanced by reinforcing with aluminium trihydrate filler (IC-A3). However, for the basalt fibres (IC-B1) the residual weight was also enhanced as compared to control formulation which was 15.84%. Similarly, both fillers were added to the system the final residual weight loss during final degradation was 16.58% which was also less as compared to the control formulations. The higher residual weight of coating (IC-B2A4) indicated that addition of aluminium trihydrate and basalt fibres could enhance the thermal stability and anti-oxidation of the coating, resulting in good fire protection performance.

The outer and inner surfaces of the control formulations after furnace test, as shown in Figure 3, presents some worm like shapes on the surface of the formulation which occurred due to graphite expansion. An uneven microstructure was observed which consists of holes that help in transference of heat of flame to penetrate inside to the substrate leading to decrease in thermal performance of coating [6]. The control formulation was reinforced with some inorganic fillers in order to enhance the microstructure of the char.

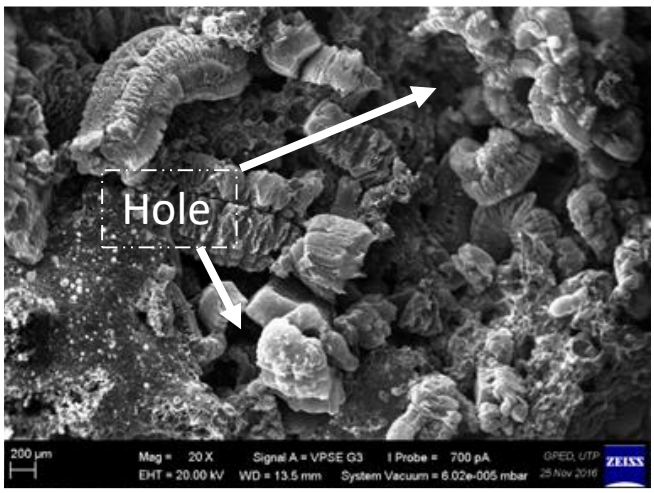

Figure 3. Microstructure of the char for CF

The microstructure of control formulation was improved by adding the inorganic filler like basalt fibres and also the ATH with variation in their weight percentages from 1-2 wt.% and 2-3 wt.%, respectively. In Figure 4 (a), IC-A4 formulation coating is stronger as we can see the presence of voids in the char. But the voids were shallow and deep which did not resist the substrate from enough heat. These voids were formed from evolution of trapped gases by blowing agent when the coating is subjected to fire.

In Figure 4 (b), showing IC-B4 in which some voids were present but these voids are not deep which protect the substrate from rise in temperature. So overall improved char microstructure was the result of the synergistic effect of fire retardant additive and inorganic fillers.

