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UNIVERSITI TEKNOLOGI PETRONAS

CHARACTERIZATION AND PROPERTIES OF VERMICULITE ON WATER-BASED ACRYLIC FIRE RETARDANT COATING

by

WAN AMALINA BT WAN ZAHARUDDIN

The undersigned certify that they have read, and recommend to the Postgraduate Studies Programme for acceptance this thesis for the fulfillment of the requirements for the degree stated.

Signature: ____

Main Supervisor: ASSOC. PROF. DR. BAMBANG ARIWAHJOEDI

Signature: ____

Co-Supervisor: ASSOC. PROF. DR. PATTHI HUSSAIN

Signature: ____

Head of Department: ASSOC. PROF. DR. AHMAD MAJDI ABDUL RANI

Date: ____

CHARACTERIZATION AND PROPERTIES OF VERMICULITE ON WATER-BASED ACRYLIC FIRE RETARDANT COATING

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WAN AMALINA BT WAN ZAHARUDDIN

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DECLARATION OF THESIS

Title of thesis	CHARACTERIZATION AND PROPERTIES OF VERMICULITE ON WATER-BASED ACRYLIC FIRE RETARDANT COATING

I, WAN AMALINA BT WAN ZAHARUDDIN

hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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______________________________	______________________________
Signature of Author	Signature of Supervisor
Permanent address:	Name of Supervisor
LOT 608, JALAN TOK GURU IBRAHIM, 18500 MACHANG, KELANTAN	ASSOC. PROF. DR. BAMBANG ARIWAHJOEDI
Date: ______________________	Date: ______________________

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DEDICATION

With love, respect and gratitude

This success is dedicated to my beloved family.

ABSTRACT

Fire retardant coating (FRC) is a vital element in the structural industry since there is an increase of the fire hazards especially in housing area. The importance of FRC is not only to provide a heat barrier to insulate the fire, but also does not generate smoke that toxic to the occupants during fire hazards. Therefore, in this research, the new formulation of water-based FRC which include a water-based acrylic resin and vermiculite as an additive was developed. The aims of this research study are to investigate the significant effect of vermiculite in enhancing the FRC and the role that acrylic resin can play. There were four formulations of coating (F1 until F4) with two different acrylic media (matt and gloss acrylic) and with and without vermiculite were applied to galvanized steel plate with thickness of 1 mm. The four formulations had been analyzed to identify the peaks. The elements of two acrylic media and vermiculite, the thermal degradation and surface morphology were investigated by using Fourier transformed infrared (FTIR) spectroscopy, X-ray fluorescence (XRF) spectroscopy, thermogravimetric analyses (TGA), and scanning electron microscopy (SEM). The heat resistance of coating was investigated by performing fire protection test for 100 minutes. For mechanical property, the shear test was conducted to measure the adhesion strength by applying the shear forces by following the ASTM 3163. TGA results for formulation F3 and F4 with presence of vermiculite showed the increase of thermally stable residue and the temperature reading from fire protection test was reduced about 150^{o}C. F3 was found giving the lowest temperature of 200^{o}C at 100 minutes compared to the other formulations. The microstructure of F3 had small porosity which is around 5 – 20 µm was observed and the shear strength of F3 was the highest compared to others, which improved about 2 times. A significant increase of shear strength, the insulation of heat and good char structure of F3 were related to the composition of the vermiculite which are aluminosilicate and enhanced with the elements in the matt acrylic i.e. SiO_2 and Al_2O_3 that were not presence in the gloss acrylic.

ABSTRAK

Lapisan tahan bakar ialah satu elemen penting dalam industri bangunan kerana ianya berfungsi sebagai penebat haba untuk melindungi struktur besi bangunan. Di samping itu, lapisan tahan bakar seharusnya tidak menghasilkan gas beracun kepada penghuni semasa berlakunya kebakaran. Oleh itu, bahan lapisan tahan bakar yang menggunakan air sebagai asas iaitu acrylic (water-based acrylic) dan vermiculite sebagai bahan tambahan digunakan dalam kajian ini. Tujuan kajian ini adalah untuk menganalisis kesan vermiculite dan peranan acrylic dalam formulasi baru lapisan tahan bakar ini. Terdapat empat jenis kategori (F1-F4) di mana dua jenis acrylic (matt dan gloss) digunakan dengan vermiculite atau sebaliknya iaitu setebal 1 mm di atas besi yang disadur. Formulasi baru lapisan tahan bakar telah diuji untuk mengetahui elemen dalam acrylic dan vermiculite, kadar penahanan haba dan lapisan mikrostruktur. Ujian ketahanan pembakaran dilakukan untuk mengetahui ketahanan lapisan tahan bakar terhadap api di mana bacaan suhu direkod di belakang substrat. Ujian ikatan lekatan antara lapisan tahan bakar dan substrat juga dijalankan. Semua bahan di dalam lapisan tahan bakar sesuai digunakan. Graf penahanan haba dan bacaan suhu di dalam ujian ketahanan pembakaran menunjukkan formulasi dengan vermiculite ialah yang terbaik iaitu F3 dan F4. Tetapi, bacaan suhu F3 yang paling rendah iaitu 200^{o}C pada masa 100 minit. Lubang yang kecil di antara 5 – 20 µm dapat diperhatikan dalam lapisan mikrostruktur F3 dan lekatan ikatan antara lapisan tahan bakar F3 dengan substrat juga yang tertinggi iaitu dua kali nilai dari formulasi yang lain. Keputusan yang amat bagus dalam ujian lekatan ikatan, ketahanan kebakaran dan mikrostruktur oleh F3 disebabkan oleh elemen dalam vermiculite iaitu aluminosilicate dan dibantu oleh elemen dalam matt acrylic iaitu SiO_2 and Al_2O_3 yang tiada dalam gloss acrylic.

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NOMENCLATURES

Al_2O_3	Aluminum dioxide (Alumina)
APP	Ammonium Polyphosphate
CTA	Chain transfer agent
DPER	Dipentaerythritol
DTG	Derivative thermogravimetric analysis
EDX	Energy dispersive X-ray spectroscopy
FRC	Fire retardant coating
FTIR	Fourier transformed infrared spectroscopy
GA	Gloss acrylic
MA	Matt acrylic
Mel	Melamine
MgF_2	Magnesium Fluoride
MMA	Methyl Methacrylate
PER	Pentaerythritol
SEM	Scanning electron microscope
SiO_2	Silicon dioxide (Silica)
TEM	Transmission electron microscope
TGA	Thermogravimetric analysis

VOC Volatile organic compound

XRF X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1 Background

Fire retardant coating (FRC) is important for construction industry such as bridges, stadiums, theme parks, petrochemical plants, offshore drilling platforms and also high rise buildings. It is even useful if the fire retardant coating can be applied to the other industries such as residential building, transportation, utilities, marine, manufacturing and military applications.

The fire protection materials issues become vital when the great fire occurred in London in 1666, where it spread throughout the city. Then, in 1871 there was a fire in Chicago and at the San Francisco earthquake in 1906 led to fire. These fires showed how a small fire could grow to encompass a building, then a group of building, and finally a portion or a complete section of a city [1]. Besides that, in 2002, investigations into the collapse of the World Trade Center have raised concern over the reliability of fire protection materials. In Malaysia, the fire mostly occurred in building structures with 3,017 cases in 2009 as shown in Figure 1.1. In 2009, the highest numbers of cases at the residential flat or building was 1,740 cases, follow by shops 377 cases, factories 320 cases and stores 116 cases [2].

In fact, prevention for structural collapse is vital as to ensure the safety of the occupants from the building. Fire retardant coatings are designed to prevent the heat, flames or fire from spreading. This coating has an ability to expand for many times of its original thickness to produce insulation layer of char when heated as shown in Figure 1.2.

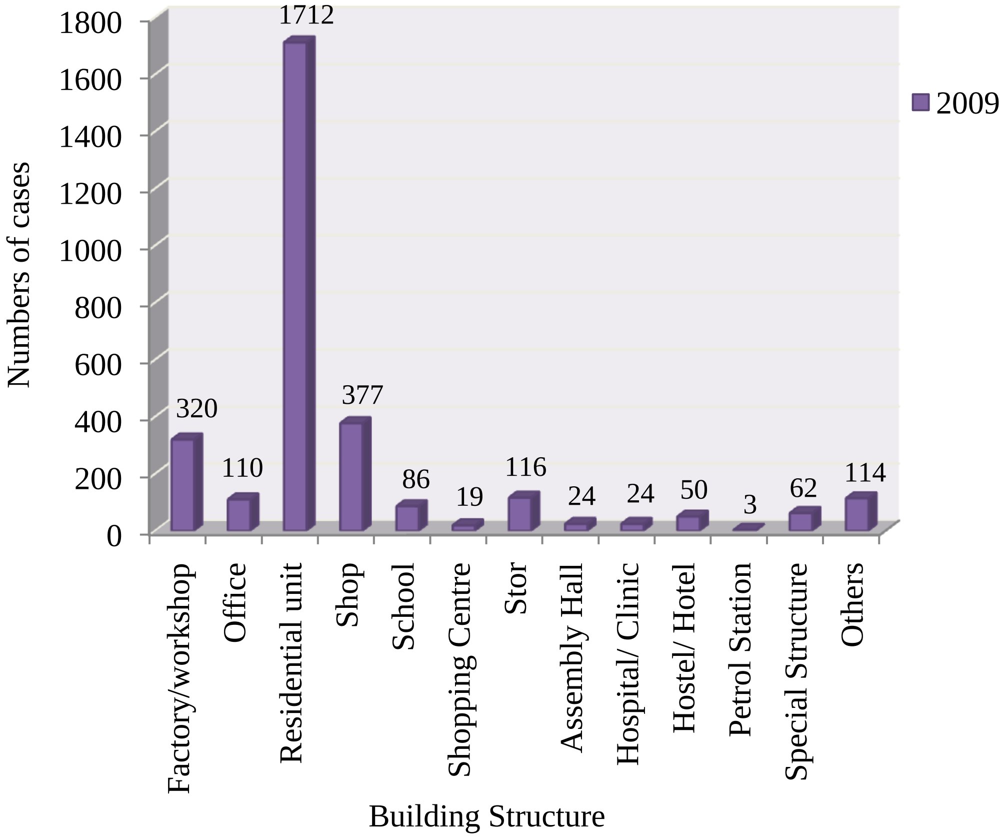


Figure 1. 1: Statistic of fire breakouts according to building categories in Malaysia for 2009 [2].

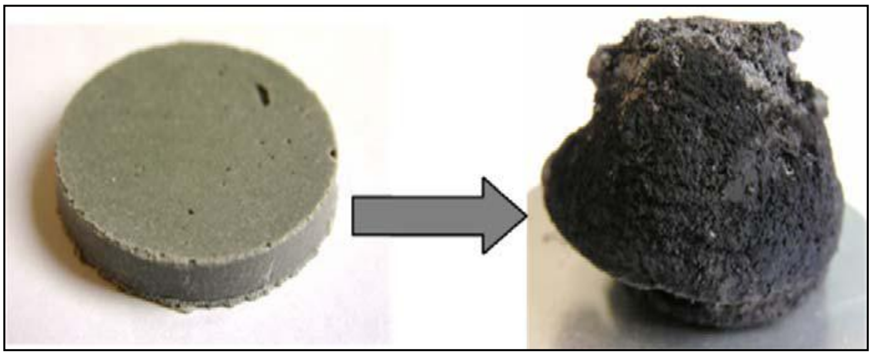


Figure 1. 2: Swelling of an intumescent coating [3]

FRC is one of the easiest and economical coatings where it can be used to metals [4], polymers [5], textiles [6], [7] and wood [8], [9]. The advantages of FRC, it does not modify the mechanical properties of the material and it can prevent the heat from spreading to the coated structure [3], [4], [10].

FRC composed of three components which are: an acid source, a carbon source and a blowing agent [3], [10], [11]. Generally, three active ingredients are ammonium polyphosphate (APP) as an acid source, pentaerythritol (PER) as carbon source and melamine (MEL) as a blowing agent [4], [11], [12], [13] . The mechanism of the FRC is as follow [3], [11]: first, the acid source breaks down to yield a mineral acid, then it takes part in the dehydration of the carbonization source to yield the carbon char, and finally the blowing agent decomposes to yield gaseous products.

