Effects of Dolomite on Thermal Performance of Intumescent Fire Retardant Coating for Structural Steel

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Department of Mechanical Engineering
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Approved:

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MAY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MUHAMMAD MUIZ HAQIMI
AHMAD SAUKI

ABSTRACT

Intumescent fire retardant (IFR) coating is designed to protect the substrate against fire. In case of fire, intumescent coating expends and form a thick porous char layer act as thermal barriers which is strong enough to protect the substrate from fire and retain its structural integrity. IFR coating consist of 3 main ingredients; an acid source (ammonium polyphosphate-APP), carbon source (expendable graphite-EG) and a blowing agent (melamine-MEL). The main objective of this project is to develop an IFR coating with reinforced of Dolomite filler and study the thermal performance, residual weight, char morphology and gaseous product of IFR coating for protection of steel substrate. The coating was formulated using the basic formula (APP-MEL-EG) with addition of Dolomite $CaMg(CO_3)_2$ as filler. Different formulation with different weight percentage of Dolomite filler composition was prepared to evaluate the performance of the IFR coating.

The thermal performance of IFR coating formulation was determined by using Bunsen burner test. The results shows that IFR 8, with 8 % of added Dolomite filler, give the better heat shielding effect compared to other IFR coating. TGA analysis was performed to determine the residual weight of the intumescent coating. The result shows that IFR coating with added filler had improved the residual weight of the coatings. At least 80% of residual weight can be improved by imparted Dolomite filler in the coating compared to IFR coating without filler. Next, the coating was tested using SEM analysis. From the analysis, it was observe that the coating with added filler shows more compact and uniform char orientation compare to the controlled sample. The speed of heat transfer from the char to steel substrate can be reduced by having uniform and multiporous char structure. Last, the IFR coatings undergo GCMS analysis in order to characterize the gaseous product after decomposition. From the result, most of the gaseous product produced is Phenol and p-Isopropylphenol. These gaseous products cannot bring much harm to the human being specifically to the victim of the fire occasion unless they inhale the gaseous in bulky compare to the halogenated based. In conclusion, the addition of Dolomite filler in the intumescent coating formulation enhances the thermal performance of IFR coating for protecting structural steel.

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List of Abbreviations

A

APP: Ammonium polyphosphate

ASTM: American Society of Testing and Materials

B

BA: Boric Acid

BS: British Standard

D

DGEBA: Diglycidylether of Bisphenol A

E

EG: Expendable Graphite

F

FTIR: Fourier Transform Infrared Spectroscopy

G

GCMS: Gas Chromatography Mass Spectrometry

I

IFR: Intumescent fire retardant

M

MEL: Melamine

P

PP: Polypropylene

S

SEM: Scanning Electron Microscopy

T

TGA: Thermogravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 Background of study

The structural steel is widely used in construction industry and offshore platforms. Steel is non-combustible materials which exhibits a good strength but begins to lose its structural properties between 470 °C and 500 °C. [1] Due to low failure temperature and high heat conducting value, the structural steel may easily collapse when its temperature reaches above 540 °C. [2, 3] Prevention from structural collapse and rapid increase in temperature has to take into consideration to ensure the safe evacuation of people from the building in case of fire. Indeed, fire protection of steel building is a main requirement of building regulation in many countries.

There are several types of fire proofing system used in industries. The most common fire proofing system is organic resin-based product, known as "intumescent coating". Intumescent coating acts as both by preventing the initial starts of fire and by delaying the spread of fire, thus can increase the escape time during the event of fire. [4] Intumescent coating is composed of three (3) fire retardant additives: an acid source (ammonium polyphosphate-APP), carbon source (expendable graphite-EG) and a blowing agent (melamine-MEL). [5] During the exposure to the heat, the coating expends and forms a thick char layer that protects the structure against fire.

The performance of the intumescent coating depends on the choice of the ingredients and their appropriate combinations. Currently, this traditional method of of the intumescent fire retardant system (APP-EG-MEL) is not satisfactory due to its poor performance of anti oxidation and fire retardancy. [5] Nowadays, extensive research had been done to improve the performance of intumescent coating. Locally inorganic fillers are added in the intumescent coating to have improvement in the char morphology, thermal insulation, mechanical properties and excellent chemical resistance. [6] One of the solutions is by adding a mineral based material (Dolomite) as filler in the intumescent coating.

1.2 Problem Statement

Recent years, intumescent coating is widely used in protecting structural steel against fire. Intumescent coatings are mostly based on a combination of char-forming material, a mineral acid catalyst, a blowing agent and a binder resin [6, 7]. However, these materials are typically organic-based materials which have some disadvantages [8]:

I. Organic additives undergo exothermic decomposition which reduces the thermal insulative value of the system.

II. The resulting carbonaceous char in some cases has a low structural integrity and the coating cannot withstand the mechanical stress induced by a fire/or by other external constrains.

III. The coating releases organic gases (potentially toxic) which are undesirable in a closed fire environment.

Inorganic filler reinforced intumescent coating is the alternative for this problem. However, inorganic intumescent coating is very vulnerable to water or moisture therefore the use of mineral based filler in intumescent coating is deemed as one of the bright solution for the situation.

1.3 Objective

To develop an intumescent fire retardant coating with reinforced of Dolomite filler and study the thermal performance, residual weight, char morphology and gaseous product produced of intumescent fire retardant (IFR) coating for protection of steel substrate.

1.4 Scope of study

The scope of study of this project will cover the effect of Dolomite as filler in intumescent coating. Thermal insulation performance will be determined by using Bunsen burner test and furnace test for char expansion. SEM test used to study the char morphology and TGA to determine the Residual weight of coating. FTIR test was used to determine the functional group of the residual char and GC-MS test is for determine the toxicity of the gas released of the IFR coating.

CHAPTER 2

LITERATURE REVIEW

2.1 Intumescent Fire Retardant (IFR) Coating

To control fire hazard effectively one can relies on excellent reactive passive fire protection such as intumescent coating. [9] Intumescent fire retardant coating is a mineral-based or organic resin-based product that can be used to protect several materials such as structural steel, wood, polymer and textile against fire. This coating if applied to the structure of a building will retard fire and slow down the spread of flame. [9] Under the action of heat, intumescent fire retardant coatings expands and forms a thick porous charred layer which acts as a thermal barrier that protects and insulate the substrate, thereby maintaining the structural integrity of the structures. [10] Another advantages of intumescent coating is, it does not modified the mechanical properties of structure and also easy to be processed. Intumescent coating is proven to protect the base structure upon fire. The coating are designed to perform under severe conditions and to maintain steel integrity for one up to three hours when the temperature of the surroundings is in excess of 1100°C [3]

An intumescent fire retardant system is made up from intumescent flame retardant (IFR) system, binder and fillers. Generally, three (3) active ingredients are used for the intumescent flame retardant (IFR) system. IFR is composed of an acid source (ammonium polyphosphate-APP), carbon source (expendable graphite-EG) and a blowing agent (melamine-MEL). [5] The three (3) active ingredients and the binder swell and form an intumescent char layer and protect the base structure from the rapid increase of temperature upon heating at elevated temperature. [4] Boric acid was used as additives in intumescent fire retardant coating system to improve the performance of the IFR coating. [11] In this work, filler added to increase the char strength. In order to form a capable intumescent coating that can ensure the protection of the structure against fire, all the formulation of the coating need to be measured in terms of physical and chemical properties to form an efficient protective char. The mechanism of intumescent is usually describe as follow [12]: first, the acid source breaks down to yield mineral acid, then it takes part in the dehydration of the carbonization agent to yield the carbon char, and finally the blowing agent decomposes to yield the carbon char, and finally the blowing agent decomposed to yield gaseous products. The later causes char to swell and hence provide insulating muti-cellular protective layer.

The ingredients are as follows:

I. Acid source: Ammonium polyphosphate (APP)

   APP is an acid source which having high chain of phosphate which its formulation describes as NH_4PO_3. APP acts both as acid source as well as blowing agent in intumescent coating. APP also acts as the source of phosphoric acid that will increase the formation of carbonaceous char and NH_3 which improve the swelling.

II. Carbon source: Expendable graphite (EG)

   The carbon source will form a carbon char when the dehydration of the mineral acid occurs. [13] When heated, the graphite starts to expend up to several 100 cm^3/g and forms a protective layer for the polymer. [11] In order to get the ideal fire retardant coating, the EG have to react with APP.

