

**Effects of Fiber Reinforcement in Intumescent Formulations for Char
Strengthening**

By

Maini Rizal B Ngatini

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Mechanical Engineering)

DECEMBER 2008

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

**Effects of Fibre Reinforcement in Intumescent Formulations for
Char Strengthening**

by

Maini Rizal B Ngatini

A project dissertation submitted to the
Mechanical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(MECHANICAL ENGINEERING)

Approved by,



(Ap. Dr. Faiz Ahmad)

Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2008

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.



MAINI RIZAL NGATINI

ABSTRACT

Fire retardant coating is used to protect structural materials against fire. It is simple and proficient passive fireproofing materials because it is designed to decrease heat transfer from a fire to the structure being protected. In this research, two formulations were prepared and tested for fire resistant properties. Glass fiber was added to the formulations to increase the strength of resulting char. All of the ingredients were mixed using high shear mixer. Once ready, the mixtures were applied on top of a metal substrate and cured in an oven. Thicknesses of the steel substrates plus the coating were recorded before and after fire testing. The samples were exposed to fire using Bunsen burner to a temperature up to 400°C. The temperatures of metal substrates were recorded at different time interval for about ten minutes. The results showed that metal substrates were protected by the char produced. For sample A, the thickness of the coating increases about 20% while sample B shows about 40% increase. Both samples (A and B) showed good intumescent behaviour. Based on the observation, sample B showed better result followed by sample A. In the case of fiber reinforcement, intumescent behaviour also recorded. The data showed that strength of the char increases in term of thermal conductivity where substrate's temperatures recorded were lower compare to sample without fiber reinforcement. Microscopic studied of the samples after exposing to fire showed irregular micro-pores were well distributed in the char. The fiber did not degrade during exposure to the fire.

ACKNOWLEDGEMENT

First of all, I would like to give thanks to ALLAH The Almighty because without His love and grace none of this would have been possible. My warmest appreciation especially to my supervisor, Ap. Dr. Faiz Ahmad for continuous support, discussions and guidance. As an advisor, he was very keen in facilitating the author to complete this project. Heartfelt appreciation is next extended to the following persons who have contributed significantly towards the project:

1. Dr Puteri Seri Melor, the Final Year Project (FYP) Coordinator July 2008, who kindly made arrangements to provide the students with all the facilities, guidance and advice throughout the research work.
2. All mechanical and chemical technicians for providing their technical assistance and sharing their specialities during conducting the laboratory work and provide a very good working environment.

Last but not least, I would like to thank my family and my friends for their continuous support, encouragement and effort in assisting the laboratory work. None of this would have been possible without them.

TABLE OF CONTENTS

CERTIFICATION	i
ABSTRACT	iii
ACKNOWLEDGEMENT	iv
LIST OF FIGURES	vii
LIST OF TABLES	viii
ABBREVIATIONS AND NOMENCLATURE	ix
CHAPTER 1:INTRODUCTION	1
1.1 Background of study	1
1.2 Problem statement	3
1.3 Objectives	4
CHAPTER 2: LITERATURE REVIEW	5
2.1 Literature review	5
CHAPTER 3: METHODOLOGY	9
3.1 Collected data: The main compositions	9
3.2 Procedure identification	14
3.3 Testing procedure	16
3.4 Raw materials and tools	22
CHAPTER 4: RESULTS AND DISCUSSION	23
4.1 Results.	23
4.1.1 Swelling	23
4.1.2 Thermal conductivity	26
4.1.3 SEM analysis	32

4.2	Discussions	37
CHAPTER 5: CONCLUSION AND RECOMMENDATION		40
5.1	Conclusion	40
5.2	Recommendation	41
REFERENCES		42
APPENDICES		43

LIST OF FIGURES

- Figure 1 Picture of Ammonium Iron (II) Sulfate.
- Figure 2 Picture of Boric Acid.
- Figure 3 Picture of Melamine.
- Figure 4 Picture of Sorbitol.
- Figure 5 Picture of Glass fiber.
- Figure 6 Schematic diagram of simplified process for preparation fire retardant coating.
- Figure 7 Picture of Sample B mixture.
- Figure 8 Picture of Sample A mixture.
- Figure 9 Sample A after cured.
- Figure 10 Sample A with fiber after cured.
- Figure 11 Sample B after cured..
- Figure 12 Sample B with fiber after cured.
- Figure 13 Sample A after exposing to fire for 10 minutes.
- Figure 14 Sample A with fiber after exposing to fire for 10 minutes.
- Figure 15 Sample B after exposing to fire for 10 minutes.
- Figure 16 Sample B with fiber after exposing to fire for 10 minutes.
- Figure 17 Graph of temperature on metal substrate versus time for **sample A (Set 1)**.
- Figure 18 Graph of temperature on metal substrate versus time for **sample B (Set 1)**.
- Figure 19 Graph of temperature on metal substrate versus time for **sample A(Set 2)**.
- Figure 20 Graph of temperature on metal substrate versus time for **sample B(Set 2)**.
- Figure 21 Structures illustration of charring layer; (a) uniformity and (b) asymmetry.
- Figure 22 SEM image of sample A without fiber reinforcement; (a) 500 X and (b) 1000 X.

- Figure 23 SEM image of sample A with fiber reinforcement; (a) 500 X and (b) 1000 X.
- Figure 24 SEM image of sample B without fiber reinforcement; (a) 500 X and (b) 1000 X.
- Figure 25 SEM image of sample B with fiber reinforcement; (a) 500 X and (b) 1000 X.
- Figure 26 Mixing equipment.
- Figure 27 Equipment setup during fire testing.
- Figure 28 Touch probe thermocouple.
- Figure 29 Side view of sample A after fire testing.
- Figure 30 Side view of sample B after fire testing

LIST OF TABLES

- Table 1 Composition of intumescent system for set 1
- Table 2 Composition of intumescent system for set 2
- Table 3 Percentage increment of thickness for **sample A (Set 1)**
- Table 4 Percentage increment of thickness for **sample B (Set 1)**
- Table 5 Percentage increment of thickness for **sample A (Set 2)**
- Table 6 Percentage increment of thickness for **sample B (Set 2)**
- Table 7 Temperature behind metal substrate for **sample A (Set 1)**
- Table 8 Temperature behind metal substrate for **sample B (Set 1)**
- Table 9 Temperature behind metal substrate for **sample A (Set 2)**
- Table 10 Temperature behind metal substrate for **sample B (Set 2)**

ABBREVIATIONS AND NOMENCLATURE

APP	Ammonium Polyphosphate
Mel	Melamine
PER	Pentaerythritol
RPM	Revolution per Minute
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscope
Wt%	Weight Percent
NH ₃	Ammonia
Td	Decompose Temperature
H ₃ BO ₃	Boric Acid
HBO ₂	Metaboric Acid
B ₂ O ₃	Boron Oxide

CHAPTER 1:

INTRODUCTION

1.1 Background of Study

Steel structure can be protected from fire or excessive heat exposure by using intumescent system. In intumescent system a carbonaceous layer also known as char, created to protect the surface of steel structure from deteriorating. A char with enhanced strength can help to protect steel structure that exposed to fire. It is believed that reinforcement of fiber in intumescent coating will strengthen the char and can protect the structure from fire. When the temperature of the coating surface reaches a critical temperature under the heat of the flame, the surface begins to melt and is converted into highly viscous liquid. Simultaneously, reactions are initiated that result in the release of inert gas with low thermal conductivity. These gasses are trapped inside the viscous fluid (formation of bubbles). The result is expansion or foaming of the coating, sometimes up to several times its original thickness, to form a protective carbonaceous char that acts as an insulative barrier between the fire and the metal substrate [1].

The intumescent concept allows a balance between the fire properties and the level of additives in the material. Generally, three main intumescent ingredients used are: an acid source, a carbon source, and a blowing agent. However, it is learned that by adding some suitable fillers and additives, the properties of the intumescent system can be increased, for example by reinforce fiber into the system. The formulation of these coatings has to be adapted in term of their physical and chemical properties to form an efficient protective char. The mechanism of intumescences is usually described as follows: first, the acid source breaks down to yield a 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 gaseous products. The later causes the char to swell and hence provides an insulating multi cellular protective layer. This shield limits at the same time the heat transfer from the heat source to the substrate and the mass transfer from the substrate to the heat source resulting in a conservation of the underlying material [2].