There are two types of FRC which are solvent-based and water-based FRC [14]. Commonly, the solvent-based were widely used as the coating to the structural materials. There are numerous advantages of the solvent-based coatings and also disadvantages. Solvent-based coatings are waterproof and better adhesion to porous surfaces. However, they give off solvent fumes during application, hence required good ventilation, it cannot be applied onto damp surfaces (incompatible with such surfaces) and applicators have to use special protective coating and special solvent to clean the equipment after used [15].

Due to an increasing requirement for public safety, the concern of the coating is not only that it can prevent the heat but also non-toxic to the people during the fire hazard. Thus, these drawbacks of the solvent-based coating have generated the interest in the invention of water-based fire retardant coatings due to its advantages which contains low volatile organic compound (VOC) content compared to conventional solvent-based coating, no solvent fumes, small amount of coalescing solvents and also contain fewer hazardous materials (non-toxic), equipment can be cleaned with water and good corrosion protection [15], [16], [17]. According to Fire and Rescue Department, Malaysia, mostly the cause of the deaths when the fire breakouts is because of the smoke generated that covered up the whole room hence obscured visibility of the occupants and drawn in the toxic smoke [18].

Therefore, in this research project, the binder for this FRC is acrylic resin which is water-based binder. Acrylic is chosen because they are slow-burning or even self extinguishing and also they do not produce harmful smoke or gases. Acrylic resin is a water-based binder where it is non-toxic, odorless, safe to use and present no harm to the environment [19], and therefore acrylic is chosen for replacing the traditional solvent-based paints. The new formulation will be established to create the new FRC that is more durable and non-toxic to people. Besides, the acrylic also can improve adhesion to metals [15]. There were researches that used acrylic as a binder in the FRC such as Wang *et al.*, 2006a used acrylic polymer and nanocomposite to see the effect of the binder on the thermal degradation and fire resistance in APP-DPER-MEL coating [20]. Besides that, Li *et al.*, 2007, also used acrylic as the binder and investigated on thermal degradation of the coating which contained MoO_3 and Fe_2O_3 [13].

In addition, there is an additive in this new formulation of the fire retardant coating which is vermiculite. Vermiculite is a natural mineral that expands when exposed to heat. Thus, vermiculite will add the expansion of the FRC to insulate the substrate from heat. From Pyro-Cote CC company, a specialized in FRC had applied vermiculite in the cement [16]. There was one research on vermiculite from Kopaonik (Yugoslavia) on the characterization and processing of that material [21]. The other researches were on the synthesizing the vermiculite in superabsorbent and hydrogel composites [22], [23], [24]. However, there is no study about vermiculite in the fire resistance coating yet. Therefore, vermiculite was used in this new formulation of FRC with other materials which consist of ammonium polyphosphate (APP), pentaerythritol (PER), melamine (MEL) and two types of acrylic binder.

In this study, galvanized steel was used as a substrate to test the formulation instead of bare steel. This is because the steel has been galvanized with zinc for corrosion resistance and no need for surface preparation before applying the coating.

In the present work, the new formulation of water-based retardant coating by using acrylic and vermiculite addition was investigated. The chemical compatibility between the acrylic binder and the other additives was investigated using Fourier transformed infrared spectroscopy (FTIR). Thermogravimetric analysis (TGA) was used to analyze the thermal degradation of the materials and determined the effect of vermiculite and synergy between the additives. The fire resistance of the coating was investigated by fire protection test. Then, the surface morphologies of the coating with and without vermiculite were examined using scanning electron microscopy (SEM). The expected results were the formulations with vermiculite give low temperature at the back of the substrate due to heat shielding effect, high thermal residue for the TGA and higher char structure integrity.

1.2 Problem Statement

FRC is the vital element in the completion of structural buildings due to the safety of the occupants during fire hazards. Steel reached it structural properties at 450 to 500^{o}C. It will become ductile and collapse in less than an hour, thus the FRC is important to ensure the occupants have more time to evacuate the building during fire hazard.

Besides that, the other issue was the smoke that generated from the fire is also toxic to the occupants; hence they also cannot escape from the building. According to Canada Wood Council, 2002 [25], the main danger to the occupants was the smoke that generated from the fire that causes 90% of deaths. Chan, 2011 [26], stated that the smokes can cover a normal living room in only 35 seconds. These are resulting in death for the occupants that trapped in the fired building even though they know the exit. Most of the FRC used materials that give off solvent-fumes which is the solvent-based FRC in particular during their application.

Thus, in this research study, the water-based binder was used to formulate the new FRC that can insulate the structure and non-toxic to the occupants during fire hazards. In addition, vermiculite was added to the new formulation of FRC where this material will be expected to enhance the insulation layer of the char to protect the underlying substrate.

1.3 Research Objectives

The aim of this research study is to formulate the new water-based FRC with addition of vermiculite, characterize the coating and test its main function which is to insulate the heat from transferring to the underlying substrate. The objectives of the study are as follows:

1. To formulate the water-based FRC based on acrylic polymer medium.

2. To compare the thermal degradation of the formulation without and with vermiculite
3. To evaluate the thermal insulation of the coating with and without vermiculite through fire protection test and the significant effect of vermiculite addition on the fire resistance of the FRC.
4. To establish the adhesion property of the water-based FRC.

1.4 Scope of Work

The scope of the study involves the formulation of the water-based FRC with addition of vermiculite. Then, the analysis of the water-based FRC is focused on the thermal degradation through thermogravimetry analysis, performance of the water-based FRC in insulates the heat by performing fire protection test and adhesion property of water based FRC. The experimental work is based on the standards and findings from the previous reported research studies and modified according to the conditions of the water-based coating.

1.5 Organization of the Thesis

The thesis is presented in five chapters. Chapter 1 describes the research background related to the function of fire retardant coating, the fire issue that brings up the concern on the fire retardant coating, the types of the fire retardant coating, the advantages and limitations of solvent-based and water-based type. In addition, the explanation on the usage of acrylic and vermiculite in this research study were given. Then, the aim and scope of study were addressed.

Chapter 2 contains in depth of previous researches about fire retardant coating, their limitations, the scarce study on the water-based acrylic as a binder, an extensive review on the fire retardant mechanism and galvanized steel properties. The theory and details study on the vermiculite, the explanation on the heat transfer through air with only focus on the mechanism of the heat transfer from the flame to the underlying substrate were described. Besides that, the variations in conducting fire protection test from previous study and adhesion test to evaluate the coating strength were elaborated.

Chapter 3 delivers the materials used in this research, the ratio of each materials and details procedure in preparing the formulations. The experimental works which are the characterization of the coating before and after fire protection test were explained in this chapter. The fire protection test, shear test and the set-up were also elaborated.

Chapter 4 presents the results obtained from the experimental works, the analyzing parts in each result and discussed the possible reasons that contribute to the outcomes. The limitations and the difficulties to gain the results were also discussed.

In Chapter 5, the conclusions of the previous chapters are drawn that met the objectives of the research. The recommendations are also addressed for the improvements in another future research work.

1.6 Chapter Summary

This chapter presents a brief overview on the fire retardant coating development, the concern for the safety issue, the important function of the coating, and the materials used in this FRC were explained in the background of this study.

The main problem was identified in the problem statement section. The problems that need to be resolved were also addressed. Then, followed with the aims of this research, the scope of works and also the thesis organization were described.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

There are many literatures review found about the solvent-based FRC which is about the mechanism of FRC, and the formulation with additives. Then, the increasing studies on the FRC with acrylic as a binder. However, no literatures could be found about previous studies on water-based acrylic resin with vermiculite in the fire retardant coating. Therefore these literatures would be able to help in explaining the results that were obtained from the new formulation of the fire retardant coating and the characterization for this new coating.

2.1 Chapter Overview

This chapter elaborates on the theory that relates to the background and literature reviews on the past research studies. The explanation on the common materials used in FRC, the mechanism of the coating, the material that used as the substrate, the significant of vermiculite, adhesion bonding and the fire protection testing.

This chapter aim is to understand the mechanism of the FRC, thus helped in this research works. The explanation also focused on the preceded research works that relate to this research.

2.2 Fire retardant coating (FRC)

FRC is a mineral based or organic resin based product functioning as fire retardant coating where it can be applied to metallic materials [4], polymers [5], textiles [6], [7], [27] and wood [8], [9]. This coating is vital to structural building in order to protect them from weakening when encounter elevated temperature in a fire. This coating has an ability to expand for many times of its original thickness to produce insulation layer of char when exposed to heat [3] that protect the substrate from the rapid increase of temperature.

Randoux *et al.*, 2002 [28] said there were two main classes of flame retardant coatings where the first class is the flame retardant coating that holds up ignition and the spread of flame while the second class is the combination of first class's function and the formation of insulating layer during the fire which also called intumescent coating. Throughout this thesis FRC term is used instead of intumescent coating.

Commonly, fire retardant coating composed of three components which are: an acid source, a carbon source and a blowing agent [3], [4], [10], [11]. Generally, three active ingredients are ammonium polyphosphate (APP) as an acid source, pentaerythritol (PER) as a carbon source and melamine (Mel) as a blowing agent [12], [13], [29], [30]. These three ingredients must have a suitable matching thermal behavior in order to have an effectively protective coating. The mechanism of this coating is, first, the acid source which is APP breaks down to yield a mineral acid, then it takes part in the dehydration of the carbonization agent (PER) to yield the carbon char and finally blowing agent decomposes to yield gaseous products [3], [11]. The surface of the FRC begins to melt and become the highly viscous liquid when the temperature reached the critical point. Meanwhile, the inert gases is released and trapped inside the bubbles in the viscous fluid. These process resulting in formation of a protective carbonaceous char that act as an insulative barrier [14] as shown in Figure 2.1. Joseph and Ebdon, (2001) [31] had illustrated the correlation between charring processes and flammability as follow:

> The higher the amounts of residual char after combustion, the lower the amount of combustible material available to perpetuate the flame and the greater the degree of flame retardance of material. Therefore, one of the ways to achieve high degrees of flame retardancy or non-combustiblity of polymeric materials is to increase the amount of char produced on combustion.

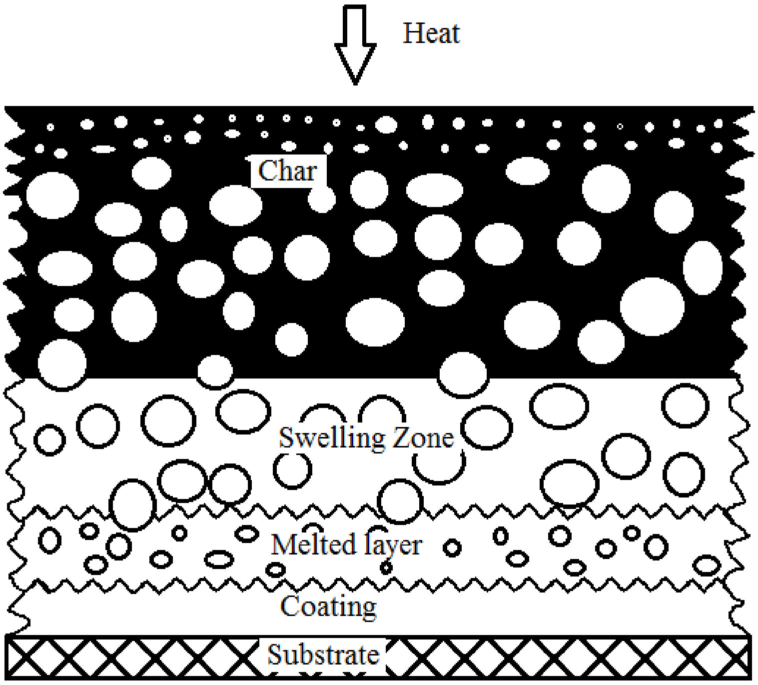


Figure 2. 1: Foaming of the FRC structure [14].

The importance of the FRC in order to function effectively is when these two mechanisms occurred, first; it degrades to form thermally stable material during the fire hazard and secondly, the thermally stable material is able to prevent the heat from transfer from the flame to the substrate [4].

Ammonium polyphosphate (APP) that used in this FRC is a high molecular weight with chain phosphate more than 1000. APP is important materials since it serves as an acid source and also a blowing agent. APP is a source of phosphoric acid that catalyzes the formation of carbonaceous char. Besides that, the ammonia gas that release from APP improves the swelling process [14].