III. Blowing agent: Melamine (MEL)

   Blowing agent decomposes to yield gaseous product during the intumescent process which will increase the char stability. [13] When mix with resin, melamine can posses fire retardant properties due to the release of nitrogen gas when it is burn or charred. [14]

IV. Binder: Epoxy resin and hardener

   Epoxy resin will be used as the binder. The binder used is a solvent free thermoset epoxy resin. The resin is the mixture of Diglycidylether of Bisphenol A (DGEBA) and an amine curing agent polyaminoamide. [12]

V. Boric acid

Boric acid, H_3BO_3 act both as intumescent agent and also char reinforce. Boric acid turns by dehydration into boron oxide between 140°C and 200°C, leading to a hard and high thermally stable residue. [3] The first step is the dehydration of boric acid that will produce metaboric acid HBO_2 (1). Further dehydration of metaboric acid will produce boron oxide B_2O_3 (2). Formation of boron oxide will form "glass like" material which can prevent the gas escape. The reaction of APP and boric acid also important as the reaction form borophosphate which provides the superior mechanical resistance of the char and promote the adhesion of the char on steel plate. [3]

$$H_3BO_3 \rightarrow H_2O + HBO_2 \qquad (1)$$

$$2\,HBO_2 \rightarrow H_2O + B_2O_3 \qquad (2)$$

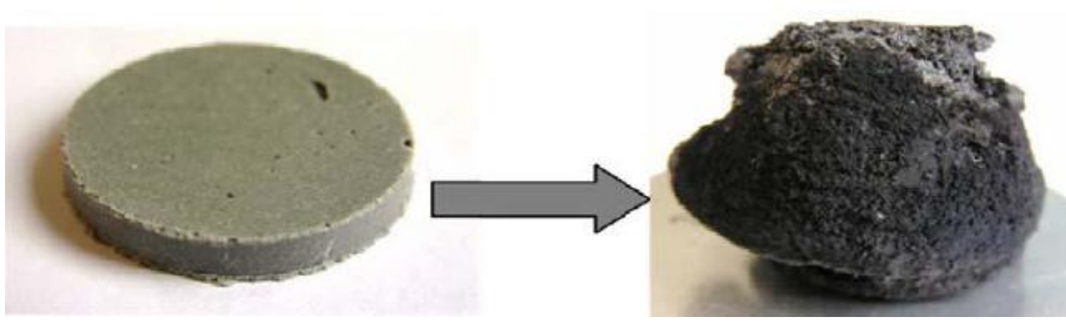

Figure 1: Swelling of an intumescent coating [4]

2.2 Effect on thermal performance of reinforced fillers in intumescent coating

To enhance the performance of the intumescent coating, several researches have been studied recently. Inorganic filler such as calcium carbonate and silica are one of the common filler reinforced in the intumescent coating. Most of the filler used are mineral based materials. In this study, it had been proven that the addition of the inorganic fillers improves the anti oxidation and thermal degradation of the coating. [15] Furthermore, it is proven that by incorporating alumina as filler in intumescent fire retardant coating, it can develop and improve the thermal efficiency and char morphology of the coating. [15] For the other inorganic fillers like talc or chalk (calcium carbonate), they are not the flame retardants in common sense. However, by diluting in the combustible polymer they will reduce its flammability and fire load. Research conducted by University of Pretoria shown that the incorporation of fillers in intumescent coating has made the char become harder and more solid even though it was lesser in volume. Moreover, some researchers have shown that effect of various inorganic fillers such as alumina ($\alpha - Al_2O_3$), calcium carbonate($CaCO_3$), silica (SiO_2) and feldspar ($KAlSi_3O_3$) on the flammability behavior of Polypropylene (PP) composite. [15] A suitable amount of fumed silica can promote the formation of compact intumescent charred layers and prevent the charred layers from cracking with effectively protects the underlying polymer from burning. [16] Furthermore, epoxy resin used as the binder with added of inorganic filler in the intumescent fire retardant coating ingredients. 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 performance [15].

2.3 Dolomite

The effect of adding inorganic filler can contribute for improvement of the residual weight, thermal expansion and char morphology of the intumescent coating. Various inorganic fillers such as silica and alumina are used to study the effect of these materials on intumescent coating. Most of the fillers used are usually mineral based materials which can improve the performance of intumescent coating. In this work, dolomite is used as the added filler to study the effect towards the performance of intumescent fire retardant coating. Dolomite is carbonate mineral composed of calcium magnesium carbonate $CaMg(CO_3)_2$. In Malaysia, dolomite which is known by the local as 'batu reput', is a primary sediment mineral and abundantly in Malaysia. [17] Dolomite chemical composition consist of 70% of calcium oxide CaO, 20% of magnesium oxide MgO and others in form of carbon and silicon oxide. According to the study from S Gunasekaran et al. 2006, thermal performance of dolomite is measure using differential thermal analysis (DTA) curve. Result shows that two peaks at 777.8 °C and 834°C. The two endothermic peaks observed in dolomite are essentially due to decarbonation of dolomite and calcite, respectively. At 750°C the dolomite structure is chance into calcite and at 950°C, the thermal decomposition reaction is complete. Furthermore, it was observed in that study, the weight loss of dolomite detected in temperature range of 600°C and 850°C was 46.6 %. Moreover, according to the study using SEM microphotograph of the untreated samples of dolomite, it shows distinct grains, however, the heat treated (950°C) samples exhibit clusters of grains conforming the thermal decomposition.

CHAPTER 3

METHODOLOGY

3.1 Experimental materials and formulation

The formulation of intumescent fire retardant coating was developed in this work. Each formulation has been coated on steel substrate. Acid source (APP), carbon source (EG), blowing agent (Melamine-MEL), additive (Boric acid-BA), epoxy resin, hardener and Dolomite filler with difference in weight percentage (1-10 wt%) were selected for developing intumescent fire retardant formulation. R is the controlled formulation while IFR 1- IFR 10 are added with Dolomite filler with difference in weight percentage.

Table shown is the portion of ingredients in the formulation:

Table 1: Composition of formulation (wt %)

Sample No.	Component (wt%)						
	APP	**EG**	**BA**	**MEL**	**Dolomite**	**Epoxy**	**Hardener**
R	11.76	5.5	11.76	5.5	0	43.42	21.71
IFR 1	11.76	5.5	11.76	5.5	1	42.76	21.38
IFR 2	11.76	5.5	11.76	5.5	2	42.10	21.05
IFR 3	11.76	5.5	11.76	5.5	3	41.44	20.72
IFR 4	11.76	5.5	11.76	5.5	4	40.78	20.39
IFR 5	11.76	5.5	11.76	5.5	5	40.12	20.06
IFR 6	11.76	5.5	11.76	5.5	6	39.46	19.73
IFR 7	11.76	5.5	11.76	5.5	7	38.80	19.40
IFR 8	11.76	5.5	11.76	5.5	8	38.14	19.07
IFR 9	11.76	5.5	11.76	5.5	9	37.48	18.74
IFR 10	11.76	5.5	11.76	5.5	10	36.82	18.41

APP: Ammonium poly phosphate, **EG:** Expendable Graphite, **BA:** Boric Acid, **MEL:** Melamine

3.2 Steel Substrate Preparation

Preparations of steel plate start with large mild steel plate with thickness of 1.5mm. The large plate has been cut into 50 x 50 mm and 100 x 100 mm plates using shear cutter machine. The plates were sent to Heat Tech Treatment Sdn Bhd for sand blasting. Sand blasting is an essential step to remove mill scale, corrosion and roughen the surface of plate as a surface preparation before coating is applied.

Figure 2: Cutting of steel substrate using shear cutter

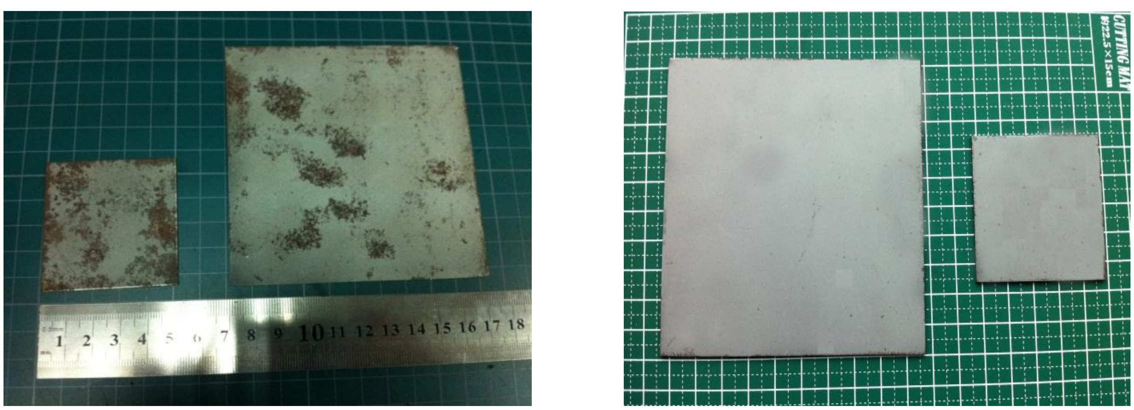

Figure 3: Steel substrate before and after undergo sand blasting

3.3 Experimental Procedure

For all IFR coating formulations, selected weight percentage of APP, MEL, BA and Dolomite filler were grounded for 1 min by using grinder. This were followed by mixing of epoxy and hardener with all ground material and expendable graphite (EG) using shear mixture at 40 rpm for 20 min. After 20 minutes, hardener is added and been mixed for another 10 minutes. Total process is 30 minutes for each sample. The formulation will then be coated on steel substrate having dimensions $(10cm \times 10cm \times 1.25mm)$ and $(5cm \times 5cm \times 1.25mm)$. The coated steel substrates were cured at ambient temperature for 1 week. Ensuring fully cured, the coatings were examined on the residual weight by using Thermogravimetric (TGA) analysis and send for GCMS analysis. Then, all the coating was tested for char formation by using carbolite furnace at 500°C for 1 hour. The char morphology was observed and analyze by using Scanning Electron Microscope (SEM). Next, the functional group of the coating will be determined by using FTIR analysis. The flow chart of the experimental procedure was shown in Figure 5.