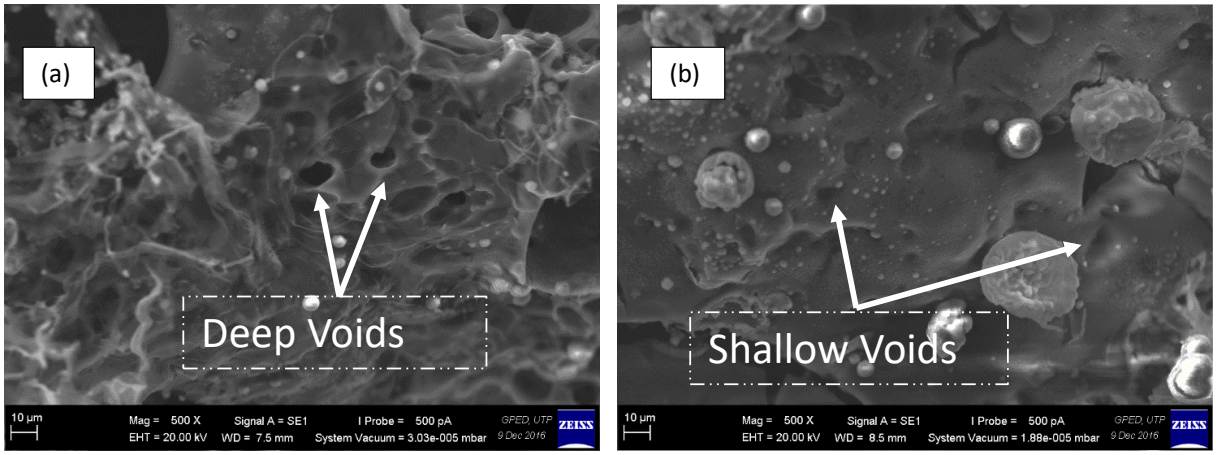

Figure 4. SEM micrographs of (a) IC-A4 (b) IC-B4 at 500°C

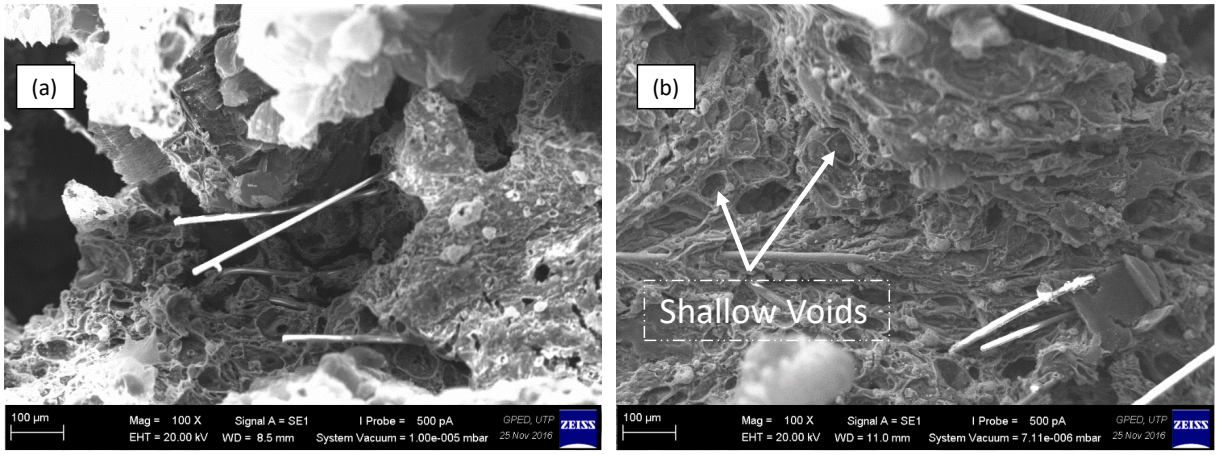

Figure 5. Microstructure of chars for (a) IC-B1A3 (b) IC-B2A4

In Figure 5 (a,b) the fillers flakes interconnected with char, the surface is visible, this structure increased char integrity and anti-oxidation of the char due filler present in char at later stages of burning.

The mechanical strength of the char is increased by addition of basalt and ATH which create a bridge between the intumescent materials. The fibres were fully covered in the coating mixture and were effective in holding the coating material to prevent fire penetration [25]. They also helped in creating a bigger char volume that can prevent the substrate from the fire. Basalt fibres and ATH are high temperature resistant materials, can withstand up to high temperature and high residual weight with less weight loss. This proved from Figure 5 (b) that IC-B2A4 produced more voids compared to the unfilled intumescent coating. Higher amount of voids produced means higher strength of char structure because these voids don't allow the heat to reach the substrate [12]. This subsequently contributes to better intumescent effect.

For elemental analysis of IFRC's char, EDS was performed as discussed in subsection 3.2. Figure 6 shows the percentage of elements in the formulations. O/C for IC-B2A4 was 0.39, which has a best anti-oxidation degree compared to all other formulations. The weight percentage of each element is obtained during EDS analysis and the weight ratio of O to C elements was determined by dividing weight % of oxygen (O) to weight % of carbon (C), hence the degree of anti-oxidation of the char is determined by O/C ratio. Lesser the values of O/C means greater weight of carbon content present in the burned coating sample, thus higher the anti-oxidation value of the char.