In this research work, the binder used was acrylic resin. The detail studies on the acrylic resin in the FRC are scarce compared to epoxy based FRC. According to Wang *et al.*, 2006a [20] that used acrylic resin said that the acrylic's function is not only as a binder, but also a carbon source in the FRC. They used two types of acrylic polymer and one acrylic nanocomposite to examine which one give better reaction with the APP-DPER-Mel. In their research work, they had found that, the acrylic that has high molecular weight and a large number of benzene rings give high melting temperature and decomposition temperature. High melting and decomposition temperature is important as the decomposition of APP is at high temperature where APP can efficiently catalyst the thermal decomposition of acrylic (as a carbon source) to initiate the char formation. Besides that, similar temperature range of the reaction of APP, DPER and Mel with decomposition of the acrylic not only initiates the char formation but also a good char structure.

Pollak (2006) [32] have stated that there are two types of fire retardant available either water-based or solvent-based coatings. Basically there are two added material to support the fire retardant coating which are the primer and topcoat. The purpose of the primer is to enhance adhesion of the fire retardant coating to the substrate while the topcoat is to provide a decorative appearance (e.g., color, gloss) or to enhance the durability of the coating. However, the primer and the topcoat must chemically compatible to the fire retardant coating. According to Pollak (2006) the water-based products might not be able to accept an epoxy, hence will not have proper adhesion.

2.3 Fire hazard in occupational area

Occupational area means the area for working, learning, staying and spending time with the family which used all the time, for instance are houses, offices, schools and hospitals. The highest numbers of fire breakouts is in residential area for 2009 was 1,712 as shown earlier in Figure 1.1. These numbers of fire cases does not decreasing since 2006. The Table 2.1 below shows the statistic of fire breakouts according to building categories from 2006 to 2008. The numbers of cases shown with highest is in housing area, followed by shops, factories, stores and kitchen which are the same for each year.

Table 2. 1: Numbers of fire breakouts according to building categories in Malaysia for 2006 – 2008 [18].

Types of Structure	**2006**	**2007**	**2008**
Housing unit	1741	1735	1775
Shop	376	365	459
Others	295	340	335
Factory	232	233	278
Stor	197	213	186
Kitchen	111	128	133
Office	103	96	86
Squatter	97	75	65
School/Institution/Hostel	75	72	74
Workshop	48	74	55
Entertainment Outlet	25	30	23
Restaurant	25	30	23
Hotel	22	22	12
Shopping Centre	8	10	11
Laboratory	4	9	10
Warehouse	7	8	6
Hospital/ Clinic	5	6	9
Total	3371	3447	3556

According to Fire and Rescue Department, Malaysia, the total fire breakouts in 2008 were 21,474 where 16.56% (3556 cases) occurred in the structural buildings [18]. Moreover, the numbers of deaths showed the upward trends since 2006 until 2008 about 10% each year. Figure 2.2 shows the statistic on fire breakouts by state for 2008 and Figure 2.3 shows the number of deaths and injuries in Malaysia for 2006 until 2008, respectively.

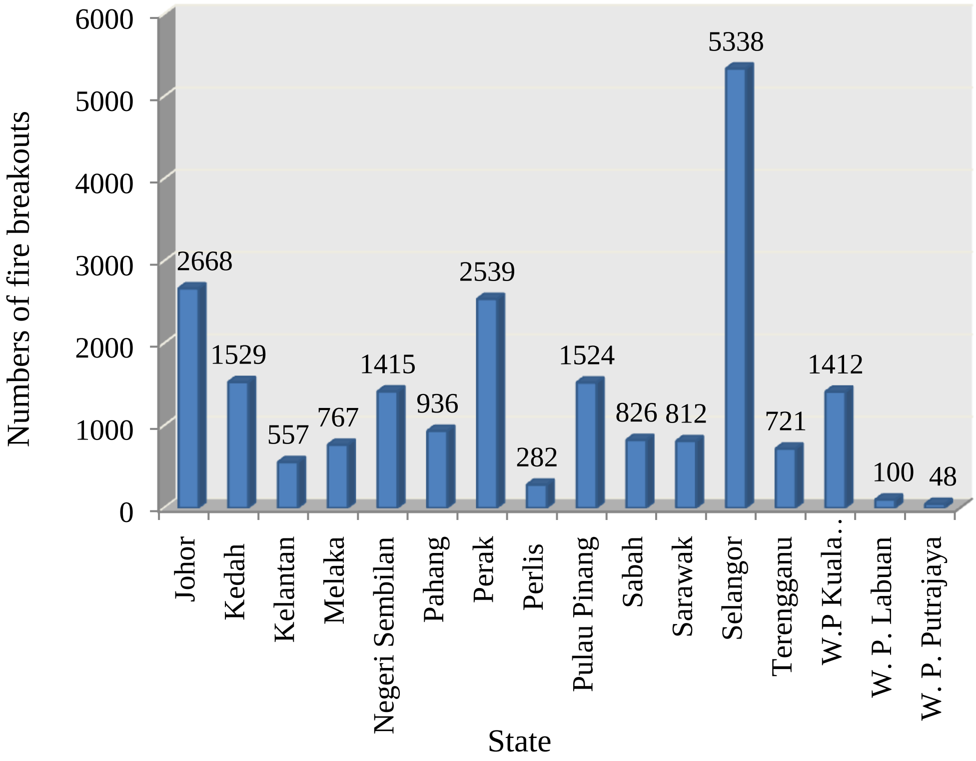


Figure 2. 2: Numbers of fire breakouts by state in Malaysia, 2008 [18].

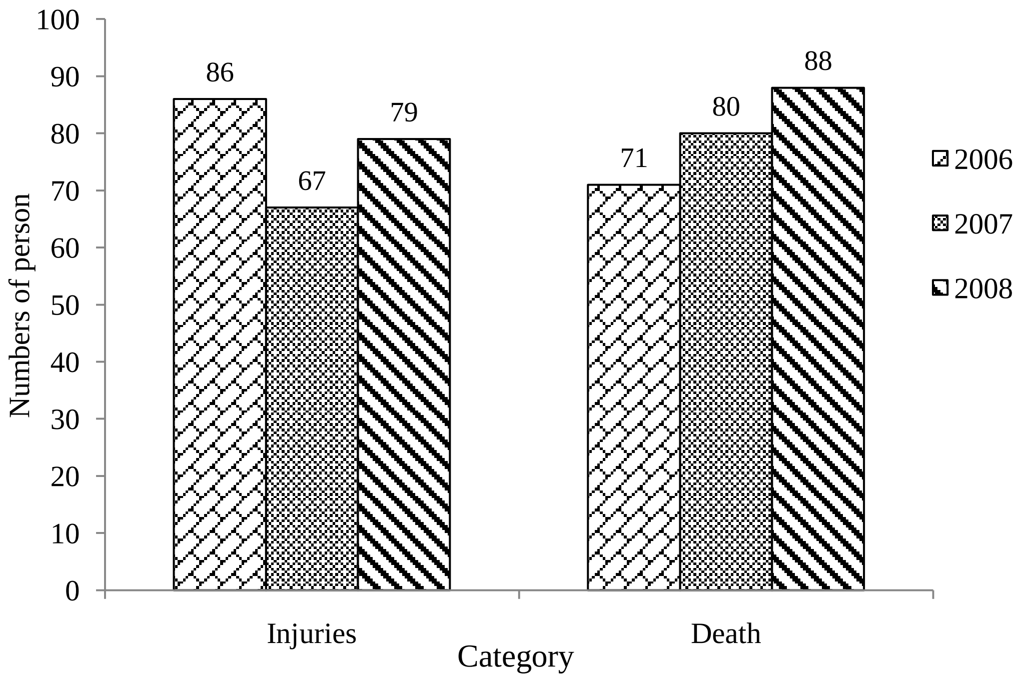


Figure 2. 3: Numbers of injuries and deaths in Malaysia for 2006 until 2008 [18].

Yatim, (2007) had studied on the fire safety in high rise building found that the cause of the deaths in fire breakouts mostly because heat and smoke released. The inhalation of smoke makes the occupants hard to breath and faint, resulting in trapped in the affected area and dead. From the research, Canada Wood Council [25] and Gormsen, *et al.*, 2004 [33] quoted that the major cause of the deaths was smoke released which is 90% of the deaths.

United Asia Fire Prevention Service Sdn. Bhd., Malaysia, (2011) [26], reported that there are two causes of the deaths which are smoke released and being burnt in the burning building. The major threat is the smoke released in the building with 75% of the deaths and only 25% attributed to burn. It can conclude that the most threat to the occupants when fire broke out is smoke. Therefore, in this research, the water-based acrylic resin was used as a binder for the coating. This material is said to be environmentally friendly since they degrade without smoke toxic.

Besides that, the phosphorus, nitrogen and silicon compounds also are said to be environmentally friendly during the decomposition at high temperature. The compounds containing phosphorus (e.g. APP), is said to be less toxic and corrosive when degrade. Low decomposition temperature yields carbon rather than carbon monoxide and resulting in the protective char layer to insulate the heat and oxygen in the air from transfer onto the substrate. For nitrogen-containing compounds (e.g. melamine) usually react with phosphorus compound to produce incombustible without toxic smoke. The produced gas forms the protective layer at high temperature. While, compounds containing silicon (e.g. vermiculite and acrylic) is an environmentally friendly among fire retardant materials. The silicon compounds produce high thermal stability material during fire when reacted with carbon, form a protective silica layer and protect the polymer residue at high temperature [34].

2.4 Acrylic resin

Acrylic resin is one of plastics (resin) generated from Methyl Methacrylate (MMA) monomer [19], [35], through polymerization process as shown in the Figure 2.4 below.

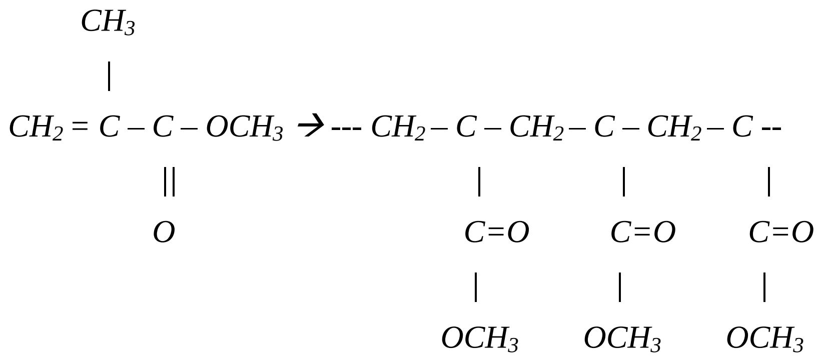


Figure 2. 4: Methyl Methacrylate (MMA) monomer going through the polymerization chemical reaction to produce acrylic resin [35].

Acrylic resin commonly used as paint for an artist. The other application of acrylate binders are paints for ceilings, walls and building fronts. Besides that, since 1957, in automotive sector, the acrylic resin was used as a binder in automotive finishes and topcoat [36].

Recently, there were studies on FRC using acrylic as a binder in FRC [12], [13], [37], onto metals [12], [20], [37], [38], wood [8], [39] and textiles [40], [41]. According to Stoye *et al.*, 1998 [36] and Wang *et al.*, 2006b [37] acrylic resin is weather resistant, water resistance, lightfastness, hard, gloss and gloss retention. Most important, acrylic resin is slow-burning or even self-extinguishing, and they do not produce harmful smoke or gases in the presence of flame [19] since volatile organic compound (VOC) is very low [42].

Dravelle *et al.*, 2004 [40], studied on the interaction of acrylic with the main composition in fire retardant coating which is ammonium polyphosphate (APP). In the studies, the thermal degradation of an acrylic binder used at the back of the textile applications was investigated. Acrylic was claimed as a carbon source because of the ability to form a carbon layer when degraded. From the thermogravimetry analysis, the material degrades slowly and stabilizes with high formation of stable residue as APP was added to the acrylic resin. Duquesne *et al.*, 2004 [4], Jimenez *et al.*, 2006 [3] and Wang and Yang, 2010 [43], explained that the binder is fundamental element in the fire retardant coating if it contributed to the expansion of char layer and ensure the formation of uniform foam structure.