In intumescent systems, it is essential that the different components included show a suitable matching thermal behavior: a random selection of a component of each three classes mentioned above does not ensure intumescent behavior in their mixture. For example, the blowing agent must decompose at a temperature above that at which the charring of the mixture begins, but before the solidification of the liquid charring melt occurs. Therefore, set of experiments need to be conducted to ensure that those materials selected to be used in this project show a suitable matching thermal behavior. The carbon rich foam layer formed also known as char have few advantages which are insulating effect, reduces further oxygen access, reduces fuel transport into the flame and prevents dripping. In this project, two samples were prepared which were sample A and sample B. Both sample used the same chemical composition except for acid source. Sample A used Ammonium iron (II) sulfate as acid source while sample B used boric acid as acid source. The rest will be further discussed throughout this report.

1.2 Problem Statement

Fire protection is very important nowadays particularly in oil and gas industry. When fire breaks out in the industry, the temperature may increase to 1000°C. Steel is generally used in the industry to design buildings, platforms, vessels and many more important components. Steel is a non-combustible material which exhibits a good ductility but it begins to lose its structural properties between 470°C and 500°C. Because of this low failure temperature, it is important to prevent any tragedy because of structural collapse, which can occur if load bearing steel elements reach a temperature above 550°C. Therefore the aim of this research is to develop intumescent coating materials which can sustain the temperature up to 1000°C and provide fire protection.

Intumescent fire-retardant systems were first developed for application in the field of coatings. Materials to be protected against the action of fire were either inert materials, such as steel, which does not contribute to the propagation of fire with volatile products but may collapse at the temperatures of flames, or reactive materials, which may chemically interact with the compounds used to develop intumescence [3]. However in this project, the temperature will be scaled down as its main purpose is to study the performance of fiber reinforcement (Glass fiber) in intumescent system. Then, with appropriate results and findings, further research will be conducted to develop intumescent coating material for real application in the industry.

1.3 Objectives and Scope of Study

The main objectives of this project are:

1. To develop intumescent formulations.
2. To reinforce fiber (glass fiber) in intumescent coating for char strengthening.
3. To observe the effect of fiber reinforcement on different set of intumescent compositions.
4. To determine the most effective formulation from the test conducted that can be used as an intumescence system.

The scope of study of this project is to develop intumescent formulations and fiber reinforcement in intumescent coating to enhance the strength of the resulting char. While conducting the experiment, information and data gathering with respect to the study will be done extensively for a better understanding. Sources of information and data were obtained from journals, text books, articles, magazines or web-sites. All data obtain will be evaluated to meet the objectives set for this project.

CHAPTER 2:

LITERATURE REVIEW

2.1 Literature Review

Several means exist for the protection of steel. They are called “passive fireproofing materials”, which means insulating systems designed to decrease heat transfer from fire to the structure being protected. These can be panels or blankets, but usually, coating such as mineral-based or organic resin-based products, known as “intumescent coatings” [1]. It is also known as one of the oldest, easiest and most efficient methods to protect a substrate against excessive heat and fire exposure. It does not change the essential properties of the material being protected, for example, it’s mechanical properties. It also can be used onto several materials including metallic materials, polymers, textiles and even wood.

The first literature report on a fire-retardant intumescent coating where a coating claimed to swell while forming a carbon layer (char) when heated is a 1938 patent by Tramm et al. However, Olsen and Bechele in 1948 were the first to use the term “intumescent”. During 1948 – 1950, Jones et al. discussing the composition of intumescent systems in terms of functions performed, defined “carbonifics”, the compounds acting as a source of carbon to build up the char, and “spumifics”, those which include the foaming effect. Vandersall has listed four categories of components that are essential to provide intumescence: an inorganic acid or a compound which generates an acid on heating between 100°C and 250°C; a polyhydric compound, rich in carbon atoms; an amine or amide; and a halogenated organic compound [3]. Nowadays, intumescent

coating can be produced using three main components which have been discussed earlier.

Because of the relatively little has been published on the chemical reactions which occur upon heating intumescent coating systems, it is difficult to know exactly the function performed by each component of the mixture. Moreover, some compounds have more than one functional group and may act in more than one way. It is assumed that the polyhydric compound performs the carbonifics function by means of the dehydrating action of the acid and the spumific function is due to the evolution of volatile products formed by thermal treatment of the amine/amide or the halogenated compound. A blowing effect may also be due to products evolved in the charring step. It has also been suggested that amines/amides may catalyze the reactions leading to the formation of char [3].

Most flame retardants act either in the vapor phase or the condensed phase through a chemical and/or physical mechanism to interfere with the combustion process during heating, pyrolysis, ignition or flame spread stages. There are two main types of flame retardants for polymers: namely the additive and reactive types. Additive type flame retardants, generally included into the polymer by physical means, have been widely used and include many of the commonly used antimony-bromine, intumescent and hydrated filler formulations available. However, a variety of problems may arise, such as poor compatibility, leaching, and a reduction in mechanical properties. The application of reactive flame retardants involves either the design of new, intrinsically flame-retarding polymers or modification of existing polymers through copolymerization with a flame-retarding unit either in the chain or as a pendant group. At the present time new polymer design lacks sufficiently versatility in manufacturing,

processing and is uneconomical, due to the expense associated with developing a new material for use [4].

Through the exact interaction of the three (3) main components which are acid source, carbon source, and blowing agent this system leads to an expansion process in which a large volume high-carbon protective layer is built up that protects the substrate below from the attack of heat. Ammonium polyphosphate (APP) is the main constituent of many intumescent flame retardant systems in coating. It initiates the intumescent process functioning as an acid source when thermal decomposition starts. The thermolysis of APP leads to the release of polyphosphoric acid. This dehydrates the carbon-supplying compound which is pentaerythritol (PER) leading to a polymer-like structure. Simultaneously, the expansion agent or blowing agent which is melamine (Mel) produces large quantities of gaseous products that swell out the high-carbon reaction mass formed. The onset of cross linking reaction leads initially to increased viscosity that prevents the gases escaping and subsequently to a solidification of the formed foam (char) [2]. However, for this project ammonium iron (II) sulfate and boric acid will be used as an alternative for APP and PER will be replaced by sorbitol.

Phosphorus compounds can increase the char yield. Formation of char means that less material is actually burned. Secondly, char formation is often accompanied by water release, which dilutes the combustible vapors. Moreover, the char can often protect the underlying structures and the char forming reactions are sometimes endothermic. A flame retardant effect results from the formation of a non combustible outward flowing vapor (water), the reduction in fuel, and in some cases the protective effect of the char. A greater degree of flame retardancy seems likely if the char resists oxidation, although even a temporary char may have some inhibitory effect. Even if the char does not

undergo oxidation, the presence of a phosphorous compound tends to inhibit complete oxidation of the carbon to carbon dioxide, and thus the heat evolution is lessened. Besides its effect in enhancing the amount of char, the phosphorus flame retardant may coat the char and therefore help prevent burning and smoldering by obstruction of the surface [5].

A composite comprises a large number of strong stiff fibers called the reinforcement, embedded in a continuous phase of a second material known as the matrix. The idea of reinforcement is not new. Over the centuries natural fibers have been widely used to improve strength and other properties of a structure. Fibers such as glass and carbon have been developed and introduced. The major advantages of composites materials are low density, high specific strength, good corrosion resistance and improved fatigue properties. Fibers can be natural or manmade, metallic, inorganic or organic. Similarly, the matrix can be metal or metal alloy, inorganic cement or glass or a natural synthetic high polymer.

Fibers are the dominant constituents of most composite systems as they act as ideal reinforcing elements providing composites with mechanical performance as well as good thermal, electrical and chemical properties. As for this project, glass fibers will be used for the purpose of char strengthening. It traps air and therefore makes good thermal insulation. Glass is the common name given to a number of mutually soluble inorganic oxides which can be cooled below their melting points without crystallization. The advantages of glass fibers are in their high tensile and compressive strengths, low cost, good compatibility and good processibility [6].

CHAPTER 3: METHODOLOGY/PROJECT WORK

3.1 Collected data: The Main Compositions.

3.1.1 Ammonium iron (II) sulfate

Ammonium sulfate is used in this project instead of APP. Ammonium sulfate has molecular weight of $((\text{NH}_4)_2\text{SO}_4)$. It is an organic compound commonly used as fertilizer. Its melting point is ranging from 235-280°C [10].



Figure 1: Picture of Ammonium Iron (II) Sulfate.

3.1.2 Boric acid

Boric acid also called boracic acid or orthoboric acid or boricum, is a weak acid often used as an antiseptics, insecticide, flame retardant, in nuclear power plants to control the fission rate of uranium, and as a precursor of other chemical compounds. Its melting point is about 169°C. It is also used as an acid source in this project [11].



Figure 2: Picture of Boric Acid.