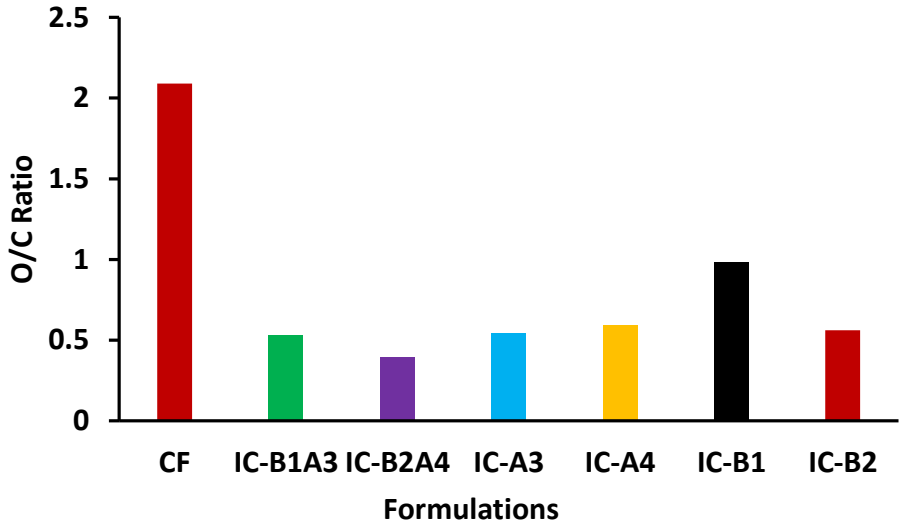

Figure 6. EDS for all coating formulations

This test was carried out on carbolite furnace at 800ºC for 1 hr. Figure 7 shows the intumescent coating thickness and char thickness of the seven formulations using equation (1). At 500ºC the coating expands and it give different char thickness. The char expansion of IC-A4 with 4 wt% of ATH is more as compared to the other formulations. The percentage expansion increased by reinforcement of ATH. Higher the value of intumescent factor and adequate adhesion prevents the underlying substrate from heat of flame.

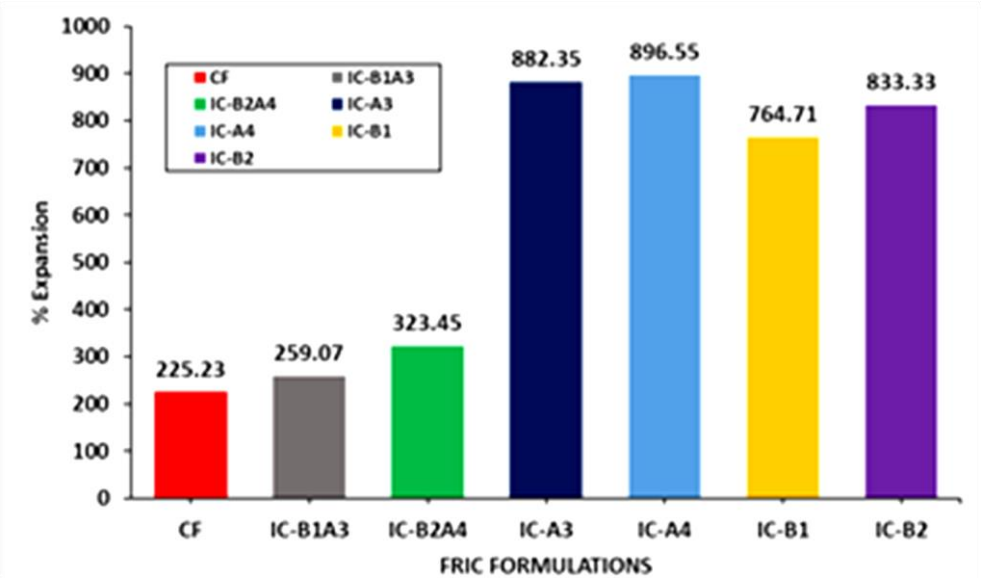

Figure 7. Char expansion percentage after 800ºC fire test

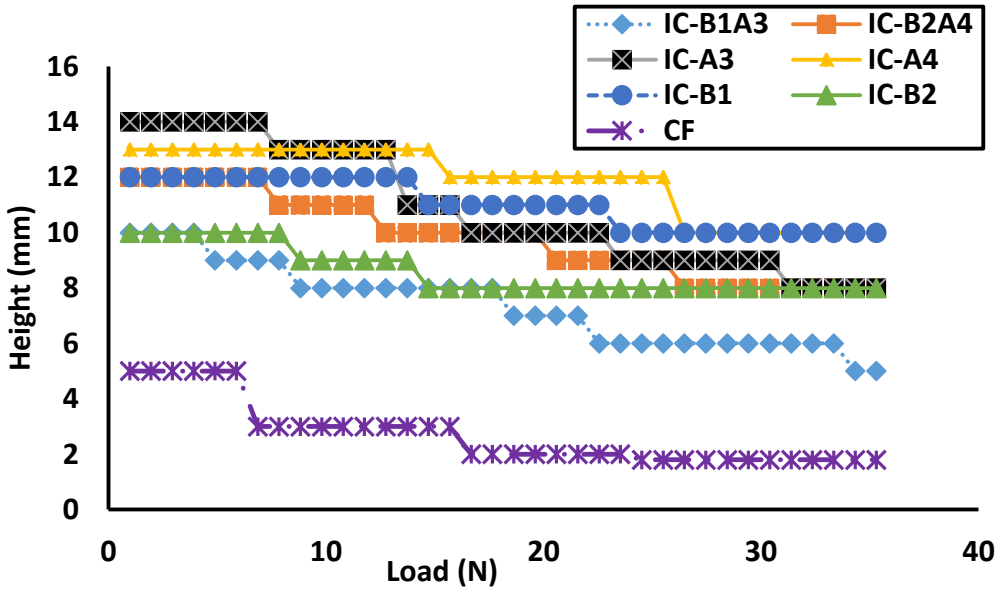

Figure 8. Char resistance of coating formulations under different loads after 500°C fire

$$Char\ Expansion = \frac{Char\ thickness}{Coating\ thickness} \times 100 \quad (1)$$