Besides that, Wang, *et al.*, 2006a [20] had studied on the effect of acrylic polymer and acrylic nanocomposite on the thermal degradation and fire protection properties of APP-DPER-MEL coating. This research also stated that acrylic was not only a binder but also a carbon source. It said that the acrylic with thermal decomposition similar to the temperature range with interaction of APP-DPER-MEL will give the formation of a thermally stable char and good char structure. This is because APP can efficiently catalyze the thermal degradation of the acrylic to form the carbonaceous layer if both have the same range of decomposition temperature.

Custodio *et al.*, 2006 [39], has done a study about the durability of waterborne acrylic varnishes for the exterior use to protect the wood from atmospheric agents where the aqueous acrylic resin is used as a binder. Acrylic resin was used due to the need of reducing the volatile organic compounds (VOCs) content in the painting industry. Furthermore, Bethencourt *et al.*, 2003 [38], also used the acrylic water-based paint but applied to the steel. They investigated the anticorrosive behavior of different formulations of the coating by using electrochemical techniques.

The other researchers which are Topcuoglu, *et al.*, 2006 [44], said the acrylic polymers and copolymers are widely used as a binder in paint formulations due to their good adhesion and film forming properties.

Therefore, in this research study the acrylic resin was used as a binder in the formulation of FRC as it is a water-based medium, capability of functioning as binder and also a carbon source and has good adhesion bonding.

2.4.1 Mechanism of decomposition for acrylic medium

Acrylic polymers in the fire retardant coating are scarcely found in the literature review. There is one study on the effect of acrylic polymer and nanocomposite with presence of nano-SiO_2 on thermal degradation and resistance of fire for fire retardant coating by Wang, *et al.*, 2006a [20]. In the studies, Wang, *et al.*, 2006a [20] used synthesized acrylic resin by methyl methacrylate and styrene, named 3F-1. The other acrylic resin was synthesized by methyl methacrylate and ethyl methacrylate, called F-936. They found that the same temperature range for interaction of APP-PER-melamine with thermal decomposition of acrylic give good fire resistance and better char structure. The process of thermal degradation for acrylic is as below:

> During the degradation of acrylic resin, a carbonic reaction and a ring-closure occur with the formation of cyclic alkenes and cyclic anhydride at high temperature. These cyclic reactions lead to the formation of a three-dimensional crosslinked char structure. The degradation reaction of acrylic resin is presented in Figure 2.5.

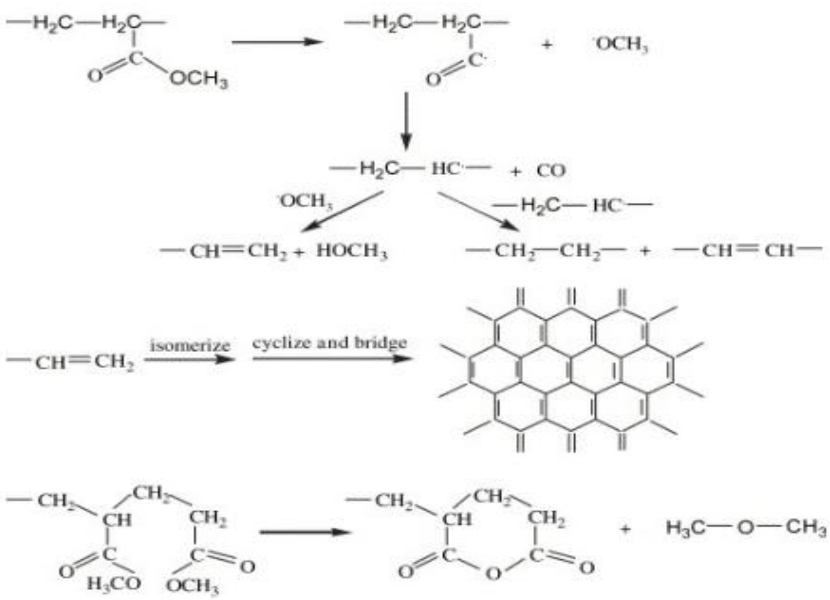


Figure 2. 5: Schematic outline of the thermal degradation of 3F-1 acrylic resin [20]

The C=C unsaturated bonds of acrylic resin are formed by radical reaction. These C=C unsaturated bonds come from chain breaking mechanisms with intermolecular or intramolecular proton transfer. The mechanism is due to disproportionation of carboxylic acid and ester functional group (HO· radicals and CH_3O· radicals). The first endothermic peak at 146.8^{o}C in DTA curve is attributed to melting of acrylic resin and the second endothermic peak at 398.1^{o}C is due to thermal degradation of acrylic resin… The high melting temperature and decomposition temperature of 3F-1 acrylic resin are attributed to high molecular weight and a great number of benzene rings in its molecular structure. The thermal decomposition of 3F-1 acrylic resin at 300^{o}C – 430^{o}C is nearly at the same temperature range with interaction of APP, DPER and Melamine at 280 – 440^{o}C.

Compared with 3F-1 acrylic resin, F-963 acrylic resin melts and decomposes at lower temperature (peak temperature: 325.8^{o}C due to low molecular weight and lack of benzene ring in its structure.

Due to the decomposition temperature range of 3F-1 is in similar range with APP-DPER-melamine, the efficient fire resistant and good char structures were obtained. For F-936, the decomposed temperature at 250 – 350^{o}C is lower than the temperature of APP-DPER-melamine at 280 – 440^{o}C, which denotes that F-936 has mostly decomposed before the efficient degradation of APP to initiate the formation of carbon char.

2.5 Vermiculite

Vermiculite is a hydrated laminar magnesium-aluminium-iron silicate resembling mica in appearance [21]. Vermiculite is a natural mineral that expand to many times its original volume when exposed to heat which is called exfoliation. There are three types of vermiculite which are unexpended, expended and single particle as shown in the Figure 2.6 below [45], [46]:

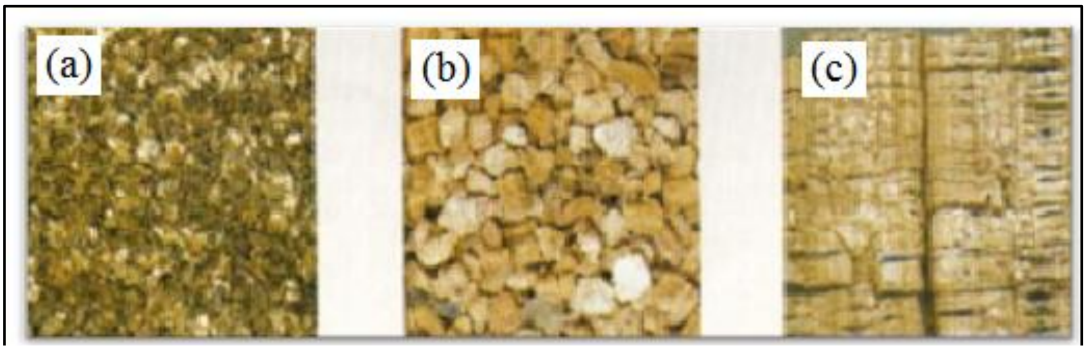


Figure 2. 6: (a) Unexpended, (b) expended, and (c) single particle vermiculite [45]

Vermiculite is used in diverse applications such as in agriculture, horticultural and construction industry [46], [47], [48]. Its properties are excellent water retention, sterile, environmental friendly, excellent insulation and also light material. In agriculture industry expanded vermiculite used as a carrier for vitamins and other nutritional substances as it is sterile and environmental friendly It also been used with the cement in construction industry as it provides a lightweight spreading material, an insulation and also as a fireproofing material [47], [48]. The typical compositions of vermiculite from Asia Pacific Vermiculite Sdn. Bhd [48] are shown in the Table 2.2 and 2.3 below:

Table 2. 2: Typical Ranges of Vermiculite for Major Components [48].

Oxide	**Mass %**
SiO_2	35 – 41
Al_2O_3	6.0 – 9.5
Fe_2O_3	6.0 – 9.5
MgO	21.5 – 25.5
K_2O	3 - 6

Table 2. 3: Typical Ranges of Vermiculite for Minor Components [48].

Oxide	**Mass %**
CaO	2.0 – 6.0
CO_2	0.6 – 2.5
TiO_2	0.6 – 1.4
F	0.2 – 0.8
Cr_2O_3	0.01 – 0.15
P_2O_5	0.2 – 2.0
Cl	0 – 0.5

Ren, *et al.*, 2010 [49], study on the synergistic effect of vermiculite on the flame retardance of polypropylene which used unexfoliated, exfoliated vermiculite and montmorillonite by using fire testing methods. The thermogravimetric analysis show the exfoliated vermiculite had increased the char residue at high temperature (650^{o}C) compared to unexfoliated vermiculite and montmorillonite. Besides that, the exfoliated vermiculite also lowering the peak values for heat release rate in the limiting oxygen index (LOI) and low smoke production rate.

In this research, exfoliated vermiculite was used as an additive in the water-based fire retardant coating.

2.6 Galvanized steel

Steel is a metal or alloy that contain mostly iron that combine with other elements. The common alloying material for iron is carbon which produced carbon steel. The carbon content is between 0.2 and 2.1 in weight % depending on the grade. The other material is chromium to produce stainless steel.

Steel is widely used in construction industry because it played critical role especially in construction such as bridges, buildings, offshore platform, for automobiles, infrastructure and machines. It is a non-combustible material where when expose to high temperature above 500ºC the strength and the stiffness of the steel decreased. If it has been exposed to a long time, the crystalline/ metallurgical structure of the steel will undergoes a transformation. Unprotected steel will visibly deform, twist and buckle. The significant heating effects of the fire could permanently alter the nature of the steel material. In order to prevent this from occur, a fire protection coating is been applied to the steel structure such as spray or brush roller as a thin film on materials [14], [50].

In this research study, galvanized steel was used as a substrate. Galvanized steel is a steel that have been coated with zinc. The purpose of this is to protect the steel from corrosion since zinc is a non-corrosive metal or as sacrificial layer. If the rust takes hold onto the galvanized steel, the zinc will be corroded first. That is why galvanized steel was used in this research as to prevent the corrosion that may affect the result.

2.7 Adhesion between coating and substrate

Generally, the coating system is widely used to coat various types of surfaces such as wood, metal and plastic, the diverse structures likes porous, homogeneous and flat, and the many possible stresses to which it may exposed such as temperature, extensibility. Because of that, it is important to have adhesion promoter to ensure the strength or a good adhesive bonding between coating material and the coated material. Adhesion is about the physical and chemically intermolecular interactions in the interface or interface layer [51], [52]. The adhesion promoter can be in a range of chemicals available includes silicones, amides, phosphates or modified polymers. Besides that, there are binders and additives. This adhesion promoter is to ensure the adhesive bonding between the coating and coated material is sufficient hence the coating functioning effectively to protect the coated surfaces.

Adhesion is important regardless of what excellent properties a coating may possess, it is useless unless it also has good adhesion. The coating's resistant to weather, chemicals, scratches or impact is only value while the coating remains on the substrate [53]. In this research, the standard test method ASTM D 3163 was used to investigate the strength of the coating to the substrate. This standard is for determining strength of adhesion in shear by tension loading.

Rich, 2001 [54] stated that there are three types of failure:

(1) cohesive failure: break in the bond line (within the same material),

(2) adhesion failure: break between substrate surface and adhesive (poor adhesion)

(3) substrate failure: break in the substrate, the bond line is stronger than the substrate (structural bonding)

According to Zhai, *et al.*, 2007 [55], the addition of nano – Al_2O_3 in the epoxy adhesive improves the adhesion of the epoxy to the steel substrate. In that study, the transmission electron microscope (TEM) was performed and proved that the nano – Al_2O_3 was finely dispersed in the epoxy adhesive. It is said that the content of 2% nano – Al_2O_3 give the highest adhesion strength with the rough surface area of the steel abraded with silicon carbide paper of 150 (150#) compared to steel abraded with 60# and polished. Besides that, with increased of wt% of nano - Al_2O_3 in the epoxy adhesive, the adhesive strength was reduced due to the surface wetting ability to the steel substrate. This condition is unfavorable to the adhesion strength. The failure modes in the study by Zhai, *et al.* were cohesive and interfacial. The Figure 2.9 below shows the illustration of failure modes can occur. The interfacial crack occurs when the adhesive-steel strength was low compared to the interfacial forces due to the applied forces. Thus in the 2% of nano – Al_2O_3, the cohesive crack was observed showing that the adhesion bonding between epoxy adhesive and steel substrate is strong compared to other sample. From these results, it indicates that nano – Al_2O_3 enhanced the adhesion at the interface.