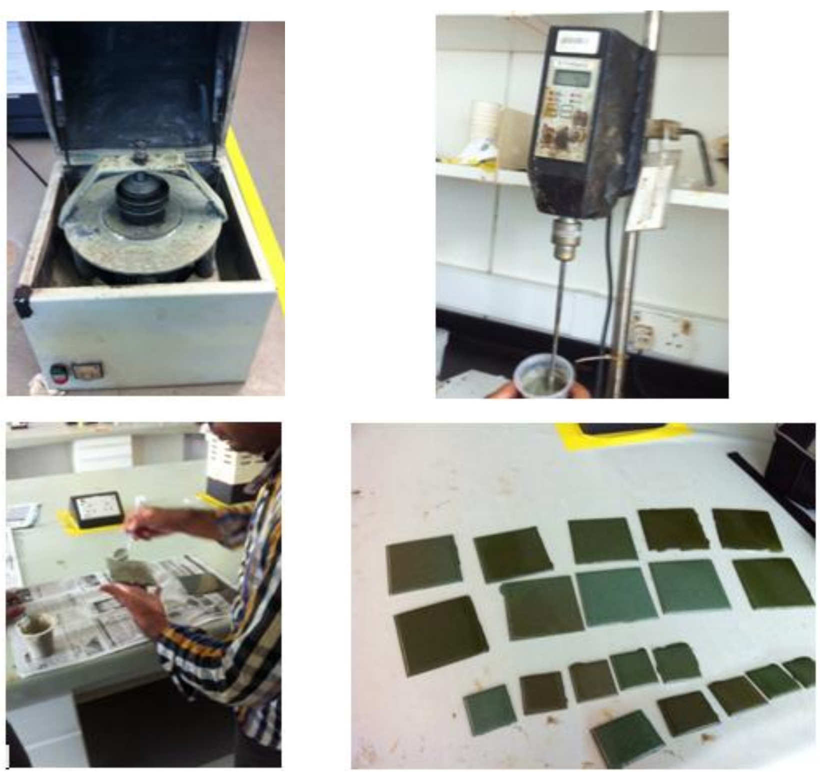

Figure 4: From top-left; Rocklabs mortar grinder, Caframo mixer, formulation applied onto steel plates using spatula and 10 cured sample formulations

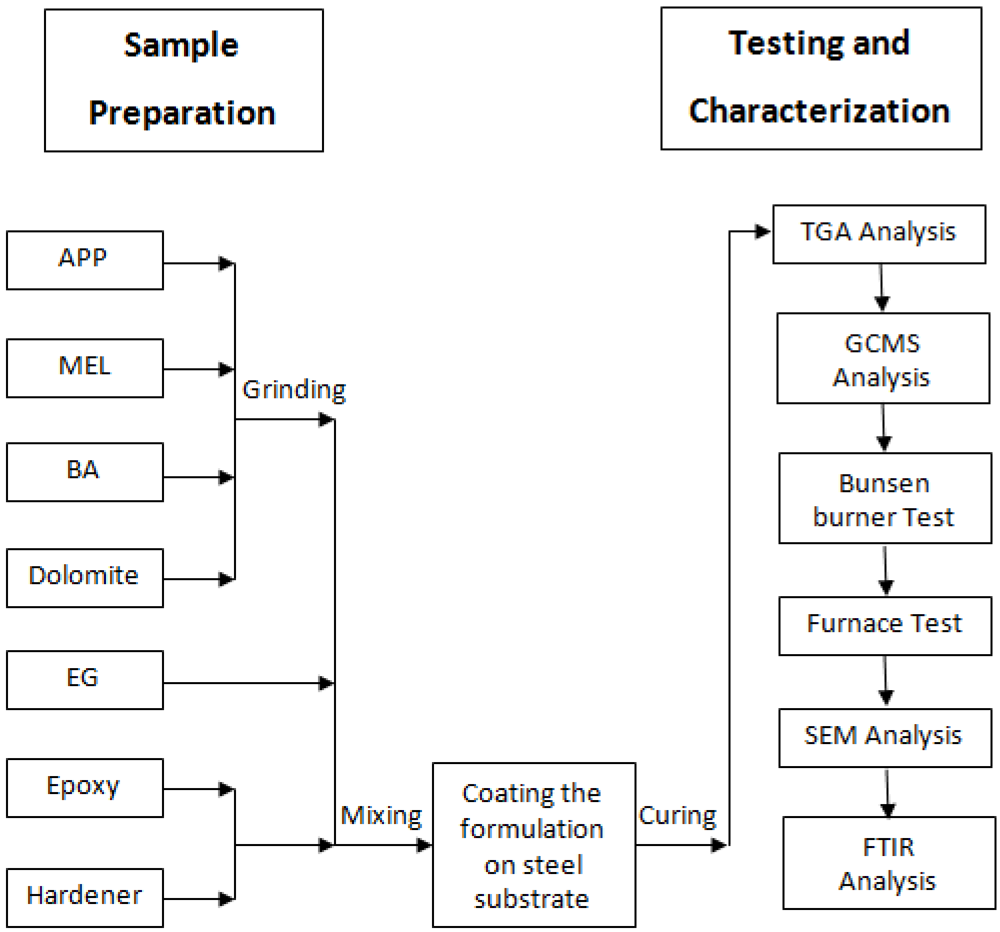

Figure 5: Experimental procedure flowchart

3.4 Testing Characterization

3.3.1 Bunsen Burner Test

Bunsen burner test were carried out to evaluate the fire performance of the intumescent coating in a real fire case scenario. For this test, steel substrate of intumescent fire retardant coating (10cm x 10 cm) was used. Bunsen burner test is used for heat shielding at 950°C according to ASTM 119. Each sample is burned for a period of 60 minutes. Thermocouple was placed at the back of the sample to determine the temperature of the sample during the testing. The temperature of the steel substrate was recorded for each minute.

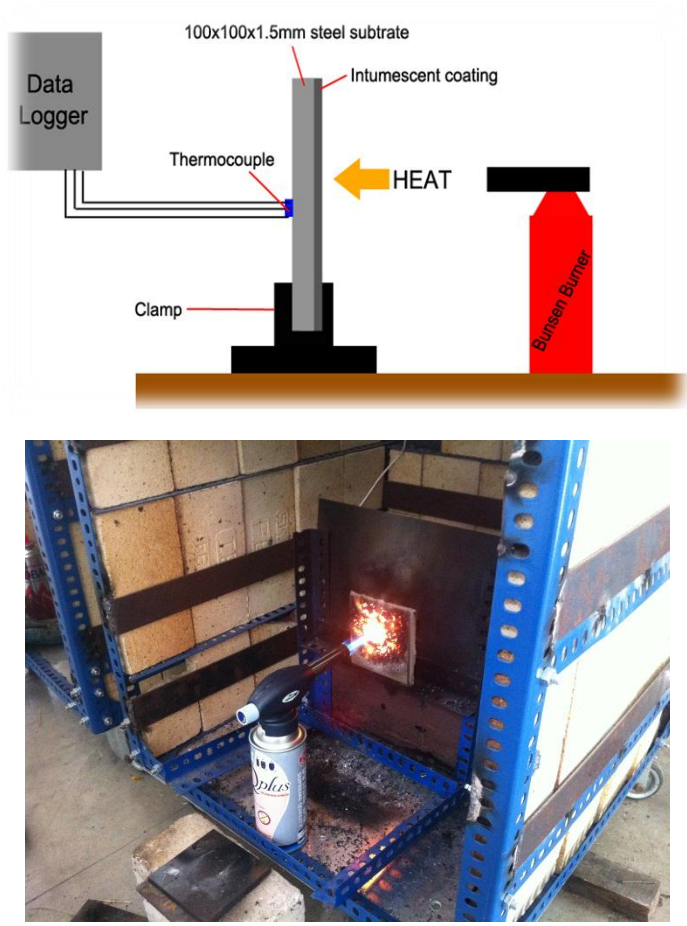

Figure 6: Bunsen burner fire test diagram (top) & Bunsen burner test on progress (bottom)

3.4.2 Furnace Test

IFR coating formulation will undergo furnace test inside the furnace chamber. Furnace fire stimulates a fire incident in a confined space, where intumescent coating sample were allowed to intumesce freely. [17] For this test, the sample will undergo progressive heating using CWF 1300 Carbolite furnace with the rate of 26°C/min from room temperature 25°C to 500°C within 30 min to follow the standard temperature/time curve in BS 476-20. The temperature was then maintained for another 30 min and after that was left to cool down under room temperature. Furnace test was conduted to study the char expansion of the intumescent coating. Apart from that, the expansion of the char after furnace test is used for another testing which are for SEM and FTIR analysis.