3.1.3 Melamine (Mel)

Melamine based flame retardants represent a small but fast growing segment in the flame retardant market. These products offer particular advantages over existing flame retardants:

- Cost effectiveness
- Low smoke density and toxicity
- Low corrosion

- Safe handling
- Environmental friendliness

In the initial stage melamine can retard ignition by causing a heat sink through endothermic dissociation in case of a melamine salt followed by endothermic sublimation of the melamine itself at roughly 350°C. Another, even larger, heat sink effect is generated by the subsequent decomposition of the melamine vapors [13].

Melamine can be regarded as a "poor fuel" having a heat of combustion of only 40% of that of hydrocarbons. Furthermore, the nitrogen produced by combustion will act as inert diluents. Another source of inert diluent is the ammonia which is released during breakdown of the melamine or self-condensation of the melamine fraction which does not sublimate.

Melamine can also show considerable contribution to the formation of a char layer in the intumescent process. Char stability is enhanced by multi-ring structures like melem and melon, formed during self-condensation of melamine [13]. In combination with phosphorous synergists melamine can further increase char stability through formation nitrogen-phosphorous substances. Last but not least melamine can act as blowing agent for the char, enhancing the heat barrier functionality of the char layer.



Figure 3: Picture of Melamine.

3.1.4 Sorbitol

Sorbitol has a molecular formula of $C_6H_{14}O_6$. It is obtained by reduction of glucose changing the aldehyde group to an additional hydroxyl group. Its melting point is $95^{\circ}C$ and boiling point of $296^{\circ}C$. Sorbitol usually used in food industries. In this project it will be used as the carbon source to produce hard forming char. Set of experiments will be conducted to prove that it can be used as carbon source in intumescent system [12].



Figure 4: Picture of Sorbitol.

3.1.5 Glass fiber

It is the common name given to a number of mutually soluble inorganic oxides which can be cooled below their melting points without crystallization. The main component is silica (SiO_2), while other oxides such as those of calcium, sodium, and aluminum, among others reduce the melting temperature and hinder crystallization [6]. Based on different chemical compositions, various grades of glass are available commercially e.g. E-, S-, R- and C-glass.

The advantages of glass fibers are in their high tensile and compressive strengths, low cost, good compatibility and good processibility. Their thermal conductivity is reasonably high compare to other materials such as plastic based composites [9]. Glass materials have a variety of applications. For example, they are used to manufacture pressure vessels, reservoirs, ships, boats and yachts, parts for car bodies, and aircraft propellers.



Figure 5: Picture of Glass fiber.

3.2 Procedure Identification

3.2.1 Gathering and Analysis of Information/data

Information and data gathering regarding intumescent coating was made by searching from various sources such as internet, books, journal, and related professionals who are expert in this field. There are many online journals can be found in the internet regarding the study that has been made concerning intumescent coating. Furthermore the books from the Information Resource Centre assist to understand the concept of intumescence system with fiber reinforcement [1, 6, 9].

3.2.2 Design/Formulation Development

At this stage, the formulation of the intumescent coating is developed. The formula consists of the type of the materials used in the intumescent coating and their compositions. In developing the formula, the properties of each material must be taken into account. The formula which is analyzed to have the optimum fire-resistant characteristic will be chosen. There are two samples which are sample A and sample B. for each of those samples; two sets of experiment were conducted. The procedure of the experiments will be explained further in the next chapter [1, 6, 9].

3.2.3 Product Development

After the intumescent formulations for char strengthening has been developed accordingly and have been justified, the intumescent material will be processed to get an intumescent product so that it can be analyzed and tested. All of the intumescent coating components weighted according to the formulation decided and mixed using liquid mixing equipment. After the mixing process was completed, the resin mixture and hardener was mixed with ration of two (2) parts resin mixture and one (1) part hardener. The samples then cured in an oven with temperature around 70°C to 80°C. The testing's standard and procedure was based on equipment manual available at the lab [1, 3, 6, 8].

3.2.4 Testing and Analysis

Once cured, the samples were tested for thermal characteristic and swelling. The thickness of the samples before and after being burned recorded using vernier caliper. At the same time, the temperature of the metal substrate also recorded using touch probe thermocouple for every one (1) minute. After that, all the data obtained were analyzed. Other test that can be done include Thermogravimetric Analysis (TGA) and also Scanning Electron Microscope (SEM). Due to few problems, TGA could not be done [9].

3.3 Testing procedure

3.3.1 Sample Preparation

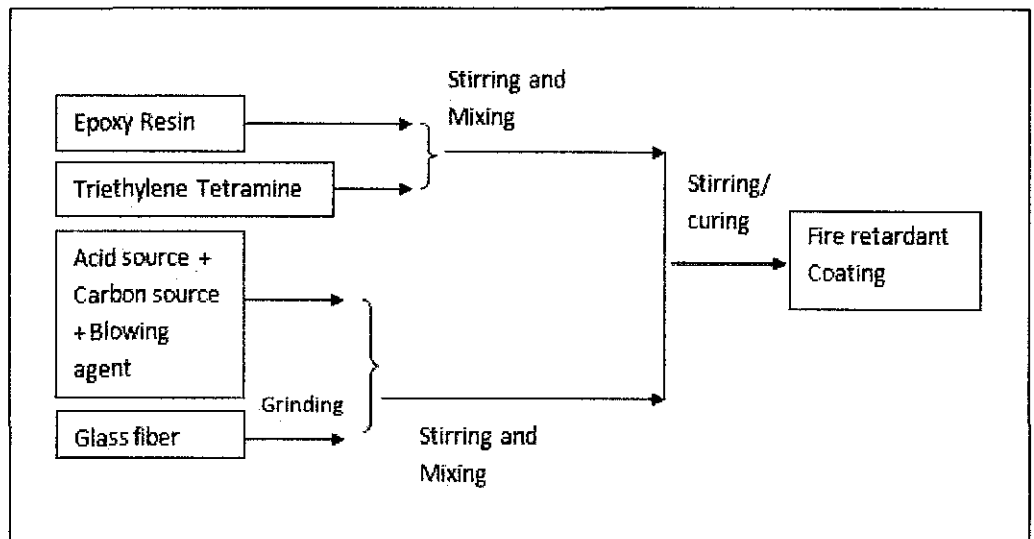


Figure 6: Schematic diagram of simplified process for preparation fire retardant coating.

The main components of the intumescent coating used in this project were:

- I. Ammonium iron (II) sulfate (Acid source)
- II. Boric acid (Acid source)
- III. Sorbitol (Carbon source)
- IV. Melamine (Blowing agent)
- V. Glass fiber
- VI. Triethylene Tetramine (Hardener)

Two set of experiments have been conducted with different chemical compositions. The following tables are the compositions for each experiment given by the weight percent (wt %) of the main components.

Set 1:

Table 1: Composition of intumescent system for set 1.

Component	Acid Source (wt %)	Carbon Source (wt %)	Blowing Agent (wt %)	Epoxy Resin (wt %)	Glass Fiber (wt %)
Sample A (Ammonium Iron (II) Sulfate)	27.8%	13.9%	18.5%	32.4%	7.4%
Sample B (Boric Acid)	27.8%	13.9%	18.5%	32.4%	7.4%

Set 2:

Table 2: Composition of intumescent system for set 2.

Component	Acid Source (wt %)	Carbon Source (wt %)	Blowing Agent (wt %)	Epoxy Resin (wt %)	Glass Fiber (wt %)
Sample A (Ammonium Iron (II) Sulfate)	32.4%	23.1%	9.3%	27.8%	7.4%
Sample B (Boric Acid)	32.4%	23.1%	9.3%	27.8%	7.4%

3.3.2 Mixing Procedure

Once all of the materials have been weighed, the next step is to mix all of the components. In order to do that, liquid mixing equipment is used. The mixing procedures are as follow:

- I. Epoxy resin was filled into a beaker.
- II. The impeller was attached to the end of shaft using chuck key and the height was set (estimated).
- III. The mixer controller was switched on and the RPM was set (50 RPM).
- IV. Other components were subsequently added into the beaker and let it well mixed.

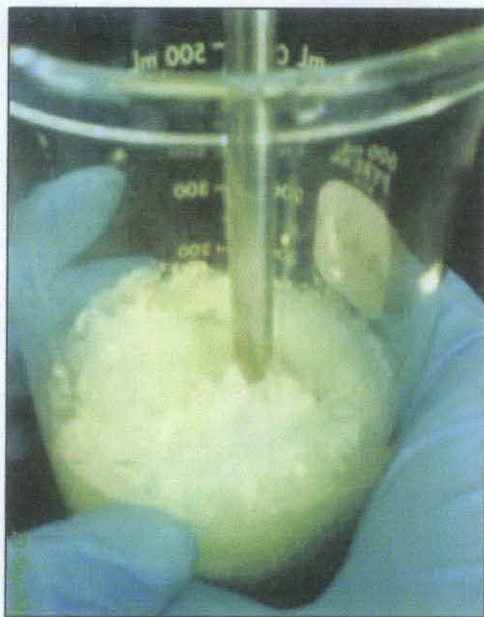


Figure 7: Picture of Sample B mixture.