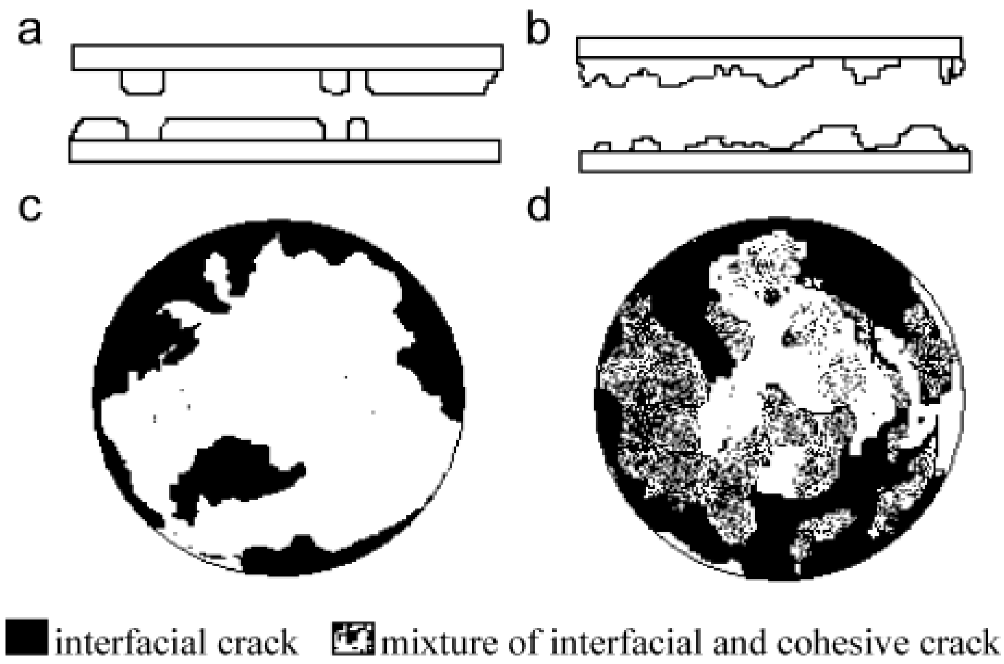


Figure 2. 7: Schematic illustration of interfacial crack (a and c) and the mixture of interfacial and cohesive crack (b and d) [55].

They further prove the significant of nano – Al_2O_3 in adhesion by performing energy dispersive X-ray (EDX) where they identified the presence of element Al at the boundary layer interface of adhesive. Besides that, nano - Al_2O_3 catalyze the epoxy adhesive to give rise to polar functional groups where it can react with steel and form some chemical bonds, resulting in carboxyl group, hence improve the adhesion.

These were supported by Hjertberg, *et al.*, 1989 [56], Friedrich, *et al.*, 2003 [57] and Brand, *et al.*, 2004 [58] that found the carboxyl group that reacted with the oxide surface of the substrate improved the adhesion bonding. Moreover, this carboxyl group showed the highest interaction with metal compared to other functional groups.

According to Kajtna, *et al.*, 2009 [59], the measurements of adhesion properties were investigated by performing tack, peel strength and shear resistance. They investigated on the effect of polymer molecular weight and crosslinking reactions on adhesion properties for microsphere water-based acrylic adhesive. Tack is an ability of the coating to adhere quickly to the substrate, meanwhile the peel strength is the ability to resist the peeling force and shear strength is the ability to resist the applied shear forces to the coated adhesive.

For peel test, they used Final test method 1 (FTM 1) with the peeling angle at 180^{o}C at speed of 300 mm/min. Then, Kajtna, *et al.*, 2009 [59] used Final test method 8 (FTM8) to determine the ability of the adhesive to withstand the forces that parallel to the surface of adhesive. The parameter of this testing was the time taken for the adhesive to slide from the standard place when applied the shear forces. The shear resistance in term of time is calculated by taking the average time taken for six strips per sample. The dimensions of the strips were 25 mm wide and had minimum length of 75 mm. Kajtna, *et al.*, 2009 also identify the bond failure with adhesive failure (interface) or cohesion failure. The improvement in cohesion failure was observed for the sample with the high molecular weight with optimum 80 wt% of gel adhesive with only used with chain transfer agent (CTA).

Xu, *et al.*, 2005 [52], studied on the interface adhesion of MgF_2, Al_2O_3 and SiO_2 with pure silver thin films (Ag). In the research, they proved that Al_2O_3 had the best adhesion bonding with Ag films compared to MgF_2 and SiO_2. Xu, *et al.*, 2005 had investigated the adhesive bonding by stripping method and humidity testing method and analyzed the surface morphology with optical microscope. The results from stripping by using adhesion test pen showed the adhesion between Ag and Al_2O_3 with no damage surface when applied the average pressure was 5 N. Then, after the samples were immersed in the water for 36 hours, the sample of Ag and Al_2O_3 had little damage compared to others, where sample with SiO_2 was peeled off from Ag and patches were observed for sample with MgF_2. The importance in adhesion is whether the physical or chemical adsorption (structure) occurred between those two films. Xu, *et al.*, 2005 further described the cause of good adhesion as follow:

> The structure of monatomic Ag is close-over hexagon atomic crystal, while Al_2O_3 is α- Al_2O_3 when substrate is 100^{o}C and structure is corundum close-over hexagon, MgF_2 is fluoritic close-over cubic structure and SiO_2 is ruleless meshwork when it deposited on Ag… SiO_2 is ruleless meshwork structure with covalent bonds; its adsorption is mainly physical…α- Al_2O_3 and MgF_2, their ion

crystal, so there are chemical adsorptions besides physical adsorptions, so their adhesion to Ag are far larger than SiO_2.

Thus, the adhesion is stronger between two materials when their structure is similar where the best adhesion with Ag film was Al_2O_3.

However there are also some limitations in conducting the testing for measuring the adhesion of the coating. Some of these are as follow according to Brown, S., 1994 [60]:

1. The adhesion of a coating to its substrate may increase or decay with time, following coating application, depending on the nature of the system and the conditions imposed during storage and/or storage. Moreover, the stress level to which a given coating – substrate system is exposed during coating application, storage, and/or service may affect the direction of such change and the rate at which it occurs.

2. Some methods used for testing adherence apply stress or energy unevenly to the coating – substrate interface in an unacceptable measure. One important consequence of this in some cases is that the stress or energy density at the locus of failure initiation is not really known. Hence, the value calculated for the adherence from the data obtained, using the conventional formulas for the case, may have an unacceptable and often unrecognized, error associated with it.

3. If the coating – substrate interface is not smooth but irregular, stresses at the crack front during adhesion failure may be more complex than assumed. This could lead to misinterpretation.

4. Undetected residual stresses within the coating – substrate system may affect adherence and confound adherence testing.

In this research work, the adhesion bonding is studied as it is one of the most important properties the FRC should possess. The FRC cannot play its role to insulate the heat from transfer to the substrate if the coating does not sufficiently adhere to the substrate.

2.8 Chapter Summary

This chapter was deeply explained on the related theoretical aspect on the fire retardant coating, fire breakouts at occupational area, acrylic resin, vermiculite, galvanized steel and adhesion between the steel and fire retardant coating. Then, the research works that were in the same interest area was explained. The findings in those research works were used as the supportive proof for the results gained in this research study.

CHAPTER 3

MATERIAL AND METHOD

3.1 Chapter Overview

This chapter presents the materials used in the new formulation of water-based FRC and the preliminary analysis on chemical compatibility testing for the materials with the acrylic resin.

Furthermore, the procedure for samples preparation was explained in this chapter. The problems faced were then explained at sample preparation and fire protection test part. Afterward, the characterization of the coating before and after fire protection test was pointed up.

Besides that, the additional testing on adhesive bonding between coating and galvanized steel substrate was presented with the guidance of ASTM D 3136 [61].

3.2 Water–based fire retardant materials

Two commercial acrylic medium from Winsor & Newton® which were matt medium, 3040821 and gloss medium, 3040820 were used as a binder. The expanded vermiculite was used as received material in this research study. Since there was no technical information for the binder and vermiculite, thus the later part explained the characterization of these two binders and vermiculite.

Ammonia polyphosphate $(NH_4PO_3)_n$ with n = 1000, phosphorus content of 31.0 – 32.0 wt.% and soluble fraction in water is less than 0.5 wt.% as an acid source was supplied from Clariant® , Sulzbach, Germany. Pentaerythritol (PER) and Melamine were purchased from Merck®. All these chemicals are used without prior purification.

3.3 Chemical compatibility testing-Fourier Transformed Infrared (FTIR) Spectroscopy

The compatibility test was to ensure there is no reaction among the additives with the binder when they mixed together. This was investigated by using Fourier transformed infrared (FTIR) spectroscopy. There was a study on the role of binder in fire retardant paint which investigates on the chemical reactivity between the binder and the additives by using FTIR [4]. In this research, each material was mixed with two binders separately according to ratio and left for 24 hours and then let it dried in ambient temperature to be tested with FTIR.

FTIR spectra were recorded using Perkin-Elmer Spectrum One spectrophometer in the wave number range of 4000 – 300 cm^{-1}. Samples were ground and mixed with KBr and the mixture was pressed into a pellet. However, samples of pure acrylic medium were used directly in solid form in diameter of 50 mm. Sixty four scans were necessary to obtain spectra with good signal-to-noise ratio [4], [40].

3.4 FRC Sample Preparations

There were four formulations, designated as F1 which is formulation number 1 until formulation number four, F4. The first two formulations which are F1 and F2 were formulations of FRC without vermiculite, while for F3 and F4 were the formulations with vermiculite.

The formulation was in the wt% ratio of 3:1:1 [62] for APP, PER and MEL respectively, then the ratio for acrylic medium to APP-PER-Mel was 2:1. The samples of F1 and F2 were APP-PER-Mel coating while samples F3 and F4 were modified by the addition of 4 wt% of vermiculite to the total ratio. Table 3.1 shows the summary of the composition of the four formulations. The samples were prepared according to the following procedure; first, APP, PER, MEL and vermiculite were pulverized for 3 minutes by using Rocklabs grinder. Then acrylic medium was added and the mixture was stirred for 20 minutes to well-mix the ingredients by using Caframo mixer. The formulation used was shown in the Table 3.1 below:

Table 3. 1: Composition of Four Formulations.

Formula	MA (g)	GA (g)	APP (g)	PER (g)	Melamine(g)	Vermiculite(g)
F1	45	-	15	15	15	-
F2	-	45	15	15	15	-
F3	45	-	15	15	15	9
F4	-	45	15	15	15	9

MA – matt acrylic, GA – gloss acrylic, APP – Ammonium Polyphosphate, PER – Pentaerythritol

3.5 Characterization of the FRC

The characterization of the coating was conducted to investigate the thermal degradation of the material and the water-based FRC by performing thermogravimetric analysis (TGA), the elemental content through X-ray fluorescence (XRF) spectroscopy and observing the microstructure of the coating and char samples by scanning electron microscopy (SEM).

3.5.1 Thermogravimetric analysis (TGA) on pure materials and four coating formulations.

TGA was carried out at heating rate of $10^{o}C$/min under flowing N_2, over the whole range of temperatures (25 - $800^{o}C$) using Perkin Elmer TGA Analyzer to determine the thermal degradation and weight loss of the coating's materials before fire protection test. The samples (approx. 10 mg) were placed in an aluminium crucible. The data was recorded using Pyris Player Data Analyzer. These analyses were performed for pure APP, PER, melamine, both acrylic, vermiculite and also four formulations which were F1, F2, F3 and F4. The acrylic media and four formulations were in solid form while vermiculite was in powder form.

3.5.2 X-Ray Fluorescence (XRF) Spectroscopy on acrylic and vermiculite.

The samples of pure acrylic media which were in the liquid form were tested for half an hour to ensure the liquid does not leaking out from the sample holder during the analysis. The other samples were in powder form with weight of 20 g each. The testing machine used was Bruker AXS, XRF S4 Pioneer.

3.5.3 Scanning Electron Microscopy (SEM)

The surface morphological structures were observed and analyzed using SEM Oxford Leo 1430. This is to observe the surface morphology of the FRC with and without vermiculite. The microstructure of the surface and char were observed before and after fire protection test, respectively.