Figure 7: Furnace Machine

3.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric (TGA) analysis is a method of thermal analysis which analyzes the physical and chemical properties changes in term of increasing temperature with constant heating rate with the function of time. TGA was performed to determine the thermal stability of the intumescent coating. TGA were carried out at 10°C/min using synthetic air (flow rate: 50 mL/min, air liquid grade), using a Setaram TG 92 microbalance. The samples (approximately 10 mg) in powder form were placed in open vitreous silica pans. The precision of the temperature measurement was 1.5°C over the whole range of temperature (20-800 °C). [3]

3.4.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a microscope that uses electron rather than light to form an image. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation make SEM is one of the most heavily used instrument in research area today. SEM can produce a very high-resolution image of a sample surface, revealing details about 1 to 5 nm in size. This is used to study the char morphology of the intumescent fire retardant coating.

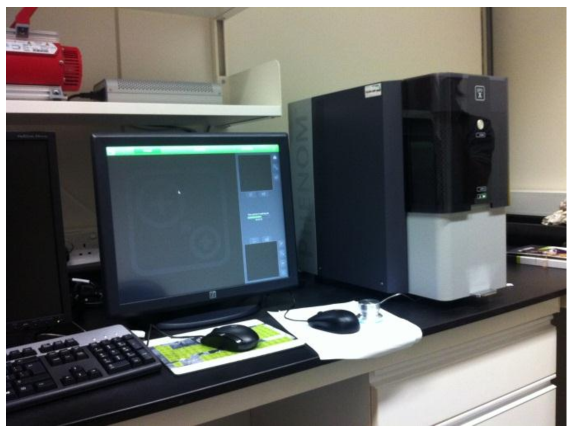

Figure 8: Phenom ProX scanning electron microscope

3.4.5 Gas Chromatography Mass Spectrometry (GCMS) test

The residues of the coating at the edge of the sample will be grind to become powder. Then, the powder will be send to the Gas Chromatography Mass Spectrometry (GCMS) laboratory to undergo the GCMS test using a PYRO-CHEM WILKS pyrolyser, Hewlett Packard 5890 Series II gas chromatograph and TRIO 1000 mass spectrometer. 10 g of the powder was placed in the pyrolyser. The process was carried out in 10 sec for 25 - 800°C. Then the pyrolysis product in the gas phase was injected into ion detector column to characterize the gaseous product.

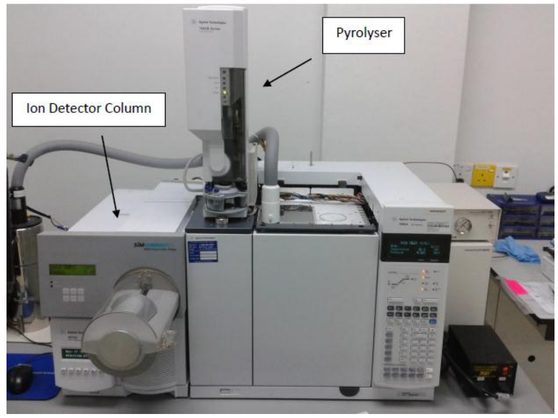

Figure 9: GCMS Testing Machine

3.4.6 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of observation, emission, photoconductivity or Raman scattering of a solid, liquid or gases. Through this analysis, the functional groups of residual char composition of the IFR coating were analyzed by Shimadzu FTIR in the range of 4000 – 400cm^{-1}.

3.5 Gantt Char

Table 2: FYP 1 Gantt Chart

FYP 1 Timeline															
No.	**Items**	**Jan**			**Feb**				**Mar**				**Apr**		
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	**Topic Selection Process**														
2	**Preliminary Research Work**														
	2.1 Literature review and analysis														
	2.2 Preparation of Extended Proposal draft														
3	**Submission of Extended Proposal**														
4	**Proposal Defence**														
5	**Project Work Baseline Preparation**														
	5.1 Discussion on experiment procedure														
	5.2 Equipment introduction and practical														
	5.3 Lab booking and schedule draft														
6	**Submission of Interim Draft Report**														
	6.1 Review interim report with SV														
	6.2 Review project work with SV														
7	**Submission of Interim Report**														
8	**Progress Planning for FYP 2**														

Table 3: FYP 2 Gantt Chart

FYP 2 Timeline															
No.	Items	May			June				July				August		
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Sample Preparation														
2	Furnace Test														
3	TGA Analysis														
4	GCMS Analysis														
5	FTIR Analysis														
6	Submission of Progress Report														
7	SEM Analysis														
8	Bunsen Burner Test														
9	Analysis of Experiment Result														
10	Pre-SEDEX														
11	Submission of Draft Report														
12	Submission of Dissertation (Soft Bound)														
13	Submission of Technical Paper														
14	Oral Presentation														
15	Submission of Project Dissertation (Hard Bound)														

CHAPTER 4

RESULT AND DISCUSSION

4.1 Heat Shielding Effect

Five different types of formulations were determined and tested for this analysis including the controlled coating sample R. The sample used for this analysis is IFR 2, IFR 4, IFR 6 and IFR 8. This testing was conducted to evaluate the thermal performance of the IFR coating formulation of added Dolomite filler compared with the controlled formulation. A direct fire by Bunsen burner can reach up to 1000˚C in just few minutes. A thermocouple was attached at the back of the steel substrate to measure the temperature of the substrate exposed to direct fire.

The temperature time curve was recorded and the data for the fire test are illustrated in Figure 10. The controlled IFR coating formulation R shows the highest temperature as it recorded to reaches up to 268°C. As shown in the graph, all the IFR coating shows same trend of graph. The temperature increases rapidly in the first 10 minutes. The next 10 minutes up to 20 minutes of exposed to direct fire, the backside temperature decreased gradually and temperature will be constant from 30 minutes up to 1 hour. For IFR coating added with Dolomite filler (IFR 2, IFR 4, IFR 6 and IFR 8), its shows that the process of heat shielding effect was improved compared to the IFR coating without filler.

As the weight percentage of Dolomite filler was increased the heat shielding effect shows better results. For IFR coating formulation IFR 8, with 8 % of added Dolomite filler, the results shows better heat shielding effect which minimum substrate temperature recorded was 190°C. From the result, it was noted that the formulation of IFR 8 give the best intumescent effect compared to others as it contains the highest percentage of Dolomite filler. Higher percentage of Dolomite gives better strength to the char formation and gives better intumescent effect. In conclusion, the higher percentage of Dolomite would enhance the heat shielding capability of the intumescent coating.

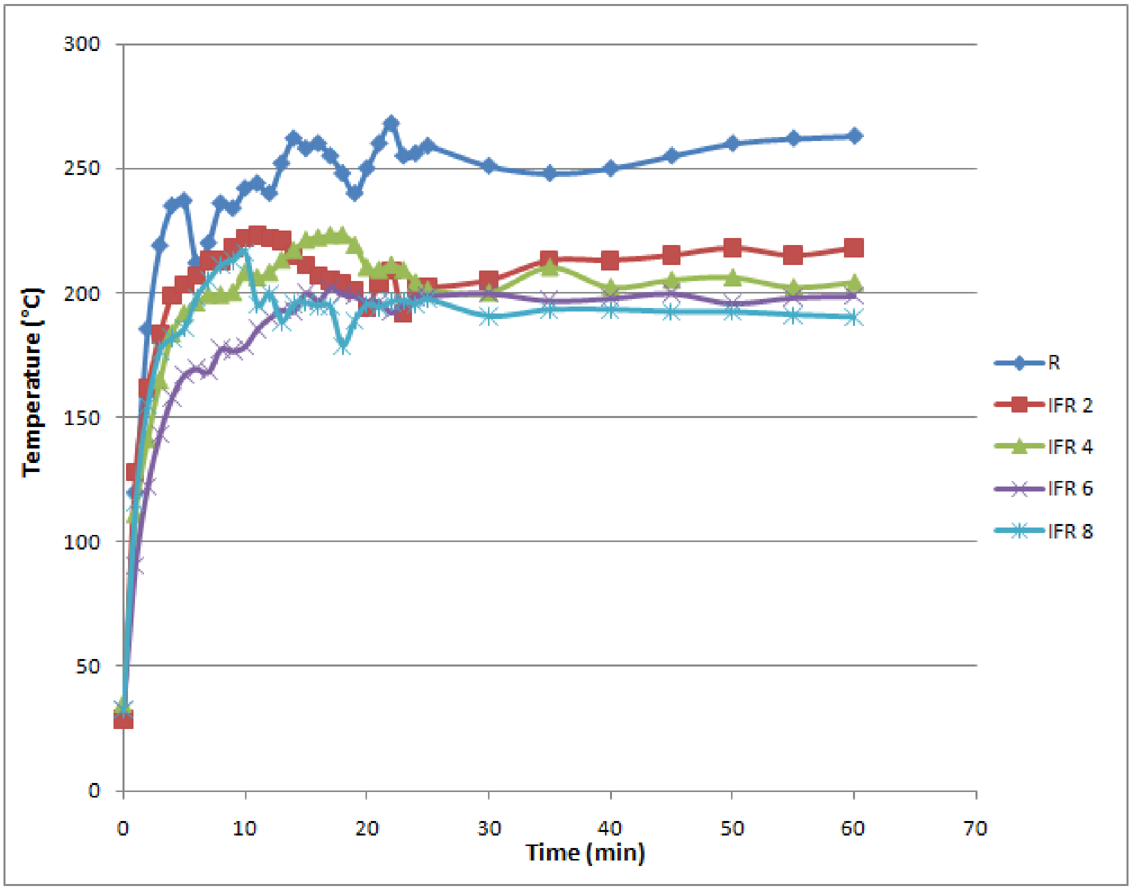

Figure 10: Time versus substrate temperature curves of IFR coating

Table 4: Temperature of steel substrate at different temperature

Time (min)	Temperature (°C)				
	R	**IFR 2**	**IFR 4**	**IFR 6**	**IFR 8**
0	32.1	28.7	34.5	32.8	32.5
5	237	203	191.6	167.1	185.6
10	242	222	208	178.7	216
15	258	211	221	200	195.9
20	250	193.7	210	196.7	195.1
25	259	202	201	199	197.4
30	251	205	199.9	200	190.6
35	248	213	210	197	193.2
40	250	213	202	198	193.2
45	255	215	205	200	192.3
50	260	218	206	196	192.3
55	262	215	202	198.3	191.1
60	263	218	204	198.9	190.2