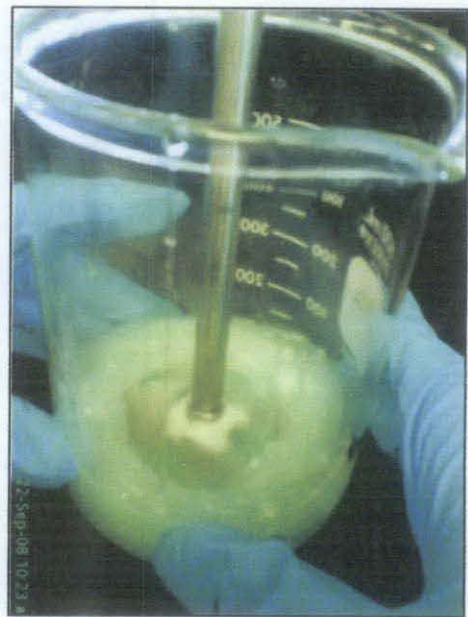


Figure 8: Picture of Sample A mixture.

3.3.3 Coating and Curing Procedure

After all of the components are well mixed, the next step is to apply the coating to the surface of metal substrate (2.5cm X 2.5 cm steel plate). The coating and curing procedures are as follow:

- I. Hardener was added to the mixture with ratio of two parts resin mixture to one part hardener.
- II. Applied the coating on the surface of metal substrate.
- III. Cured the sample in the oven to let it dry and hard (70°C-80°C).



Figure 9: Sample A after cured.



Figure 10: Sample A with fiber after cured.



Figure 11: Sample B after cured.



Figure 12: Sample B with fiber after cured.

3.3.4 Fire Testing Procedure

After the sample was dried and hardened, the next step is to burn it. The procedures of fire testing are as follow:

- I. Thickness of the metal substrate and the coating was measured using caliper.
- II. Hold the sample tightly using steel holder. Initial temperature behind the metal substrate was recorded using touch probe thermocouple.
- III. Turned on a Bunsen burner and focused the tip of the burner to the coating.
- IV. Temperature of the metal substrate was recorded every one (1) minute for about 10 minutes.
- V. Thickness of the burned sample was measured and recorded.

All of the tests were conducted according to the lab manual and also equipment adheres to the standards and manuals to safeguard safety throughout experiment. Please refer to figure 13 to figure 16 pictures of samples after exposed to fire.

3.4 Raw Materials and Tools

3.3.1 Raw Materials

- Acid source – Ammonium iron (II) sulfate and boric acid.
- Carbon source – Sorbitol.
- Blowing agent – Melamine.
- Binders – Epoxy resin.
- Hardener.

3.3.2 Tools

- Liquid Mixing Equipment – To mix the components.
- Weighing balance – to compute the weight of each component.
- Burner – To burn the sample.
- Temperature measurement tools – To analyze the temperature behind the metal substrate.

CHAPTER 4:

RESULTS AND DISCUSSION

4.1 Results

4.1.2 Intumescent behavior of coating (Swelling)

When the coating is exposed to fire or heat, the intumescence effect started to occur. The surface begins to melt and converted to highly viscous liquid. Concurrently, reactions are initiated with the release of inert gases of low thermal conductivity. These gases are trapped inside the viscous liquid and this process is observed with the formation of bubbles during the fire testing procedure. The result is the expansion or foaming of the coating (swelling), sometimes up to several times of its original thickness. This insulative layer or also known as char acts as an insulative barrier between the fire from the Bunsen burner used and the metal substrate. The result of the fire testing for the two set of experiments are as follow:

Table 3: Percentage increment of thickness for sample A (Set 1).

Set 1	Initial thickness (mm) before burn.	Final thickness (mm) after burn	% increase
Sample A	7.40	8.24	11.35%
Sample A + Glass fiber	7.76	8.32	7.22%

Table 4: Percentage increment of thickness for sample B (Set 1).

Set 1	Initial thickness (mm) before burn.	Final thickness (mm) after burn.	% increase
Sample B	7.80	10.22	31.03%
Sample B + Glass fiber	8.02	9.32	16.21%

Table 5: Percentage increment of thickness for sample A (Set 2).

Set 2	Initial thickness (mm) before burn.	Final thickness (mm) after burn.	% increase
Sample A	7.51	8.95	19.17%
Sample A + Glass fiber	9.94	11.03	10.97%

Table 6: Percentage increment of thickness for sample B (Set 2).

Set 2	Initial thickness (mm) before burn.	Final thickness (mm) after burn.	% increase
Sample B	6.82	9.46	38.71%
Sample B + Glass fiber	8.57	10.53	22.87%



Figure 13: Sample A after exposing to fire for 10 minutes.



Figure 14: Sample A with fiber after exposing to fire for 10 minutes.



Figure 15: Sample B after exposing to fire for 10 minutes.



Figure 16: Sample B with fiber after exposing to fire for 10 minutes.

Please refer to appendices section for more picture of samples and equipments setup during fire testing procedure.

For experiment set 1, the percentage increment of thickness for sample B is higher compare to sample A. This pattern also observed during experiment set 2. In experiment set 1, Sample A without fiber reinforcement recorded 11.35% increment while with fiber reinforcement the percentage increment recorded is only 7.22%. For sample B, the percentage increment of the thickness is higher as being mention earlier. Sample B without fiber reinforcement recorded 31.03% increment while with fiber reinforcement the percentage recorded is 16.21%.

For experiment set 2, sample A without fiber reinforcement recorded 19.17% increment while with fiber reinforcement the percentage increment recorded is 10.97%. For sample B, without fiber reinforcement the increment is 38.71% while with fiber reinforcement the percentage increment is 22.87%.

4.1.3 Temperature of steel substrate

The temperature behind the metal substrate during fire testing for both sets of experiment is observed using touch probe thermocouple. This test is carried out to monitor the change in temperature of the metal substrate upon exposed to fire or heat. Due to insufficient equipments, the temperature of the coating could not be recorded to compare with the temperature behind the metal substrate. However, temperature of uncoated metal substrate is recorded by using the same equipment setup. The results are as follow:

Set 1:

Table 7: Temperature on metal substrate for sample A (Set 1).

Time Set 1	1 st min (°C)	2 nd min (°C)	3 rd min (°C)	4 th min (°C)	5 th min (°C)	6 th min (°C)	7 th min (°C)	8 th min (°C)	9 th min (°C)	10 th min (°C)
Uncoated	99.0	112.0	167.1	186.2	209.3	212.5	216.4	223.5	231.0	239.4
Sample A	50.5	73.9	85.1	93.4	97.6	105.7	112.3	116.5	110.4	104.6
Sample A + Glass fiber	40.2	57.1	82.4	88.2	94.3	102.8	105.9	116.2	102.5	94.3

Table 8: Temperature on metal substrate for sample B (Set 1).

Set 1 \ Time	1 st min (°C)	2 nd min (°C)	3 rd min (°C)	4 th min (°C)	5 th min (°C)	6 th min (°C)	7 th min (°C)	8 th min (°C)	9 th min (°C)	10 th min (°C)
Uncoated	99.0	112.0	167.1	186.2	209.3	212.5	216.4	223.5	231.0	239.4
Sample B	60.8	91.1	94.0	97.9	100.3	105.7	109.6	103.8	98.2	97.3
Sample B + Glass fiber	40.3	62.2	70.6	79.4	83.05	86.3	99.1	104.5	97.2	93.3

Set 2:

Table 9: Temperature on metal substrate for sample A (Set 2).

Set 2 \ Time	1 st min (°C)	2 nd min (°C)	3 rd min (°C)	4 th min (°C)	5 th min (°C)	6 th min (°C)	7 th min (°C)	8 th min (°C)	9 th min (°C)	10 th min (°C)
Uncoated	99.0	112.0	167.1	186.2	209.3	212.5	216.4	223.5	231.0	239.4
Sample A	47.5	68.0	79.3	88.4	97.1	103.7	110.2	115.5	109.4	101.3
Sample A + Glass fiber	38.9	51.4	79.6	85.8	92.1	101.3	104.8	112.7	101.4	91.3

Table 10: Temperature on metal substrate for sample B (Set 2).