3.6 Fire Protection Test

The fire protection test was to assess the heat resistance of the coating protecting the substrate and the heat shielding ability of the resulting char. The coating was applied onto the 100 x 100 mm^2 galvanized steel substrate. The coating was exposed to butane portable gas torch as the experimental setup for this fire protection test is shown in Figure 3.1. A K type thermocouple and Anritsu AM-8000K, a digital data logger were used to record the temperature readings for every 1 minute at the back of the substrate and repeated for triplicate results. The distance of the fire with sample was kept constant at 6 cm. Besides that, the angle of the sample was also kept constant at 30^o. The temperature was recorded every minute for total duration of 100 minutes.

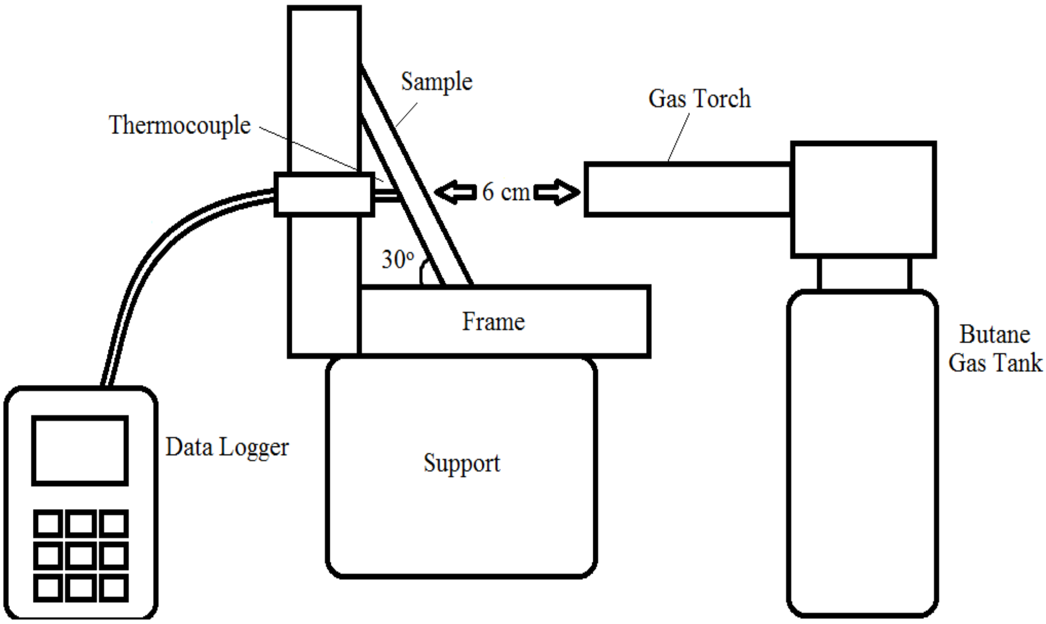


Figure 3. 1: Experimental setup for fire protection test

At first, the experiment setup for the fire protection test was done with the vertical Bunsen burner as shown in the Figure 3.2.

Figure 3. 2: Coating was faced downwards with vertical Bunsen burner

This setup was failed because during the fire protection test, the coating at certain time melted and falls off onto the Bunsen burner. This is probably because of formulation with first ratio was very dilute.

Then, the position of the sample is changed to be in slanted position and horizontal Bunsen burner was used as shown in Figure 3.3 which modified from Chou *et al.*, 2009 [29]. However, the fire from the Bunsen used was not strong enough and the temperature has to be recorded manually from the J type thermocouple every minute.

Figure 3. 3: Second trial of fire protection test.

In the end, the butane Bunsen burner and K type thermocouple with Anritsu AM-8000K were used. The Anritsu AM-8000K is a digital data logger that automatically record the back temperature of the galvanized steel substrate for every minute for 100 minutes.

The setup of fire protection test is differed from Chou *et al.*, 2009 [29] on the position of the sample where they hang up the sample on top of the fire in 45^o. However, the distance from the end of the torch is the same which is 6 cm.

3.7 Shear test of FRC

In term of performance of the coating, the ability of the coating to adhere properly to the material is most crucial element. The coating might flake away or detach from the surface due to the poor adhesion bonding thus allow moisture or corrosion products degrade the coating film at the damage areas. Moreover, if the coating is not adheres sufficiently to the structure the coating will not perform their function to protect steel structure from the heat efficiently. Thus, in this research work, shear test was performed to know the strength of the coating adheres to the galvanized steel substrate.

The test was conducted to further analyze the strength of the coating adheres to the galvanized steel substrate in terms of mechanical properties ASTM D 3163 was used as the standard test procedure for this testing [61]. The dimensions of the samples for this test were illustrated in Figure 3.5 below.

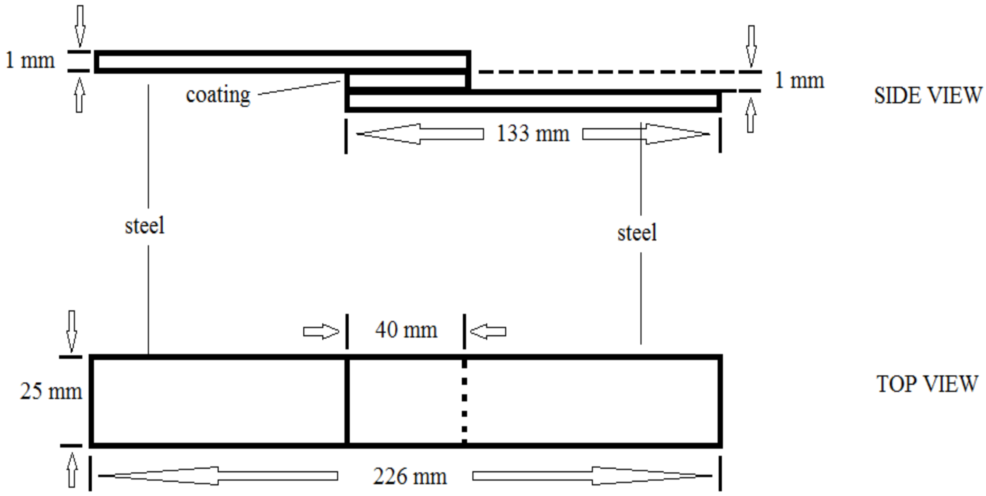


Figure 3. 4: The dimensions of the shear test sample.

The standard test method was to determine the strength of the adhesion coating to the substrate in shear by tension loading. The pre load for this testing was set to 50N with speed of cross head was 0.05 in. /min (1.3mm/min) [61]. Five samples for each formulation were repeated to obtain accurate result. The experiment was performed as shown in the Figure 3.6 below:

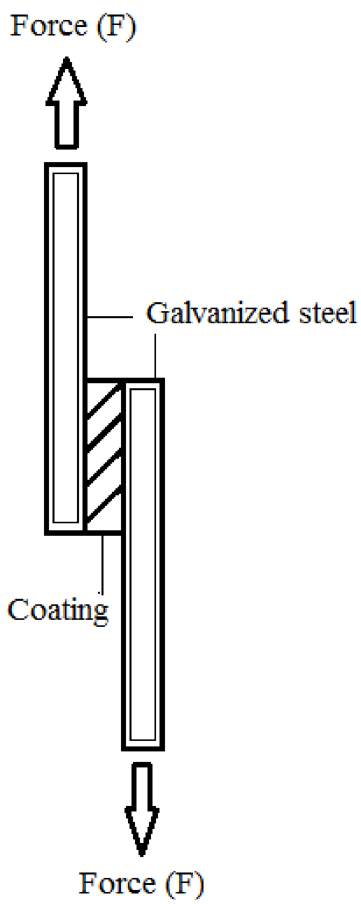


Figure 3. 5: The shear test setup

3.8 Chapter Summary

This chapter was successfully explained on the material used to formulate the water-based acrylic fire retardant coating which was APP, PER, Melamine, acrylic media and vermiculite. The characterization of the coating was investigated by performing thermogravimetric analysis (TGA), X-ray fluorescence (XRF) spectroscopy and scanning electron microscopy (SEM). The effect of vermiculite addition in the FRC was investigated by fire protection test and adhesion to the galvanized steel substrate by performing shear test.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Chapter Overview

This chapter illustrates and elaborates mainly on analyzing the results from FTIR spectroscopy for the compatibility testing, the elemental contents of the vermiculite and two acrylic binders from XRF analysis and the coating characterization on thermal degradation of each material and the coating before fire protection test. The fire protection test was also explained in details including the experimental setup, the graph of the result obtained and images of the coating before and after the experiment. Besides that, the morphology of the coating by SEM was presented with figures of microstructure of the coating before and after fire protection test. Morphology after fire protection test was focused at the inner structure of the char. The last testing was to determine the adhesive bonding between the coating and the galvanized steel substrate by describing the results of the shear test.

4.2 Samples of FRC

At first, the samples were prepared by weighing the material according to the ratio, then mix them up with the acrylic resin and been stirred for 20 minutes. The Figure 4.1 shows the image of F1 after been stirred for 20 minutes.

Figure 4. 1: Consistency of the resulting formulation F1 after mixing.

After that, the mixture was applied onto the 100 x 100 mm^2 galvanized steel substrate that was placed in the aluminum mold to fix the thickness of the coating for about 1 mm as shown in Figure 4.2 below.

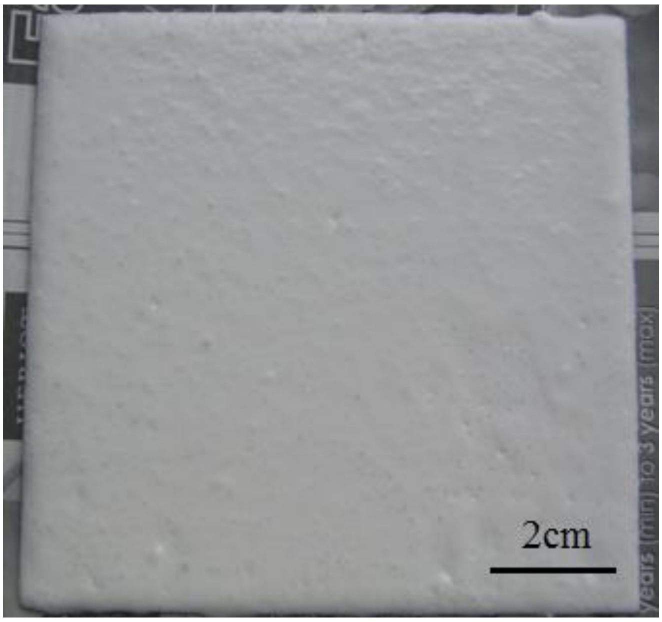


Figure 4. 2: Formulation F1 after application on one side surface of the galvanized steel plate

Finally, the coated galvanized steel substrate was dried for about three weeks at ambient temperatures as shown in Figure 4.3.

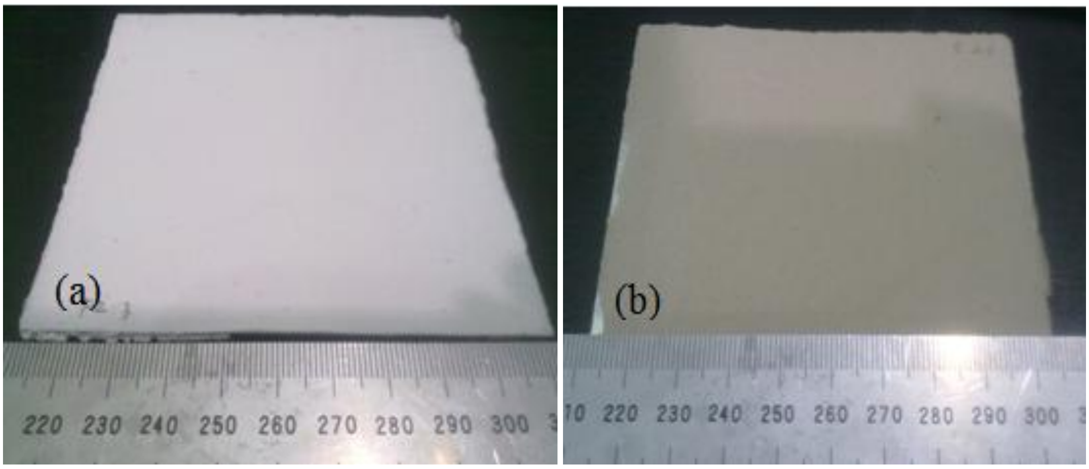


Figure 4. 3: Samples after dried (a) sample F2 and (b) sample F4. (Scale divisions are in mm)

4.3 Fourier Transformed Infrared (FTIR) Spectroscopy

The aim of FTIR analysis was to investigate the compatibility of fire retardant coating materials with acrylic resin. The presence of additional peaks in the result of FTIR spectrum were observed and compared with FTIR spectrum of the pure materials. If there are additional peaks, the reactivity between the materials occurred, thus it does not compatible with each other since it already react when first mixed up.