4.2 Effect of Dolomite on residual weight of intumescent fire retardant coating.

Thermogravimetric analysis (TGA) is used to determine the residual weight of each IFR coating formulation. TGA curve for every IFR coating with difference weight percentage of Dolomite filler are presented in Figure 11. Each coating formulation shows the same trend of curve. There are significance changes of slope and this shows that the degradation process occurs at 3 main stages. The difference in the curve where sample R started to degrade earlier at 250 °C compare to IFR1 up to IFR10 which degrade around 350°C. From the result, it shows that the addition of Dolomite filler delayed the process of degradation of the intumescent coating.

For the IFR coating with added of Dolomite filler, as the temperature increasing higher than 350°C, the coatings started to degrade gradually. At this stage, it is where the coating ingredients such as APP, EG, MEL and BA decomposed and produced inert gases such as ammonia and carbon dioxide to form insulating char layer. [5] The process of intumescent occurred at the same time as the coatings degrade at the temperature of 150°C until 550°C. [6] At the later stage from 550°C up to 800°C, the non combusted residue chars acts as insulation layer and protecting the steel substrate. [6] The residue weight of each coating at different temperature is show in Table 5 below.

The highest residue weight was achieved by coating IFR 4 with 34.182% residue weight. Then it was followed by IFR 10 (33.957%), IFR 7 (32.957%), IFR 6 (32.41%), IFR 5 (31.068%), IFR 8 (30.068%), IFR 9 (28.855%), IFR 3 (25.944%), IFR 2 (24.957%) and sample R (8.84%). From the result, it shows that the addition of Dolomite filler for IFR coating formulation shows higher residual weight compared to IFR coating sample R. From the analysis it is proven that the addition of Dolomite fillers had improved the residual weight of the coatings. At least 80% of residual weight can be improved by imparted Dolomite filler in the coating compared to intumescent coating without filler. The coating with the higher 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. [5]

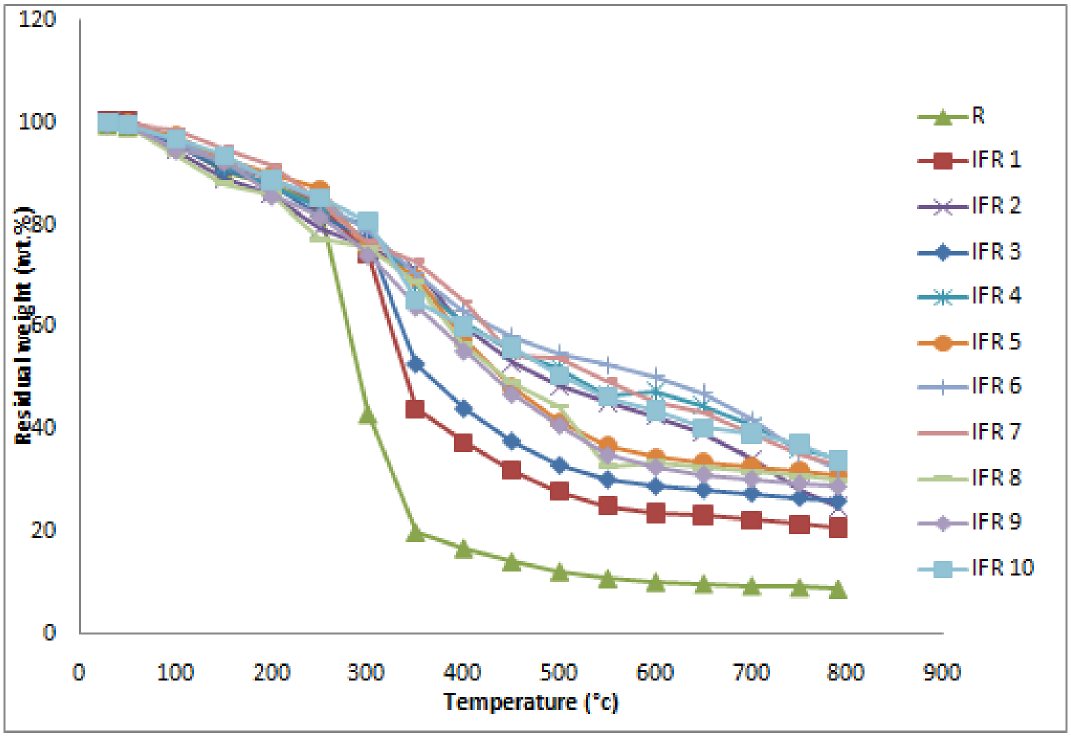

Figure 11: Residual weight of IFR

Table 5: Residual weight (wt %) of IFR coating at different temperature

Sample	Temperature (°C)				
	400	**500**	**600**	**700**	**800**
R	16.874	12.326	10.32	9.542	8.884
IFR 1	37.473	27.929	23.660	22.354	20.855
IFR 2	60.188	48.548	42.685	34.204	24.957
IFR 3	44.112	32.979	28.912	27.513	25.944
IFR 4	60.768	52.040	47.389	40.768	34.182
IFR 5	57.608	41.601	34.656	32.678	31.068
1FR 6	63.052	54.986	47.214	42.008	32.416
IFR 7	65.101	49.564	43.314	39.23	32.975
IFR 8	56.608	44.601	33.656	31.676	30.068
IFR 9	55.473	40.929	32.660	30.354	28.855
IFR 10	60.188	50.548	43.685	39.204	33.957

4.3 Char morphology of intumescent fire retardant coating

The char morphology of IFR coatings was tested by using Scanning Electron Microscopy (SEM). The coatings were burned at 500°C for 1 hour in carbolite furnace before undergo SEM analysis. From the results, on the outer surface of the char structure (Figure 12 – 14), there is expendable graphite like worm structure. This worm type structure acts s function of fiber which can enhance the resistance of char structure to deformation. [6] These characteristic are favorable which helps to get an efficient insulation layer and fire resistance of char structure. [18] This fiber like structure occurred when the expendable graphite was exposed to the heat source. [6]

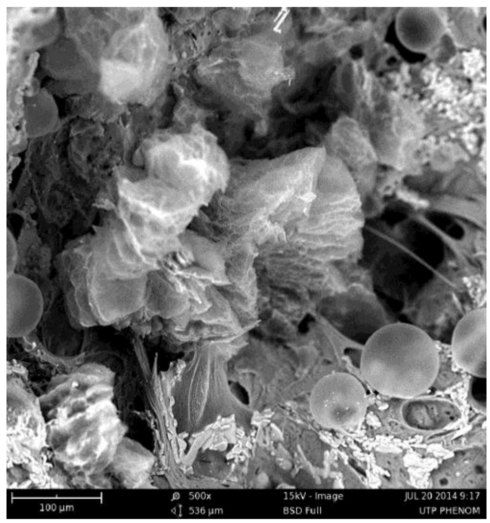

Figure 12: SEM image of sample R fibrous structure

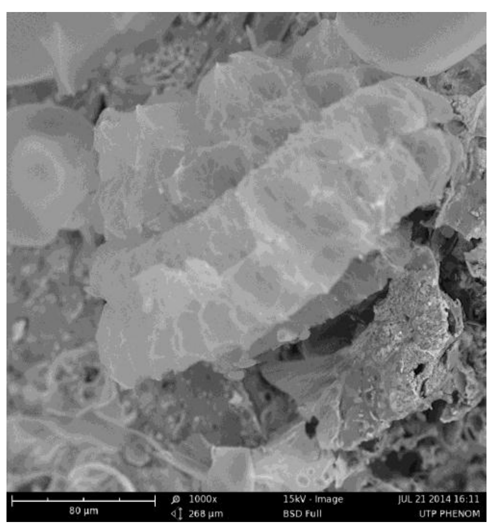

Figure 13: SEM image of sample IFR 5 fibrous structure

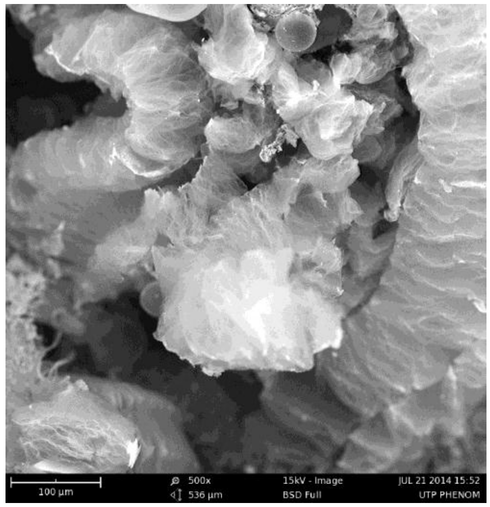

Figure 14: SEM image of sample IFR 8 fibrous structure

During heating, the intercalation compound (sulphuric acid) in the crystal structure of graphite decomposed into gases product (carbon dioxide and water). The decomposition of the intercalation compound produce a strong push forced between the graphite lattices, so the graphite basal planes can be pushed apart. During the expansion, the fused resin can stick a large amount of expendable graphite. That is why the expendable graphite is embedded in the char structure in a fibered way. [19]