Time	1 st min (°C)	2 nd min (°C)	3 rd min (°C)	4 th min (°C)	5 th min (°C)	6 th min (°C)	7 th min (°C)	8 th min (°C)	9 th min (°C)	10 th min (°C)
Set 2 / Uncoated	99.0	112.0	167.1	186.2	209.3	212.5	216.4	223.5	231.0	239.4
Sample B	58.2	86.5	93.6	96.9	99.2	104.8	108.3	99.7	96.5	93.3
Sample B + Glass fiber	36.4	50.7	68.9	76.5	81.3	84.2	97.6	101.8	96.5	90.9

Set 1:

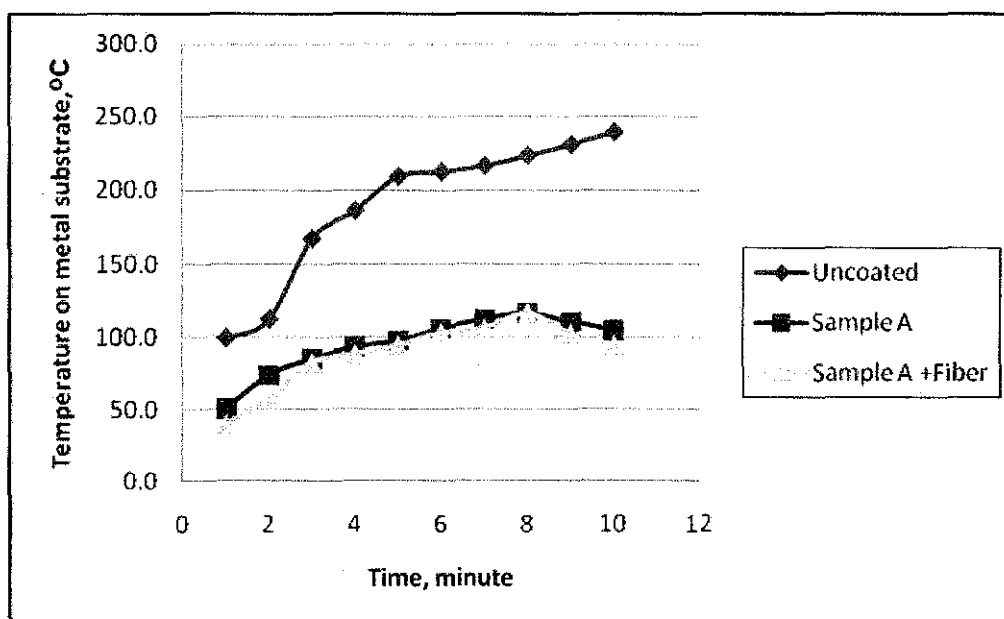


Figure 17: Graph of temperature on metal substrate versus time for sample A.

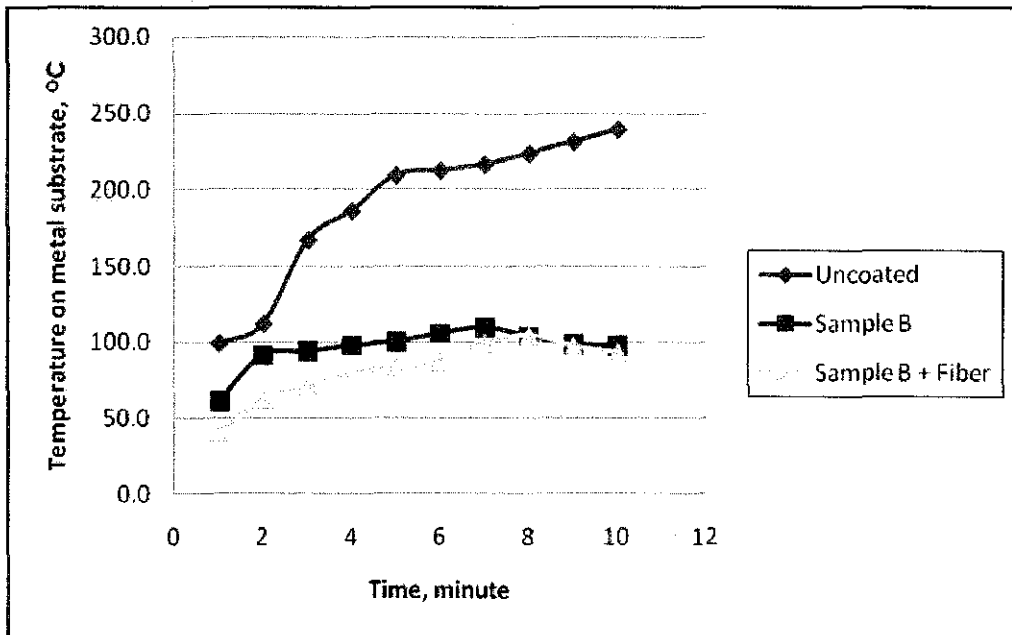


Figure 18: Graph of temperature on metal substrate versus time for sample B.

Set 2:

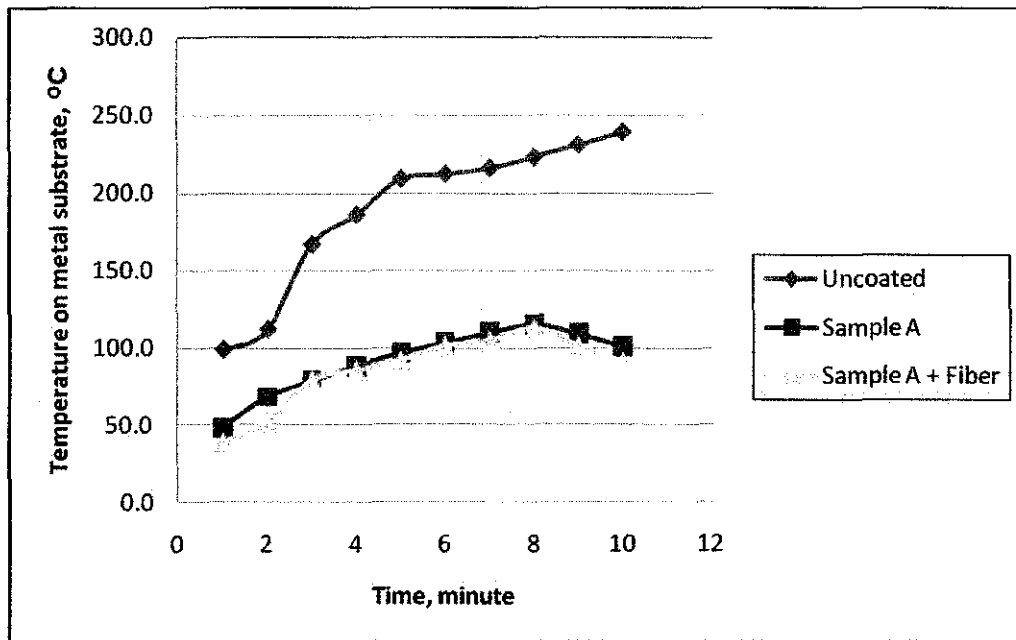


Figure 19: Graph of temperature on metal substrate versus time for sample A.

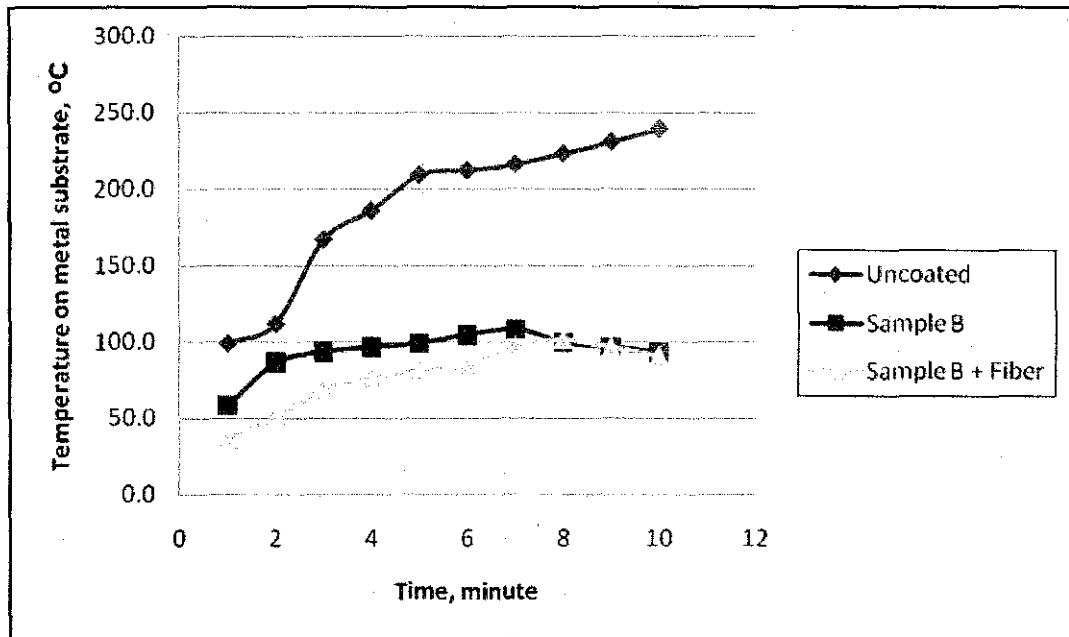


Figure 20: Graph of temperature on metal substrate versus time for sample B.