There were eight samples which are pure matt acrylic, pure gloss acrylic, APP, PER and also melamine with both acrylics. Figure 4.4 shows the comparison between pure matt and pure gloss acrylic.

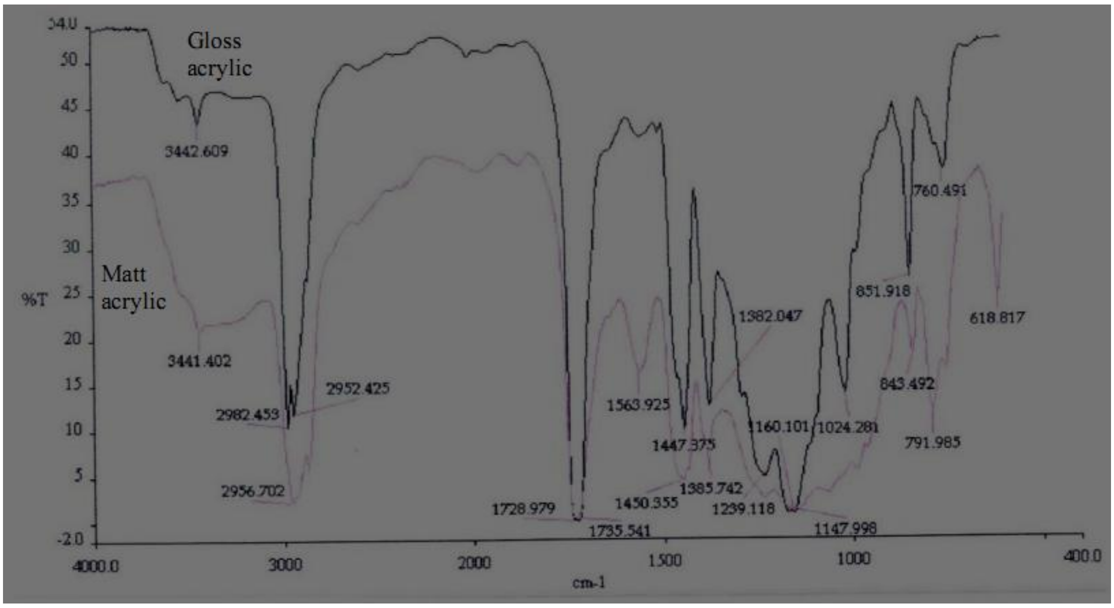


Figure 4. 4: FTIR spectrum of pure matt acrylic and pure gloss acrylic

Based on the results shown in Figure 4.4, the spectrum of gloss and matt acrylic show absorption bands at 3,442 and 3,441 cm^{-1} (N-H), 2,982 and 2,956 cm^{-1} ($H-CH_2-H$), 2,952 and 2,800 cm^{-1} ($C-CH_2-C$), 1,728 and 1,735 cm^{-1} (C═O acid), 1,447 and 1,450 cm^{-1} (C-OH acid), 1,382 and 1,385 cm^{-1} (CH_3-CRRR*), 1,147 and 1,160 cm^{-1} (C-O-C), respectively. The Table 4.1 below shows the summarized infrared peaks for the acrylic resin.

Table 4. 1: The summarized infrared peak assignments for the gloss and matt acrylic

Assignment Peaks	**Gloss acrylic (cm^{-1})**	**Matt acrylic (cm^{-1})**
N-H	3441	3442
$H-CH_2-H$	2982	2956
$C-CH_2-C$	2952	-
C═O acid	1728	1735
C-OH acid	1447	1450
CH_3-CRRR*	1382	1385
C-O-C	1160	1147

The spectra of APP with both acrylics are shown in Figure 4.5 where the percentage of transmittance for different acrylic is differed from each other. However, the absorption patterns were similar. The transmittance for APP with matt acrylic is higher than APP with gloss acrylic. These spectra were compared with pure APP that was analyzed by Wu, *et al.*, 2007 [63] and this is shown in Figure 4.6. The mixture of APP and two acrylics were given the similar absorption peaks as the pure APP in Figure 4.6. The typical absorption peaks of APP include 3,202 and 3,196 cm^{-1} (N–H), 1,252 cm^{-1} (P=O), 1,077 and 1,089 cm^{-1} (P–O symmetric stretching vibration), 882 and 879 cm^{-1} (P–O–P asymmetric stretching vibration) and 1,018 cm^{-1} (symmetric vibration of PO_2 and PO_3) [40], [63]. One peak that shows the existence of acrylic is at peak 1,734 and 1,736 cm^{-1} (C=O acid) respectively.

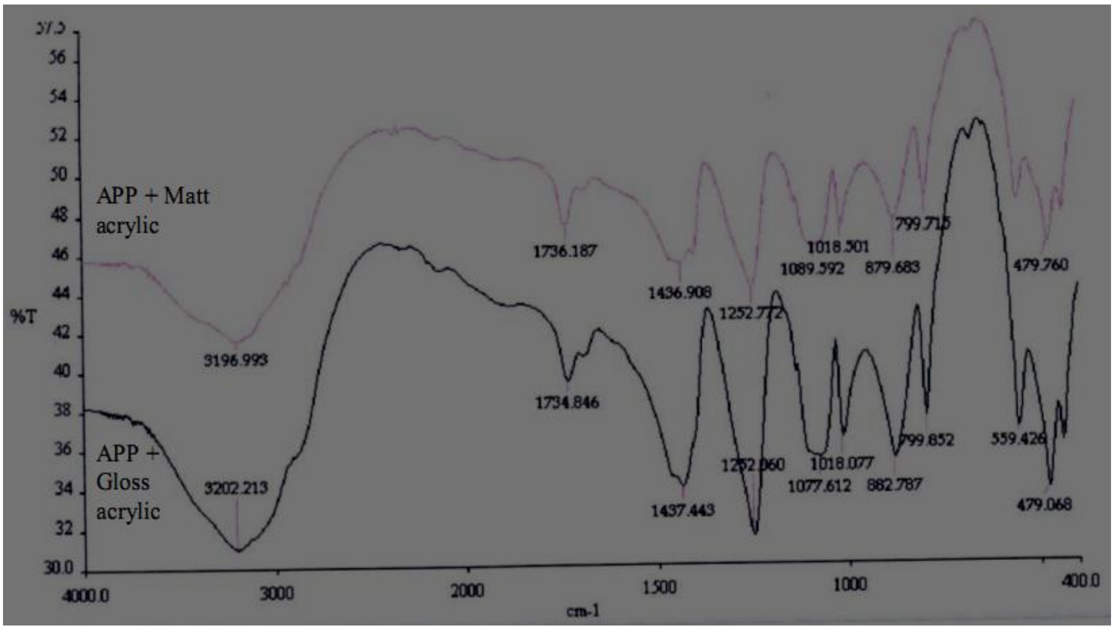


Figure 4. 5: FTIR spectrum of APP with matt and gloss acrylic respectively.

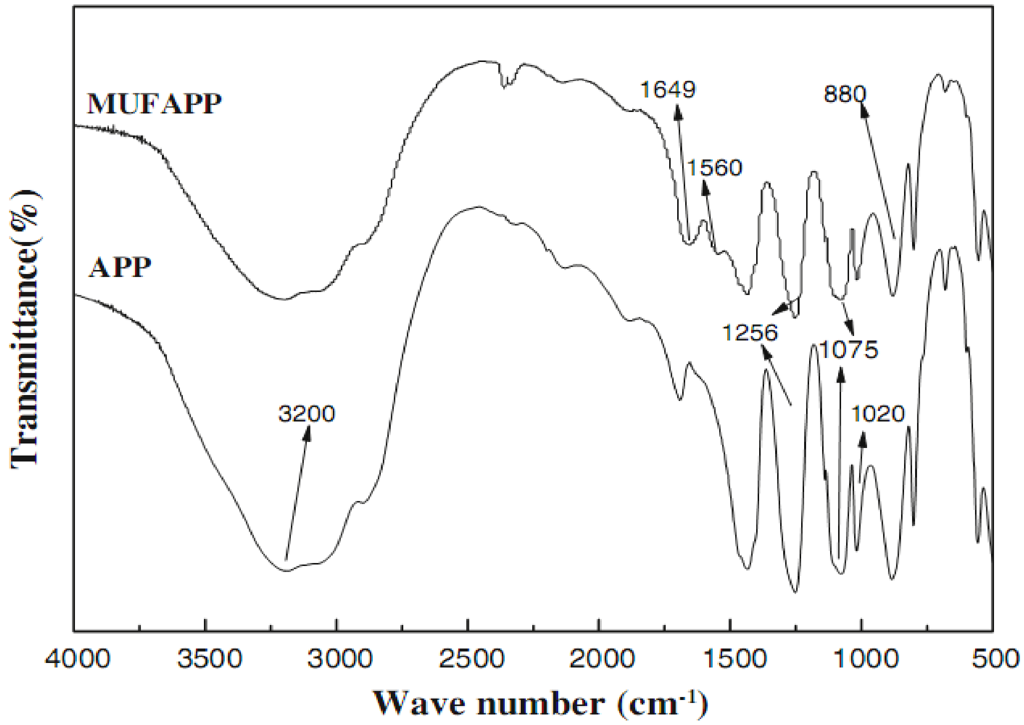


Figure 4. 6: FTIR spectrum of APP from Wu, *et al.*, 2008 [63].

The identified peaks for APP and both acrylics were shown in the Table 4.2

Table 4. 2: The summarized infrared peak assignments of APP, matt and gloss acrylic

Assignment Peaks	APP (cm^{-1})	Matt and Gloss acrylic **(cm^{-1})**
N–H	3202, 3196	
P=O	1252	
P–O symmetric stretching vibration	1077, 1089	
P–O–P asymmetric stretching vibration	882, 879	
symmetric vibration of PO_2 and PO_3	1018	
C=O acid		1734, 1736

FTIR spectra of PER with matt and gloss acrylic gave same peaks as shown in Figure 4.7. The stretching vibration peaks of O-H band is 3,325 cm^{-1}, C-H band is 2,886 cm^{-1}, C-O band from 1,015 cm^{-1} to 1,231 cm^{-1} [64]. The identified peaks of acrylic were 2,955 (H-CH_2-H) and 1,385 cm^{-1} (CH_3-CRRR*) [40].

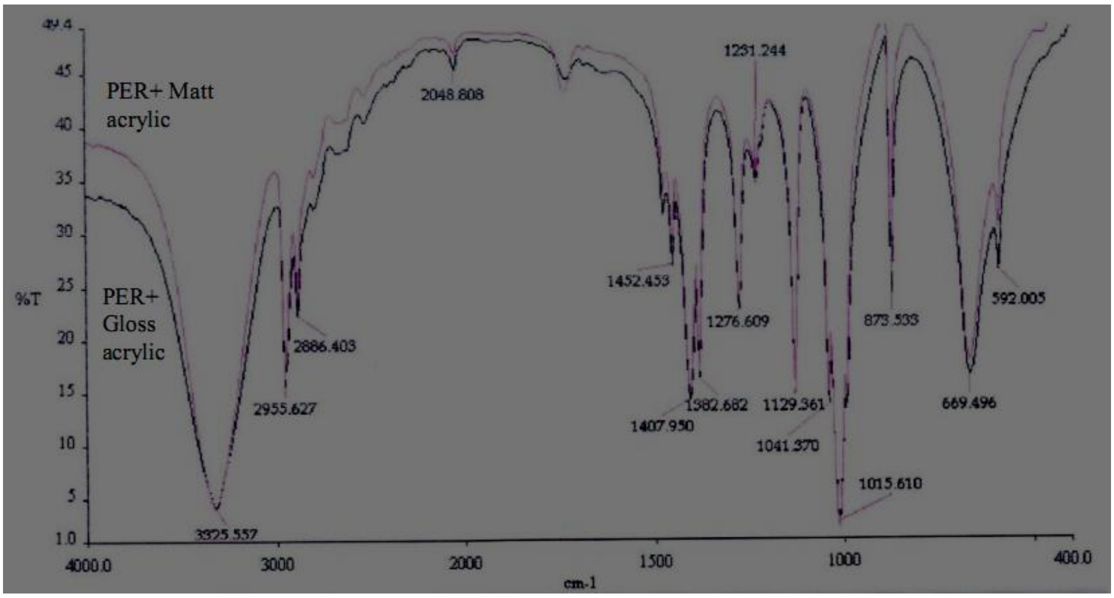


Figure 4. 7: FTIR spectrum of PER with matt and gloss acrylic

The identified peaks for PER and both acrylics were shown in the Table 4.3

Table 4. 3: The summarized infrared peak assignments for PER, matt and gloss acrylic.