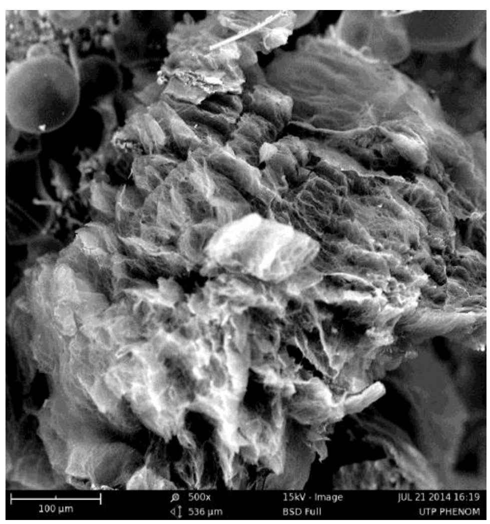

Figure 15: SEM image of cellular stucture of sample R

With higher magnification as shown in Figure 15 - 17, the outer surface of the char show compact and uniform of char structure. This foam char structure provides a shield that insulates the steel substrate from radiant heat and direct contact with the flame. [20] The multiporous char structure can block heat transferring to the steel substrate and protect the steel substrate from fire. [6] The speed of heat transfer from outer surface of char to the steel substrate depends on the resistance of the substrate to fire. That is why the expansion effect and compact char structure are important to the fire resistant properties. [5]

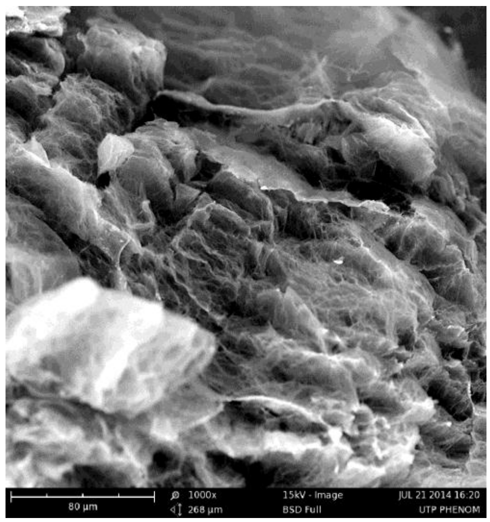

Figure 16: SEM image of cellular stucture of sample IFR 5

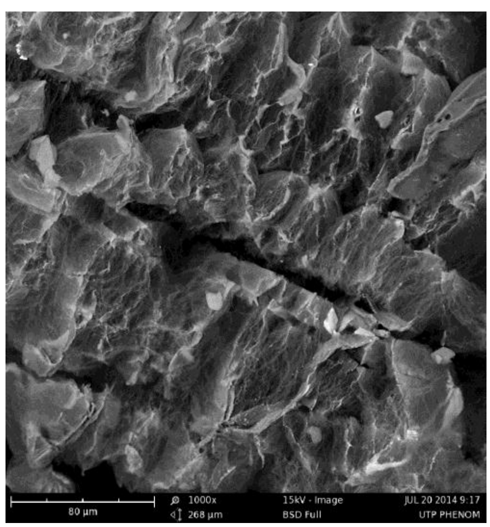

Figure 17: SEM image of cellular stucture of sample IFR 8

In conclusion, the speed of heat transfer from the char to steel substrate can be reduced by having uniform and multiporous char structure. 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. [21] Thus, it can enhance the anti-oxidation of the char layer and improved thermal stability.

4.4 Gas Chromatography Mass Spectrometry (GCMS)

Gas Chromatography Mass Spectrometry (GCMS) analysis was performed to analyze the gaseous product formed during the burning of intumescent fire retardant coating. The residues of the coating at the edge of the sample are ground. Then, the powder will be send to the laboratory to undergo the GCMS test using a PYRO-CHEM WILKS pyrolyser, Hewlett Packard 5890 Series II gas chromatograph and TRIO 1000 mass spectrometer. Then the pyrolysis product in the gas phase was injected into ion detector column to characterize the gaseous product. IFR formulation of sample R and IFR 1 – IFR 7 were selected to undergo GCMS analysis.

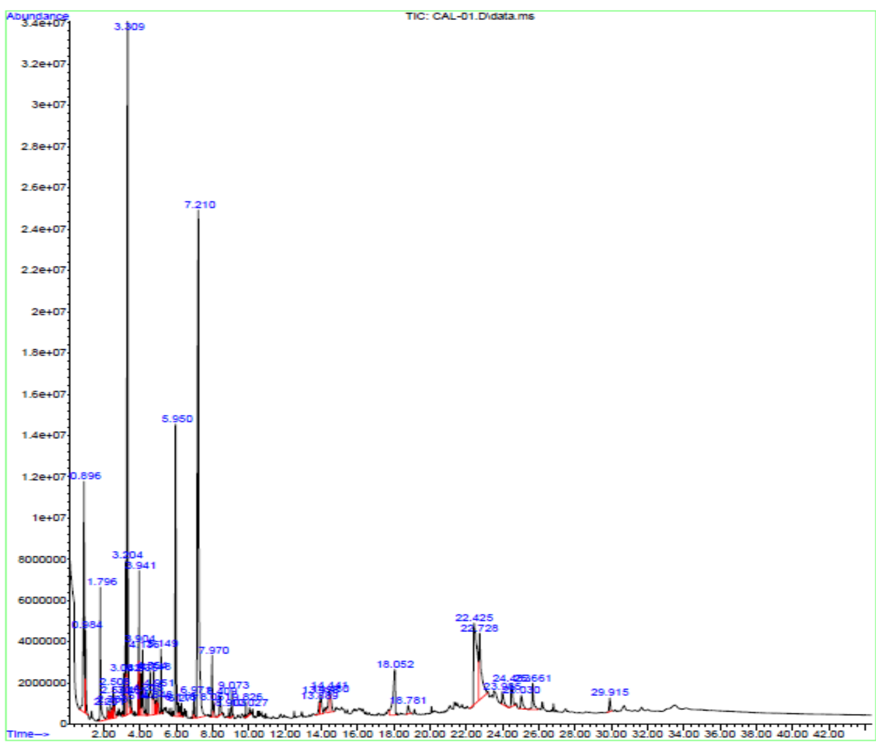

Figure 18: GCMS result for sample R

Table 6: Gaseous product for sample R

Peak Retention Time (min)	ID	Quality
3.309	Phenol	95
	Phenol	95
7.210	p-Isopropenylphenol	95
	Benzene, 1,2,3,5-tetramethyl	87
5.950	Phenol, 4 – (1-methylethyl)	94
	Phenol, 3-(1-methylethyl)	91

Figure 18 above shows the graph of no. of existing peaks for gaseous produced vs the retention time for formulation without filler. The result shows dominant gaseous product is Phenol and p-Isopropenylphenol. The dominant gaseous product produced on sample R is shown in Table 6.