The char's strength was quantified with respect to the char height after applying load. The stiffer char resists the deformation and it was translated by the smaller change in the height of the char. Abrupt drop in the height means that the char strength is low. Figure 8 shows the plot between char height as it was loaded by various weights up to 35.316N. For CF, at a load of 10.791N the height of the char decreased by an amount of 2 mm which means that the char ruptured which decreased the strength. The change in height remains constant from 25.525N onwards. On the other hand the fire retardant intumescent coatings do not follows the same trend because of the crispy and brittle structure. By adding ATH and BF in the formulations made some tiny holes after burning and swelling which resulted higher strength of the char. Among all, the IC-B2 shows higher strength which remained almost rigid and its height didn't decrease after applying 14.715N load onwards. As for as the first height reduction is concerned, IC-B1 formulation was the best among all which resisted against the applied load until 13.734N, remaining all samples got height reduction earlier than IC-B2. The first drop in thickness due to the compression force may be attributed to collapse or rupture of the rough peak of the char's top layer. Successive reduction in char thickness happened because of further damage of the top surface. The increase in mechanical strength of the fibre reinforced chars was anticipated. Though, high temperature may have decreased basalt fibres' performance, FRIC produced higher strength char than the unreinforced coating.

XRD results for the control formulation consisted of three main peaks. Char was composed of carbon and inorganic compounds like boron phosphate due to the presence of boric acid in the formulation. These were the key factors to oxidize the char from high temperature. CF showed the presence of boron phosphate, boric acid and carbon at 2^{θ} values of 24.5332, 26.639 and 40.02 respectively. Boron phosphate was formed due to reaction between boron oxide and decomposition products of APP i.e. polyphosphoric acid. Boron phosphate was also present there because it is a hard intumescent char and it is stable up to 1200ºC.
When the coating was added with 2 wt.% of basalt fibres (BF) filler, char was found to be composed of carbon, boron phosphate. The ICDD 98-015-0372: for Boron Phosphate, 00-025-0284 for Carbon and

98-002-4711 for boric acid. The presence of these compounds in the char confirms the strength of the char that can withstand at high temperature [13]. The XRD for the IC-B1 is shown in the Figure 9.