From the graphs sketched, it is obvious that with intumescent coating the temperature behind metal substrate is lower compare to the uncoated metal. With fiber reinforcement in the coating, the temperature behind metal substrate is slightly lower compare to sample without fiber reinforcement. The present of glass fiber lowered the thermal conductivity of the coating to protect the metal substrate. The result obtained in experiment set 1 is better from experiment set 1 in term of temperature behind metal substrate.

For experiment set 1, the highest temperature recorded of the steel substrate without fiber reinforcement is 116.5°C while with fiber reinforcement is about 104.5°C. The different in temperature shows that the steel substrate is better protected if the coating reinforced with fiber. The same situation happened for experiment set 2 but with different temperature readings as shown in the tables and graphs.

4.1.4 SEM analysis

The charring layer protects the matrix materials, and its protective property depends on the physical and chemical structure of the charring layer. Researches indicate that there are other elements in the charring-layer structure [9]. But the non-charring layer element is easy to be oxygenated and very unstable on chemistry aspects. There are two ideal types of charring structures namely uniformity and asymmetry.

For uniformity type of structure, there are great deals of integrated closed honeycomb pores. That type of structure can form adequate temperature gradients in the charring layer and protect the molten mass and matrix below. The other structure which is asymmetry has many channels and apertures and the gas and molten mass of polymers can overflow to the entry of the flame-region. Therefore, the isolation effect of heat transfer is inferior. This type of structure is non-ideal.

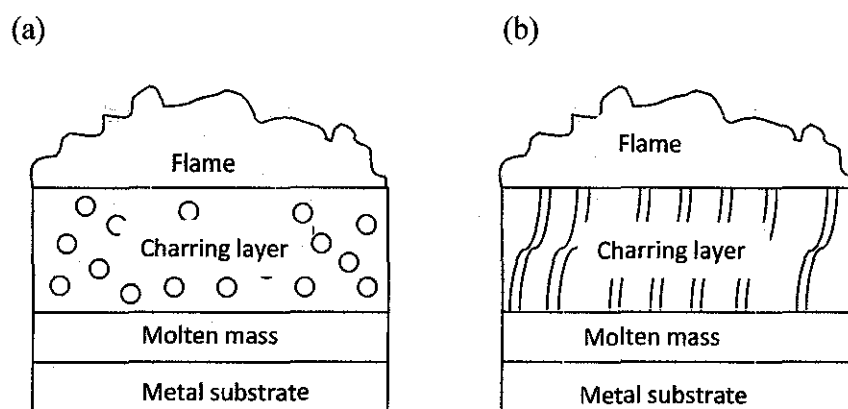
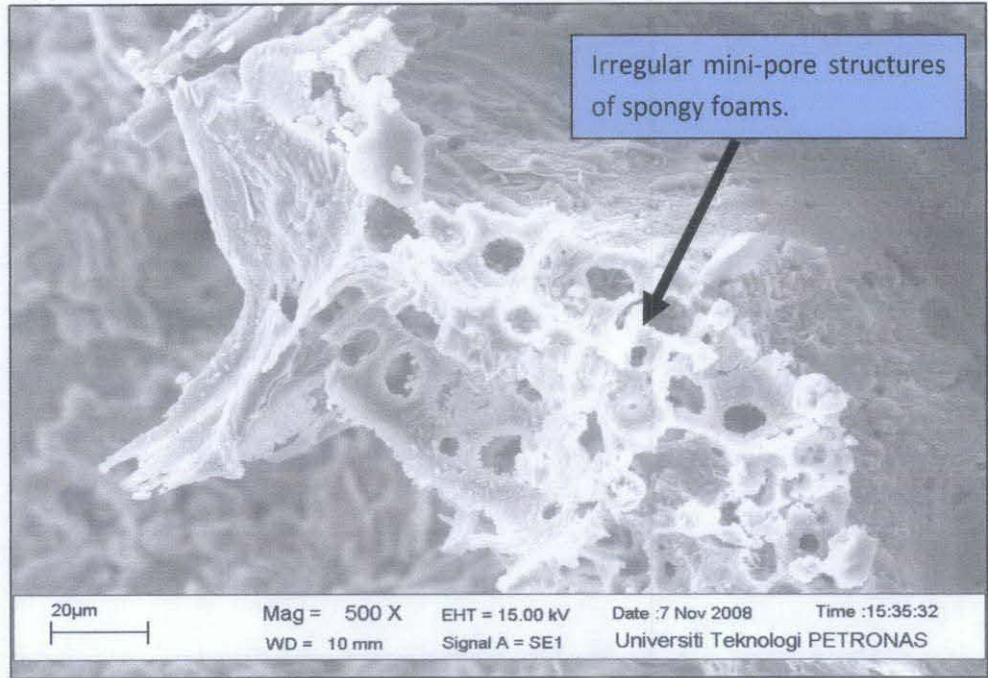


Figure 21: Structures illustration of charring layer; (a) uniformity (pores) and (b) asymmetry.

Results from SEM analysis are as follow:

(a)



(b)

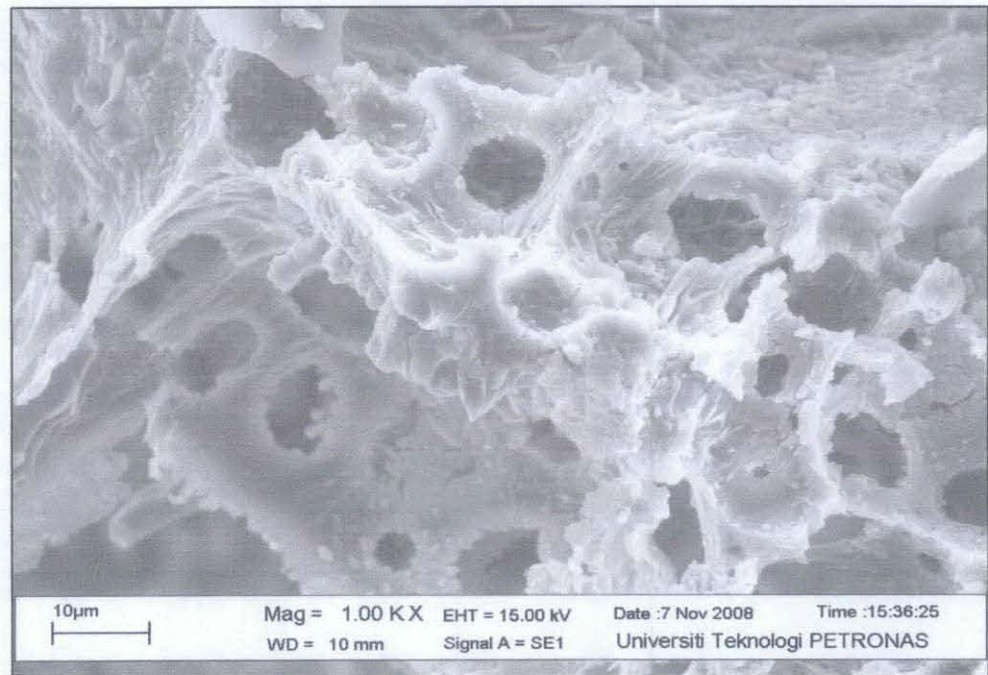
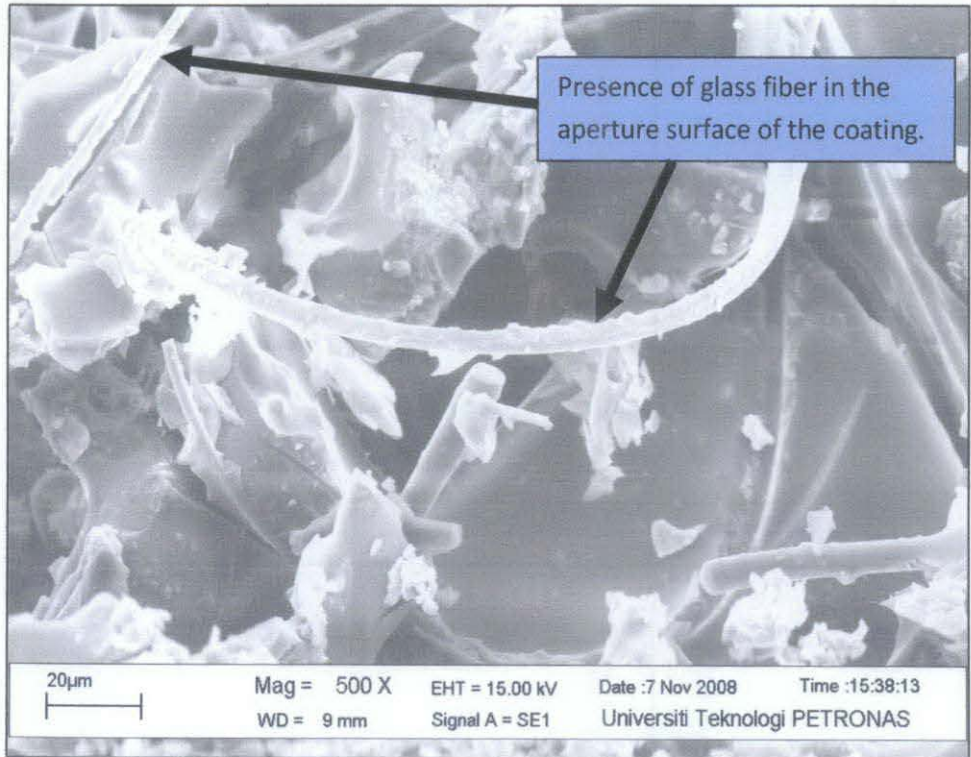