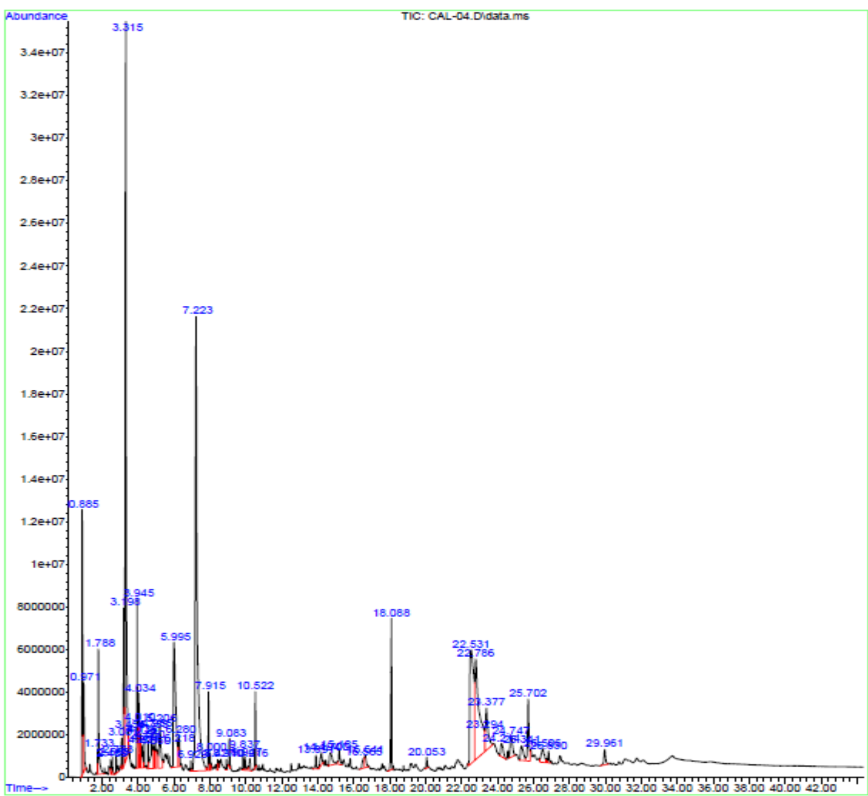

Figure 19: GCMS result for sample IFR 3

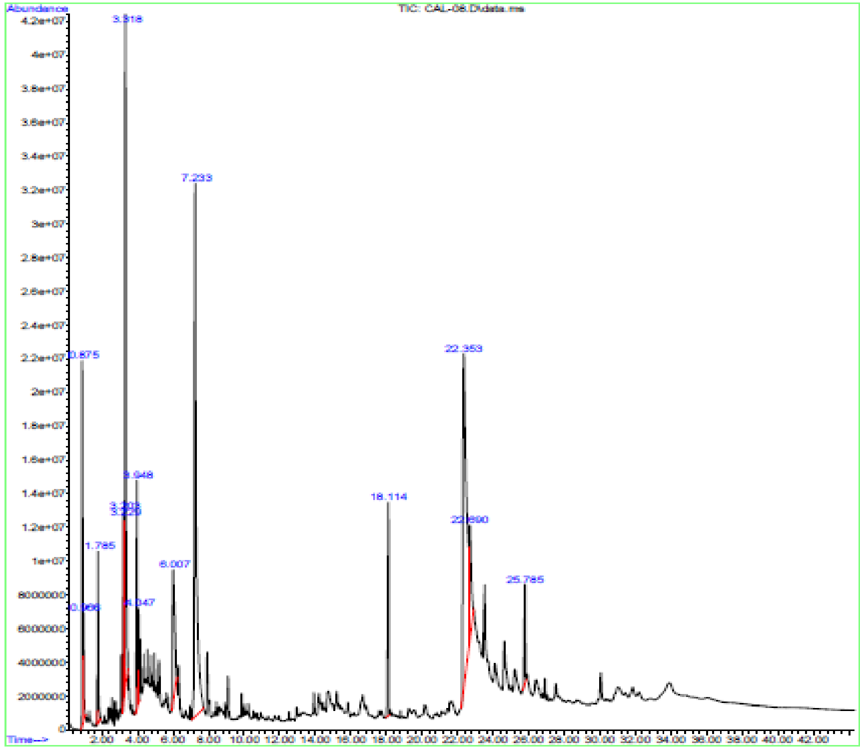

Figure 20: GCMS result for sample IFR 7

Table 7: Gaseous product for sample IFR 1 – IFR 7

Sample No	Retention time, Peak (min)	ID	Quality
IFR 1	3.297	Phenol	96
	7.187	p-Isopropenylphenol	95
IFR 2	3.299	Phenol	95
	7.196	p-Isopropenylphenol	93
IFR 3	3.315	Phenol	96
	7.223	p-Isopropenylphenol	95
IFR 4	3.310	Phenol	97
	7.202	p-Isopropenylphenol	93
IFR 5	3.296	Phenol	96
	7.177	Benzene Alcohol	89
IFR 6	3.310	Phenol	97
	7.210	p-Isopropenylphenol	93
IFR 7	3.318	Phenol	97
	7.233	p-Isopropenylphenol	95

Table 8: Gaseous product of IFR coating sample R (controlled) obtained at 800°C

IFR sample R No of Peak	Retention time (min)	Percentage of gaseous product (%)	Suspected compound name
1	0.896	6.501	Carbamic acid, monoammonium salt
2	0.984	1.721	2-Propenal
3	1.796	2.566	Toluene
4	2.201	0.289	Pyridine, 2-methyl-
5	2.363	0.350	Benzene, 1,3-dimethyl-
6	2.508	0.513	Pyridine, 3-methyl-
7	2.570	0.496	1,3,5,7-Cyclooctatetraene
8	3.082	0.394	Benzaldehyde
9	3.204	3.333	Aniline
10	3.309	17.841	Phenol
11	3.461	0.303	Benzyl chloride
12	3.514	0.108	Benzene,1-methyl-2-1-methylethyl
13	3.904	0.884	Phenol, 2-methyl-
14	3.941	1.509	Benzeneacetic acid,
15	4.035	0.906	2-(4-Aminophenyl)ethylamine
16	4.136	1.463	Phenol, 4-methyl-
17	4.335	0.277	Benzofuran, 2-methyl-
18	4.554	2.408	Benzyl Alcohol
19	4.748	1.180	2-Propenal, 3-phenyl-
20	4.848	0.315	Benzene, 1-butynyl-
21	4.951	0.345	alpha.-Benzylphenethylamine
22	5.149	1.092	Phenol, 4-ethyl-
23	5.950	7.046	Phenol, 4-(1-methylethyl)-
24	6.118	0.364	Quinoline
25	6.277	0.297	Isoquinoline
26	6.971	0.506	Phenol, 2-methyl-5-(1-methylethyl
27	7.210	20.891	p-Isopropenylphenol
28	7.970	1.044	Quinoline, 8-methyl-
29	8.061	0.353	Quinoline, 3-methyl-
30	8.409	0.661	1H-Indole, 2-methyl-
31	8.903	0.151	Benzofuran, 3-methyl-2
32	9.073	0.557	Benzofuran, 3-methyl-2
33	9.826	0.218	Trans-pDimethylaminocinnamonitril
34	10.027	0.195	Quinoline, 2,6-dimethyl-
35	13.889	0.422	Phenol, 2-(phenylmethyl)-
36	13.958	0.887	Phenol, 2-(phenylmethyl
37	14.441	1.001	Phenol, 2-(1-phenylethyl)-
38	14.480	0.743	Phenol, 2-(1-phenylethyl)
39	18.052	2.924	Phthalic acid, butyl hexyl ester
40	18.781	0.391	[1,1'-Biphenyl]-2-ol
41	22.425	7.863	Phenol, 4,4'-(1-methylethylidene)
42	22.728	4.601	Theobromine TMS derivative
43	23.985	0.671	Alpha-methylbenzylidene
44	24.483	1.092	Silane, dimethyl(4-acetylphenoxy)
45	25.030	0.759	Silane, dimethyl(4-acetylphenoxy)
46	25.661	1.090	3-amino-2-iodo-toluene
47	29.915	0.480	1H-Indole,3-phenyl-2-(2'-pyridyl)

Table 9: Gaseous product of IFR coating sample IFR 5 obtained at 800°C

IFR sample R No. of Peak	Retention time (min)	Percentage of gaseous product	Suspected compound name
1	0.886	5.572	Carbamic acid, monoammonium salt
2	0.971	2.099	2-Propenal
3	1.792	1.960	Toluene
4	3.204	4.173	Aniline
5	3.296	17.106	Phenol
6	3.941	2.024	(R)-(-)-2-Phenylglycinol
7	4.028	1.169	Pyridine, 2-ethyl-
8	6.007	6.499	Phenol, 4-(1-methylethyl)-
9	7.177	22.988	p-Isopropenylphenol
10	7.896	0.970	Quinoline, 8-methyl-
11	18.090	4.218	Dibutyl phthalate
12	22.363	23.534	Phenol, 4,4'-(1-methylethylidene)
13	22.716	7.689	Thiophene

Figure 19 and 20 above shows the graph of no. of existing peaks for gaseous produced vs the retention time for sample IFR 3 and IFR 7 respectively. The dominant gaseous product produced on sample IFR 1 – IFR 7 is shown in Table 7 based on peak retention time. The percentage of gaseous product produced by IFR coating formulation R and IFR 7 was shown in Table 6. As the result shows that, IFR 7 produced less type of gas compared to IFR coating formulation R. This indicates that the addition of Dolomite filler reduced the type of gaseous product that been produced by IFR coating without filler.

Based on the result from GCMS test, the higher correlation area in the above graph is picked as the dominant gas. For the coating with no filler (R), the higher correlation area happens at retention time of 3.309 minutes. During this period, the machine integrates the graph and gives 3 choice of possibility gaseous. The gas with higher quality has been picked as the exact one which is Phenol that has quality of 95. For all sample, it produce the same type of gases as their dominant. Phenol is also known as carbolic acid of Hydroxybenzene with molecular formula$C_6H_5OH$and boiling point at 40.5°C. According to New Jersey Department of Health, Phenol can affect someone during inhalation of the gas and may be absorbed through the skin. [22]

Another gas that is produced is p-Isopropylphenol at all formulations. This gas has molecular formula of $C_9H_{10}O$. According to the Material Safety Data Sheet for p-Isopropenylphenol by Chembase, the inhalation of this gas in bulk can cause the individual having headache, dizziness, nausea, shortness of breath, coughing and insomnia. [23] However, this health effect can be overcome by taking the victim to fresh air immediately.