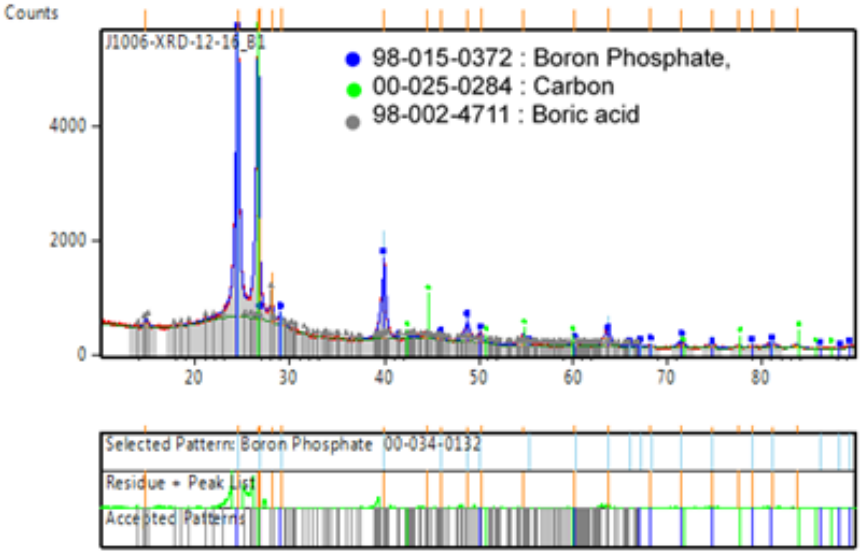

Figure 9. XRD spectra for IC-B1

5. CONCLUSION

This research involves investigation of aluminium trihydrate and basalt fibres for application as fillers for intumescent coatings which can be potentially used for protection of steel structures, in case of fire. Control formulation was developed using flame retardants such as ammonium polyphosphate, expandable graphite, melamine and boric acid as an acid source, carbon source, blowing agent and flame retardant additive, respectively. The intumescent percentage was increased by using aluminium hydrate 4 wt.% and basalt as 2 wt.% IC-B2A4 among all formulations. The microstructure of control formulations was uneven and consists of deep and shallow cracks which reduced the strength of char. However, the microstructure was improved by using aluminium hydrate 4 wt.% and basalt as 2 wt.% IC-B2A4; which yielded less cracks and increased the strength of the char. According to EDS analysis, oxygen to carbon ratio (O/C) for IC-B2A4 was significantly enhanced by 49%. XRD results showed that the char obtained after furnace test for control formulation was composed of carbon, boron phosphate and boric acid. These are highly thermal stable compounds that can prevent the char from oxidization. The final residual weight of the char at 800°C for IC-B2A4 was 35.32% which is the highest residual weight among all formulations. Thus, the preliminary results indicate that newly prepared formulation can withstand high temperature to protect the steel substrate.

References

[1] J. Wang, W. H. Song, M. Zhang, and Z. Chen, *Ind & Eng Chem Res,* **53**, 11249, 2014.
[2] J. S. Emma G, *The New York Times,* Vol., 2015.
[3] M. Jimenez, S. Duquesne, and S. Bourbigot, *Therm Acta,* **449**, 16, 2006.
[4] M. Jimenez, S. Duquesne, and S. Bourbigot Ind & Eng Chem Res, **45**, 7475, 2006.
[5] G. Wang and J. Yang, *Surf & Coat Tech,* **204**, 1186, 2010.
[6] G. Wang and J. Yang, *Prog in Org Coat,* **70**, 150, 2011.
[7] S. Bourbigot, M. Le Bras, S. Duquesne, and M. Rochery, *Mac Mat & Eng,* **289**, 499, 2004.
[8] A. Dasari, Z.-Z. Yu, G.-P. Cai, and Y.-W. Mai, *Prog in Poly Sci,* **38**, 1357, 2013.

[9] M. Jimenez, S. Bellayer, B. Revel, S. Duquesne, and S. Bourbigot, *Ind & Eng Chem Res,* **52**, 729, 2013.
[10] A. Riva, G. Camino, L. Fomperie, and P. Amigouet, *Poly deg & stab,* **82**, 341, 2003.
[11] N. Amir, F. Ahmad, and P. S. M. Megat-Yusoff, " *Adv Mat Res*, 504, 2013.
[12] N. Amir, A. A. Majid, and F. Ahmad, " in *MATEC Web of Conf*, 2016.
[13] M. Zia-ul-Mustafa, F. Ahmad, S. Ullah, N. Amir, and Q. F. Gillani, *Prog in Org Coat,* **102**, 201, 2017.
[14] H. Aziz and F. Ahmad, *Prog in Org Coat,* **101**, 431, 2016.
[15] G. Li, G. Liang, T. He, Q. Yang, and X. Song, *Poly deg & stab,* **92**, 569, 2007.
[16] C.-S. Chou, S.-H. Lin, and C.-I. Wang, *Adv Pow Tech,* **20**, 169, 2009.
[17] C.-S. Chou, S.-H. Lin, C.-I. Wang, and K.-H. Liu, *Pow Tech,* **198**, 149, 2010.
[18] G. Li, J. Yang, T. He, Y. Wu, and G. Liang, *Surf & coat Tech,* **202**, 3121, 2008.
[19] S. Ullah, F. Ahmad, and P. S. M. M. Yusoff, *Jour of App Poly Sci,* **128**, 2983, 2013.
[20] W. F. Mohamad, F. Ahmad, and S. Ullah, *Asi Jour of Sci Res,* **6**, p. 263, 2013.
[21] Q. Liu, M. T. Shaw, R. S. Parnas, and A.-M. McDonnell, *Poly Comp,* **27**, 41, 2006.
[22] T. Czigány, *Poly Comp*, ed: Springer, pp. 309, 2005.
[23] *EXPRESS Polymer Letters,* 2007.
[24] R. Otáhal, D. Veselý, J. Násadová, V. Zíma, P. Němec, and P. Kalenda, *Pig & Res Tech,* **40**, 247, 2011.
[25] M. Kumar, M. Kumar, and S. Arora, *Jour of the Ind Acad of Wood Sci,* **10**, 125, 2013.

Corrigendum: Effect of basalt fibres reinforcement and aluminum trihydrate on the thermal properties of intumescent fire retardant coatings

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Muhammad Yasir[1], Norlaili Binti Amir[1], Faiz Ahmad[1], N. Syahirah Rodzhan[1]

Mechanical Engineering Department, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak, Malaysia

Corresponding author email: norlailiamir@utp.edu.my

Description of corrigendum:

A section in the paper on page 9 after section 5 is missing. The missing section is as below:

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