Figure 22: SEM image of sample A without fiber reinforcement; (a) 500 X and (b) 1000 X.

(a)



(b)

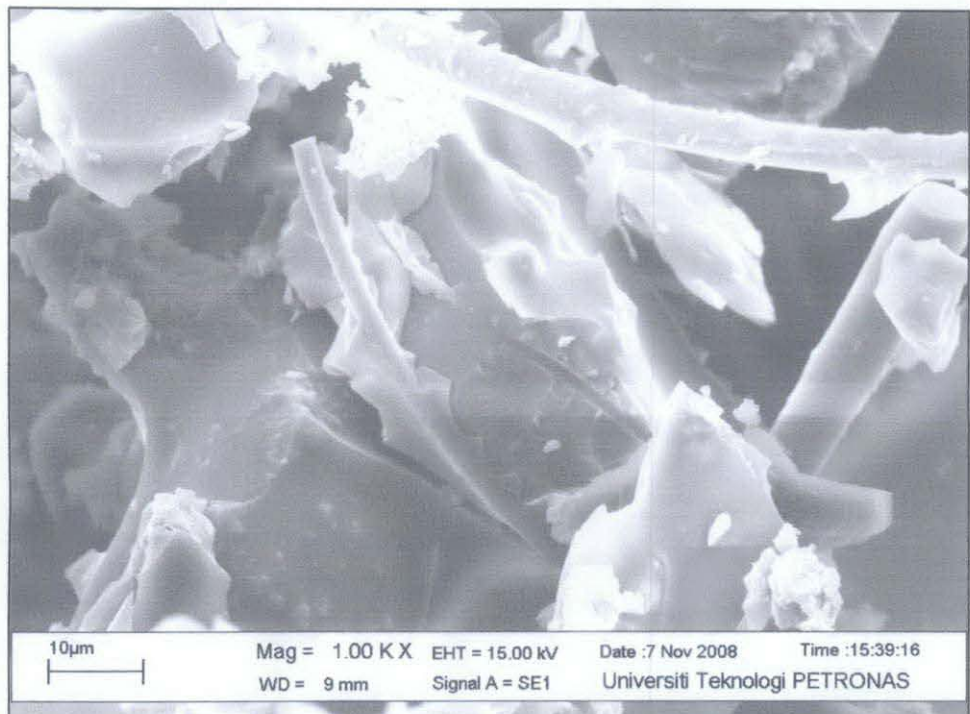
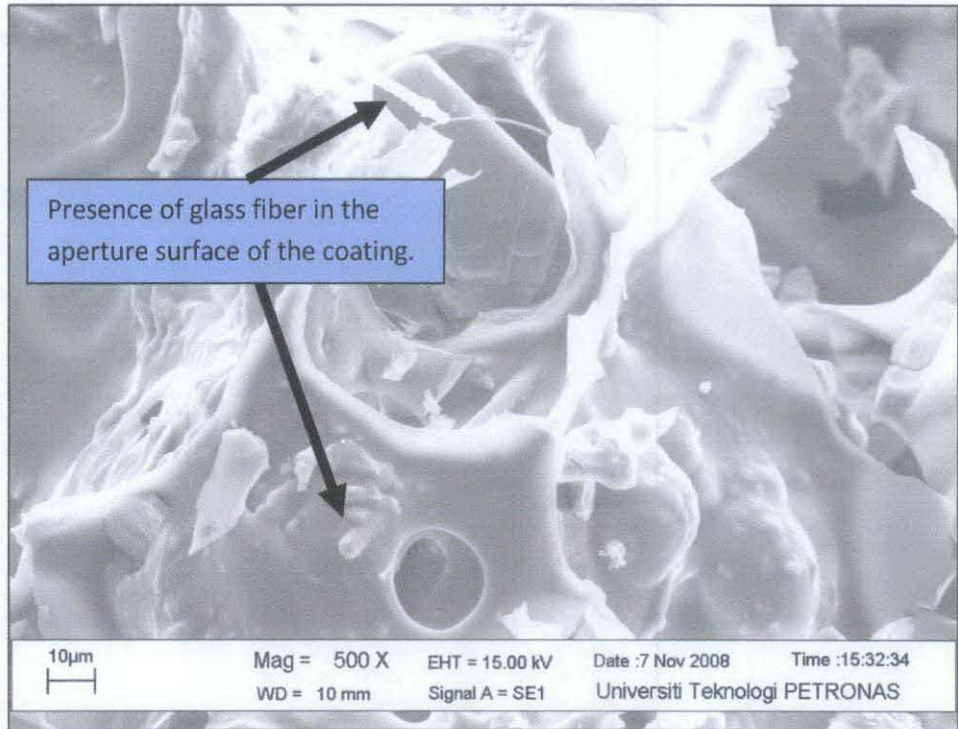


Figure 23: SEM image of sample A with fiber reinforcement; (a) 500 X and (b) 1000 X.

(a)



(b)

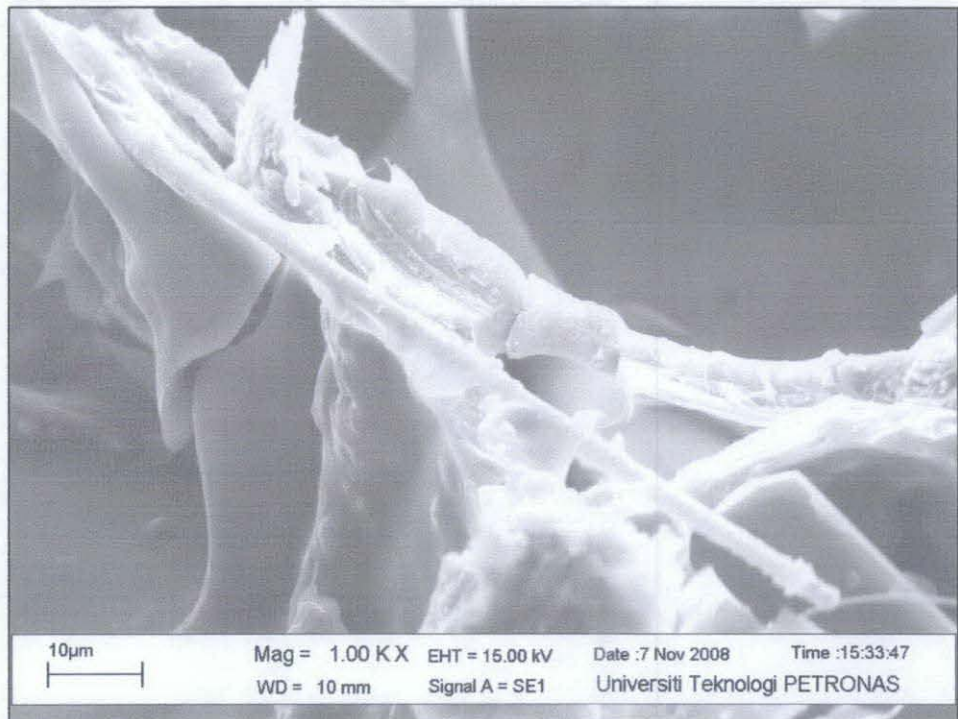


Figure 25: SEM image of sample B with fiber reinforcement; (a) 500 X and (b) 1000 X.