Through the observation, the entire sample resulting with the same type of dominant gaseous produced which is phenol and p-Isopropylphenol. These gaseous products are from the mineral based which is carbon compound or known as organic compound. All of them contain carbon element in their respective molecular weight. Organic compound has been used frequent in human daily life application from the medicine until the vehicles that use organic compound. These gaseous products cannot bring much harm to the human being specifically to the victim of the fire occasion unless they inhale the gaseous in bulky compare to the halogenated based.

4.5 Fourier Transform Infrared Spectroscopy (FTIR)

The coating samples were analyzed by FTIR, and FTIR Spectra for intumescent coating without filler and coating sample IFR 1 – IFR 7 are shown in Figure 21 and Figure 22. The ingredients used to prepare the IFR coating added with Dolomite as filler were same as those used to prepare the controlled sample R, except of addition of Dolomite according to the weight percentage respectively. The spectra of IFR coating sample R and IFR 1 – IFR 7 are illustrated in Figure 21 and 22. All spectra of the coatings that were tested give same trend and type of spectra. There were also some main peaks appeared in all spectra that shows the functional groups of reaction. The spectrum of char IFR 4 in Figure 21 shows peaks at 3411.76, 3221.28, 2924.36, 2851.54, 2257.70, 1622.37, 1432.16, 1188.81, 1085.31, 928.67, 623.77, 545.45 and 469.93 cm^{-1} which were identified. At peaks of 1432.16 cm^{-1} and 1622.37 cm^{-1} assigned to the amino groups of NH_2 are due to (melamine and APP) and C=C of cured epoxy, respectively. [24] At the region above 2100 cm^{-1} the weak bands was shown at 3221.28 and 3411.76 is correspond to the presence of boric acid in residual char. [24]

The spectrum char of IFR 7 formulation in Figure 22 shows peaks at 3428.57, 2918.76, 2851.54, 2263.30 1627.97, 1434.96, 1088.11, 920.27, 878.32, 620.97, 509.09 and 467.13cm^{-1}. At peaks of 1434.96 cm^{-1} and 1627.97 cm^{-1} assigned to the amino groups of NH_2 are due to (melamine and APP) and C=C of cured epoxy, respectively same as been discussed for IFR 4. [24] At the region above 2100 cm^{-1} the weak bands was shown at 3428.57 is correspond to the presence of boric acid in the residual char. [24]

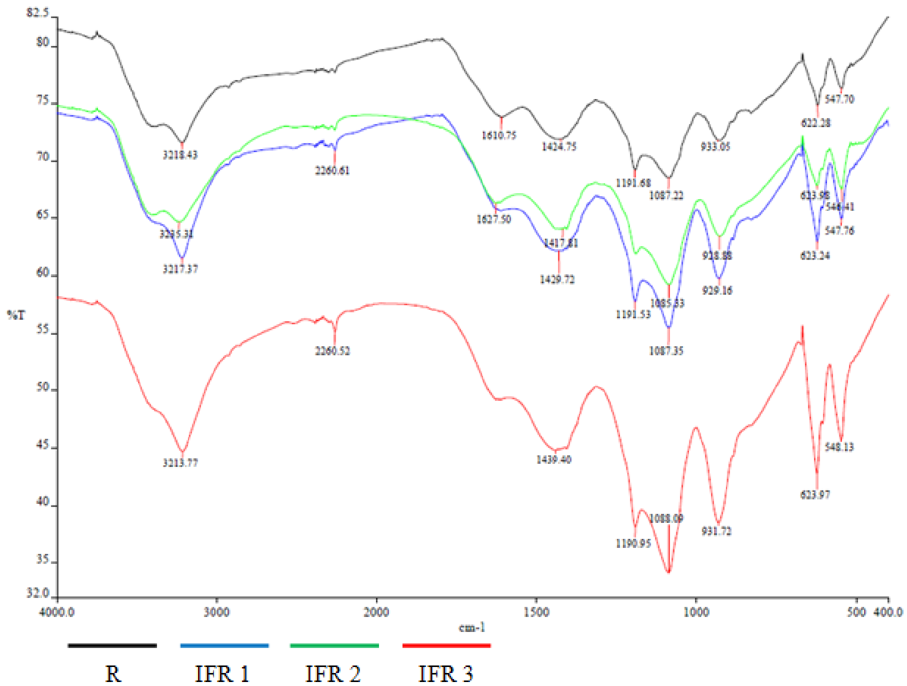

Figure 21: FTIR result for sample R – IFR 3

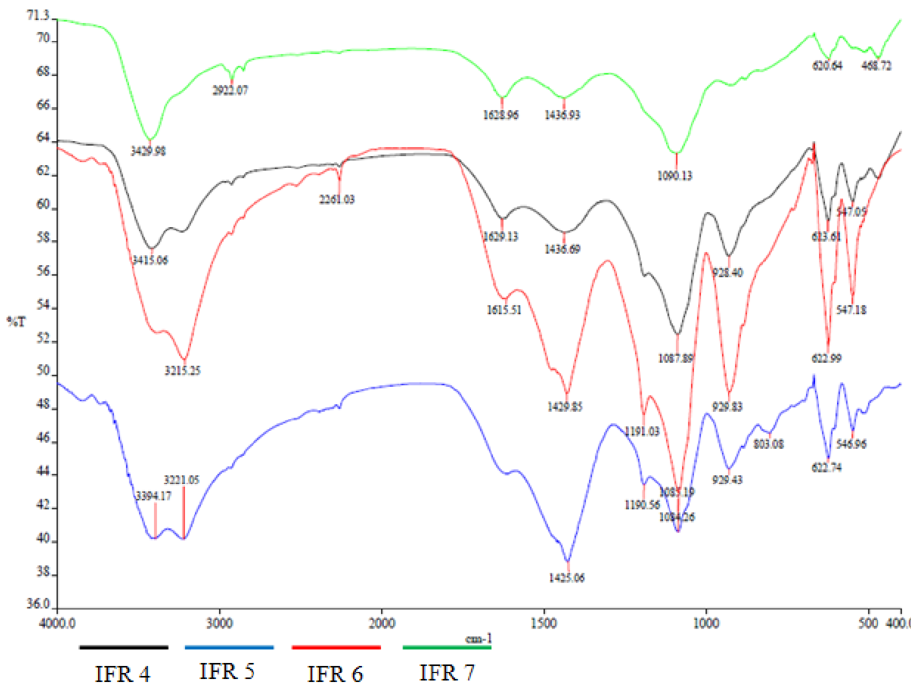

Figure 22: FTIR result for sample IFR 4 – IFR 7

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study was taken with objectives to develop mineral based intumescent fire retardant coating and study thermal performance, residual weight, char morphology and gaseous product of intumescent fire retardant (IFR) coating for protection of steel substrate. Bunsen burner test was done to evaluate the performance of heat shielding effect of the IFR coating formulation. From the results, sample IFR 8, with 8 % of added Dolomite filler, gives better heat shielding effect compared to other IFR coating. The lowest substrate temperature was recorded is 190°C for IFR 8. From this result we can noted that IFR 8 give the best intumescent effect as it contains the highest percentage of Dolomite filler. Higher percentage of Dolomite gives better strength of char formation thus gives better intumescent effect. Hence, the higher percentage of Dolomite would enhance the heat shielding capability of the intumescent coating which was helpful in reducing the substrate temperature.

TGA analysis were done to determine the residual weight of the coating with added Dolomite filler compare to controlled formulation of without filler. From the analysis it is proven that the addition of Dolomite fillers had improved the residual weight of the coatings. At least 80% of residual weight can be improved by imparted Dolomite filler in the coating compared to intumescent coating without filler. Thus, the addition of Dolomite filler improves the anti oxidation and thermal degradation of the coating.

Based on SEM testing, the result shows compact and uniform of char structure of the coating. The coating sample with added of Dolomite filler shows more compact and multiporous char structure compared to coating without filler. The multiporous char structure can block heat transferring to the steel substrate and protect the steel substrate from fire. Furthermore, the speed of heat transfer from the char to steel substrate also can be reduced by having uniform and multiporous char structure. In conclusion, by incorporating Dolomite filler, it can form the uniform and multiporous char structure which can enhance the anti-oxidation of the char layer and improved thermal stability.

GCMS analysis were performed to analyzed the gaseous product that been formed during the burning of intumescent fire retardant coating. Through the observation, the entire sample resulting with the same type of dominant gaseous produced which is phenol and p-Isopropylphenol. These gaseous products are from the mineral based which is carbon compound or known as organic compound. These gaseous products cannot bring much harm to the human being specifically to the victim of the fire occasion unless they inhale the gaseous in bulky compare to the halogenated based.

5.2 Recommendation

It is recommended to carry out further study with similar objective for:

1. To compare the performance of intumescent fire retardant coating with added of Dolomite filler with other type of reinforcement like alumina and kaolin clay.
2. To carry out X-ray Diffraction (XRD) test to study more on the composition of the intumescent coating with added of Dolomite filler. Currently, XRD facilities at UTP are not functioning, and this testing should be included in the next study.

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