From all of the figures shown earlier, the structure of the charring layer of sample B inclines to be more compact and more homogeneous. The intension of charring layer improves largely and the effect of the flame retardant is better as being shown in the swelling and thermal conductivity tests. Different aperture surface tensions in the course of gas cavities during burning lead to the asymmetry abscess. While for sample A, there are quite many irregular mini-pore structures of spongy foams in the charring from figure 22. The intumescent layer is compact and spongy. These criteria are good heat insulation properties. The intumescent charring layer with many mini-pores acts as the effect of the flame retardant, heat insulation and protecting inner matrix materials.

Presence of glass fibers in the coating for both sample A and B improves the heat insulation effect. In this project, chopped glass fibers about 3-mm long were used and distributed in a random manner and held together with a resin binder. The fiber did not degrade during exposure time instead buried in the coating structure thus increase its strength.

4.2 Discussions

During early stage when the temperature is slightly low, ammonium iron (II) sulfate has nearly no any weight lost. As the temperature increasing, it starts losing weight. It decomposes to release the gas of NH_3 and Sulfuric acid. The weight lost will get bigger in the later stage where it starts to decompose. Sorbitol starts decompose and loses weight at temperature approximately above 95°C . The weight loss is mostly due to it dehydrating intra-molecularly then dehydrogenizing, charring and ruptures of chemical bonds. While the weight loss of Mel gets to 100% under temperature approximately 350°C . Ammonia (NH_3) released dilute the oxygenous concentration, blow the charring layer and form intumescent foam charring layer [9].

The weight loss of the coating in the early stage is small which come from the fraction substance and resin decomposing, solvent and other volatilization vaporization. The key weight loss begins some way in the middle of the experiment when ammonium sulfate decomposes to release NH_3 and sulphuric acid acid. They will react with sorbitol to form the charring framework. At the same time, the vesicant ammonia begins to release NH_3 gas. It blows the charring layer to form a compact, firm and black charring layer. The matching of decompose temperature (T_d) of ammonium sulfate, sorbitol and Mel is the key factor to form an ideal charring layer. In addition to that, glass fiber reinforcement in the system will eventually improve the thermal strength of the char produced. This is due to its properties that have been discussed earlier [9].

Borax, boric acid and borates derivatives are actually well known as flame retardants materials. It can gives off water upon heating, which can provides a heat sink, a fuel diluents, a propellant for the fuel out of the flame zone and also a

blowing agent for the glassy intumescent coating. Boric acid has a two-step degradation mechanism; a first step between 100°C and 140°C and a second step in the temperature between 140°C and 200°C leading to a thermally stable material. It is possible to assume that boric acid and/or its degradation products are main components of the final protective structure developed when the intumescent coating is exposed to fire. The first step of degradation is attributed to the dehydration of boric acid into metaboric acid (1). The second step corresponds to the dehydration of metaboric acid into boron oxide (2):



Boric acid turns by dehydration into boron oxide in the second step of dehydration, leading to a hard and high thermally stable residue. As boric acid releases water and forms a hard glass, it can play the role of blowing agent, to hold the combustion char together and provide structural integrity to the char [1].

Composite structures can be divided into two polymeric structures which are fiber and resin. Both of them are present in the intumescence system. They behave differently in a fire depending upon their respective thermal stabilities. Composite structures which are layered normally burn in layers. When exposed to fire, the resin of the first layer degrades and any combustible products formed are ignited. Then the heat penetrates the adjacent fiber layer. The fiber used in this project is glass fiber which categorized as inorganic fiber. Inorganic fiber will melt or soften when heated causing its degradation and any products formed will then move to the burning zone through the fibrous layers.

CHAPTER 5:

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In the studied intumescent formulation, all of the three main components used which are acid source, carbon source and blowing agent seem to show a particularly interesting effect. When all of the components mixed together in presence of an epoxy resin and glass fiber, an intumescent effect develops. Formation of black and thick insulating layer or also known as char observed with certain amount of percentage increment of its initial thickness. Sample B predominantly shows better intumescent effect compare to sample A. The intumescent effect also can be observed with different composition used in the two sets of experiment conducted. Set 2 shows better result compare to set 1. Results obtained confirmed the objectives set for this project.

The study of an intumescent system can be quite complicated and requires a variety of techniques in order to arrive at an understanding of the operation of that system. In addition to thermal analysis, one must be able to characterize the solid residues and do model compound studies in order to identify the intermediates that may be involved in the overall reaction. The characterization of the char is quite complex and requires special techniques for solid-state characterization. Modeling studies further enable one to understand the overall reaction scheme.

5.2 Recommendation

From the results obtained, it can be said that further study and improvement can be made. Some of the improvements that can be made during conducting experiment are:

- I. Conduct experiment in an appropriate place where the results are not affected by the surrounding.
- II. Conduct experiment with complete and suitable equipments to ensure the accuracy of results obtain.
- III. Refer to available standards and manuals for each of the testing procedure to make sure experiment run smoothly and safely.

Besides that, other tests like Scanning Electron Microscope (SEM) can be done to study the charring layer that protects the metal substrate. There are two ideal typical charring structures which are uniformity and asymmetry. For uniformity, there are great deals of integrated closed honeycomb pores that can form adequate temperature grads in the charring layer and protect molten mass and matrix below. The other structure which is non-ideal called asymmetry has many channels and apertures. These attributes allow the gas and molten mass of polymers overflow to the entry of the flame-region. Thus the isolation effect of heat transfer is inferior.

REFERENCES

1. M. Jimenez, S. Duquesne, S. Bourbigot, *Intumescent fire protective coating: Toward a better understanding of their mechanism of action*, *Thermochimica Acta* 449 (2006)16-26.
2. <http://www.mindfully.org/Plastic/Flame/Ammonium-Polyphosphate-FlameApr02.htm>.
3. Arthur F. Grand, Charles A. Wilkie, *Fire Retardancy of Polymeric Materials*, Marcel Dekker, Inc. New York, 2000.
4. Sheng Zhang, A. Richard Horrocks, *A review of flame retardant polypropylene fibers*, Centre for Materials Research and Innovation, Bolton, 2003.
5. Eckold G, *Design and Manufacturing of Composite Structures*, Cambridge, Woodhead, 1994.
6. A R Horrocks, D Price, *Fire Retardant materials*, Woodhead Publishing Ltd, Cambridge, 2001.
7. Phillips L N, *Design with advanced composite materials*, London, Springer- Verlag, 1998.
8. Gy. Marosi, *Role of interface modification in filled and flame-retarded polymer systems*. Department of Organic Chemical Technology, Budapest University of Technology and Economics, Hungary. 2001.
9. Jun-wei Gu, *Study on preparation and fire-retardant mechanism analysis of intumescent flame-retardant coatings*, Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, China. 2007.
10. [http://en.wikipedia.org/wiki/Ammonium_iron\(II\)_sulfate](http://en.wikipedia.org/wiki/Ammonium_iron(II)_sulfate).
11. http://en.wikipedia.org/wiki/Boric_acid.
12. <http://en.wikipedia.org/wiki/Sorbitol>.
13. <http://en.wikipedia.org/wiki/Melamine>.

APPENDIX

APPENDIX 1: Pictures of samples and equipments setup.



Figure 26: Mixing equipment

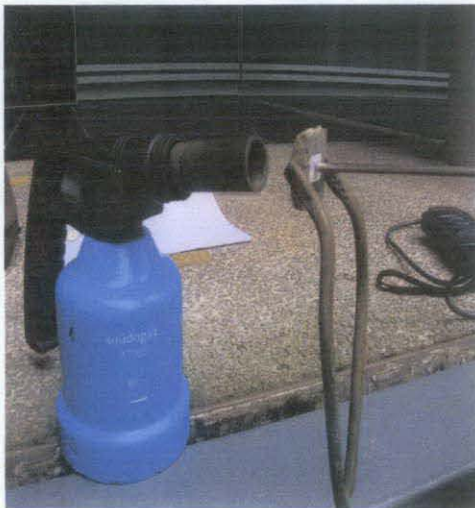


Figure 27: Equipment setup during fire testing.



Figure 28: Touch probe thermocouple



Figure 29: Side view of sample A after fire testing



Figure 30: Side view of sample B after fire testing