Assignment peaks	**PER (cm^{-1})**	**Matt and gloss acrylic (cm^{-1})**
O-H band	3325	-
C-H	2886	-
C-O	1015 - 1231	-
H-CH_2-H	-	2955
CH_3-CRRR*	-	1385

Figure 4.8 shows melamine with both acrylics. The absorption peaks of N-H are in the range of 3,332 to 3,496 cm^{-1} and from 1,551 to 1,652 cm^{-1}. The peak band of 1,027 cm^{-1} shows the same peak for pure gloss acrylic.

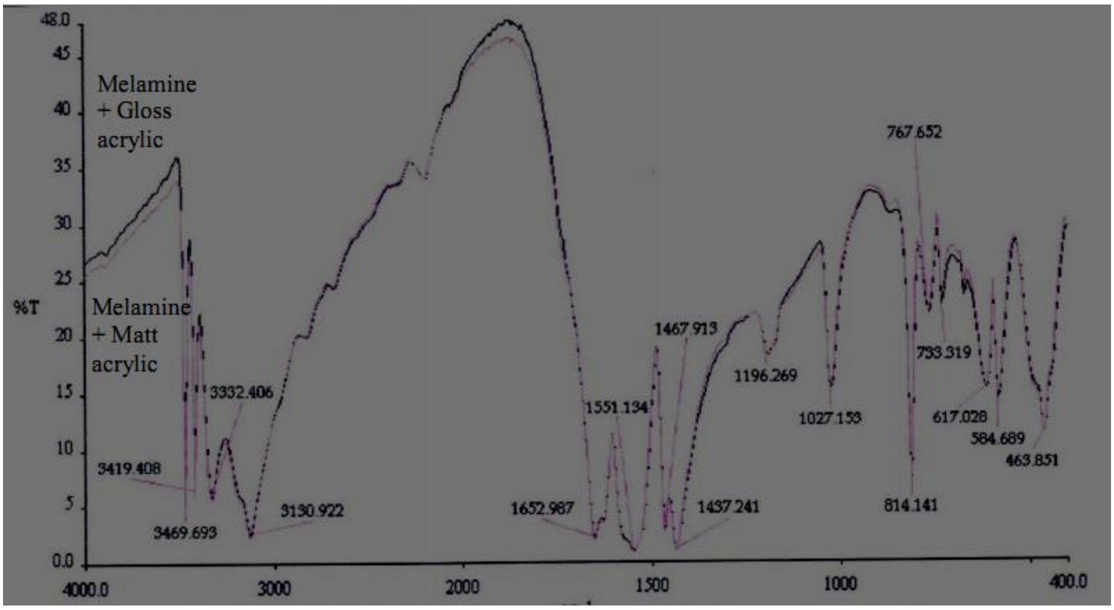


Figure 4. 8: Melamine with matt and gloss acrylic.

The identified peaks for Melamine and both acrylics were shown in the Table 4.4

Table 4. 4: The summarized infrared peak assignments for Melamine, matt and gloss acrylic.

Assignments peak	**Melamine (cm^{-1})**	**Gloss acrylic (cm^{-1})**
N-H	3332 to 3469 and	-
	1551 to 1652	-
C-O-C	-	1027

From all of these spectra, the components were found to be compatible with acrylic resin since there is no additional peaks were observed. However, the FTIR analysis of this FRC should be done in further details in future to identify the peaks and reactions occurred.

4.4 FRC Characterization

4.4.1 X – Ray Fluorescence (XRF): Pure acrylic media

The elements contained in matt and gloss acrylics are shown in Table 4.5. There are different main elements in the acrylic media where in matt acrylic there are silicon, calcium and phosphorus while for gloss acrylic there are phosphorus, calcium and sulfur.

Table 4. 5: Composition of Two Acrylic Media

Element	**Matt acrylic (*Mass %*)**	**Gloss acrylic (*Mass %*)**
Si	74.30	-
Ca	15.10	28.40
P	7.15	43.50
S	1.83	19.80
Fe	1.12	4.70
Al	0.33	-
Cu	0.17	3.60

This indicates that the oxide additives used by the manufacturer to produce the matt acrylic were silicon (Si) and aluminium (Al).

4.4.2 X – Ray Fluorescence: Vermiculite

Table 4.6 below shows the composition of the vermiculite used in this research.

Table 4. 6: Composition of Vermiculite

Oxide	Mass (%)	Oxide	Mass (%)
SiO_2	43.90	Rb_2O	0.07
MgO	23.28	MnO	0.07
Fe_2O_3	10.77	Cr_2O_3	0.04
Al_2O_3	10.40	NiO	0.03
K_2O	7.11	ZnO	0.03
CaO	1.90	SrO	0.02
TiO_2	1.42	CuO	0.01
P_2O_5	0.95		

The main oxides in vermiculite were silica, magnesia, ferric oxide and alumina. These main components will affect the reaction of the fire retardant coating during fire hazard.

It is important to identify the elements in acrylics and vermiculite since they play important role in reaction within FRC which is to form a good char structure and thermally stable ceramic material at high temperatures. For instance, the SiO_2 is important in creating the Si-O-Si networks that protect the insulating materials at high temperatures and a mechanical reinforcement of the protective materials [34], [37].

4.4.3 Thermogravimetric analyses (TGA) on pure materials and four formulations.

The thermogravimetry was performed on pure acrylic media and vermiculite since there was no information regarding the properties on those materials from supplier. Besides that, four formulations of water – based fire retardant coating before fire protection test also need to be analyzed using TGA to identify their thermal behavior, promptly know the effect of vermiculite addition in the formulation.

TGA thermogram curves of two acrylic mediums are shown in Figure 4.9. There are two degradation steps for matt acrylic. The first step presents with the weight loss of 17% at 150^{o}C. Then, the major degradation step cause the weight loss of matt acrylic is 64% at 401.9^{o}C (as shown in the Figure 4.10). At the end of the degradation, the residual mass is 16%

For gloss acrylic there are two steps where the first major degradation step with a maximum weight loss of 88% is at 412^{o}C. Then, the second step presents the maximum of weight loss of 4% at 520^{o}C. From Figure 4.9, the obvious different in residual weight where matt acrylic give higher thermally stable residue than gloss acrylic. This is because of the different compositions in matt acrylic which contain Al and Si as shown in Table 4.5 where these components were said can enhances the formation of stabilize material at high temperature [40], presumably in the form of alumino silicate ceramics.

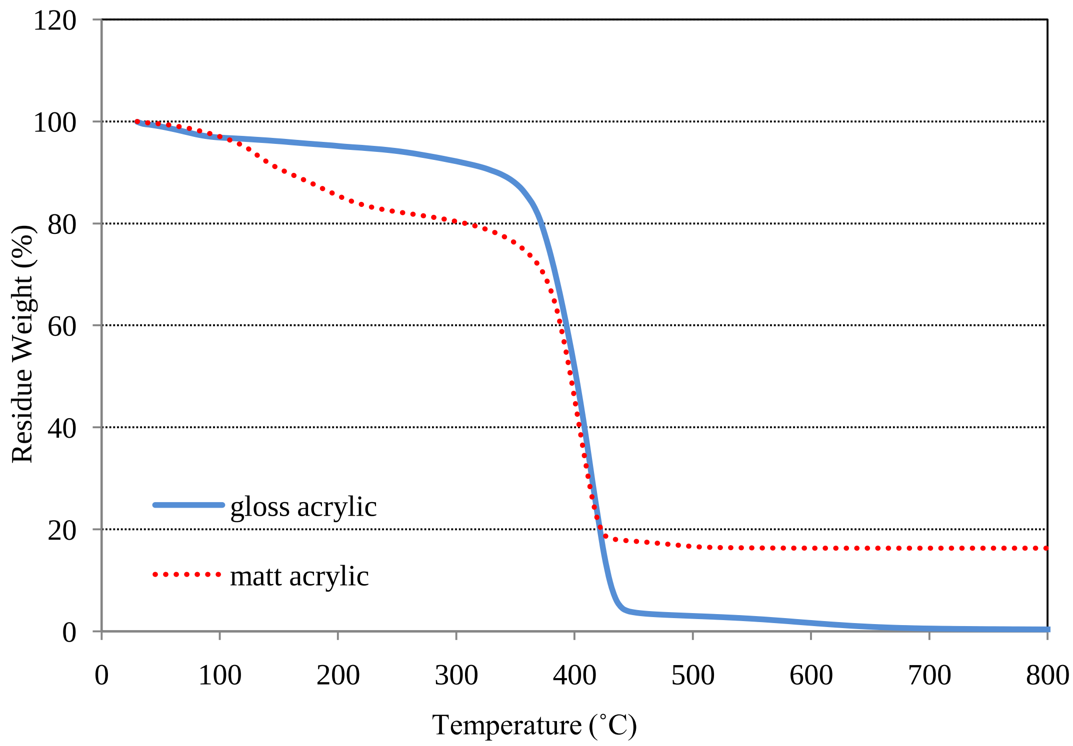


Figure 4. 9: TGA curves of matt and gloss acrylic

From the derivative thermogravimetry (DTG) curve in Figure 4.10, the matt acrylic starts to melt on 129.8°C and decomposed peak at 401.9°C. For gloss acrylic in Figure 4.11, at temperature 71.3°C it started to melt and decomposed peak at 412.0°C.

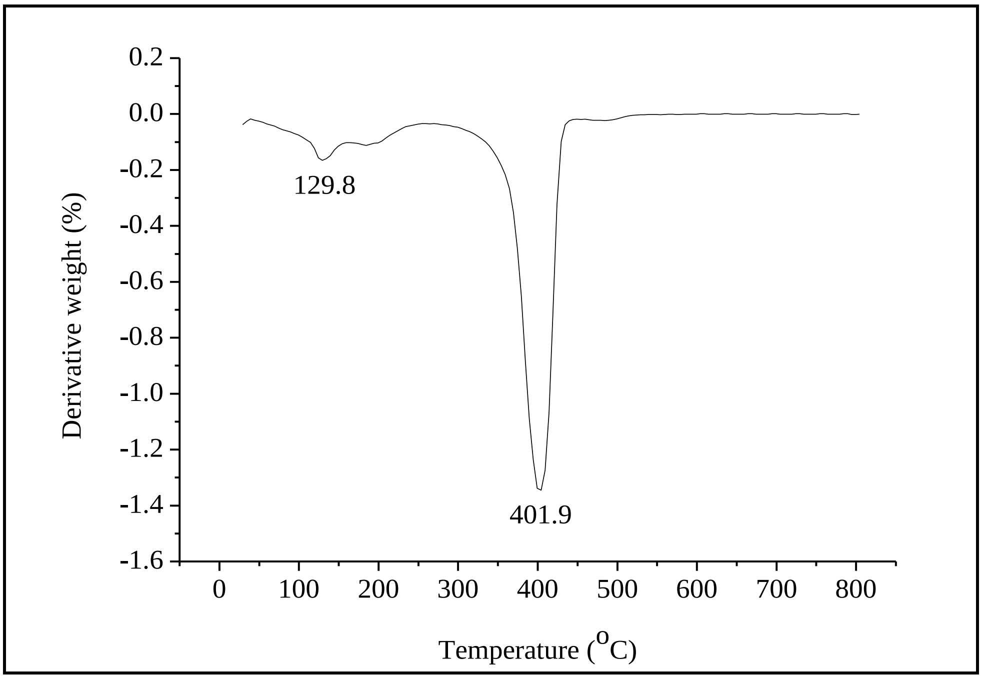


Figure 4. 10: DTG curve of matt acrylic

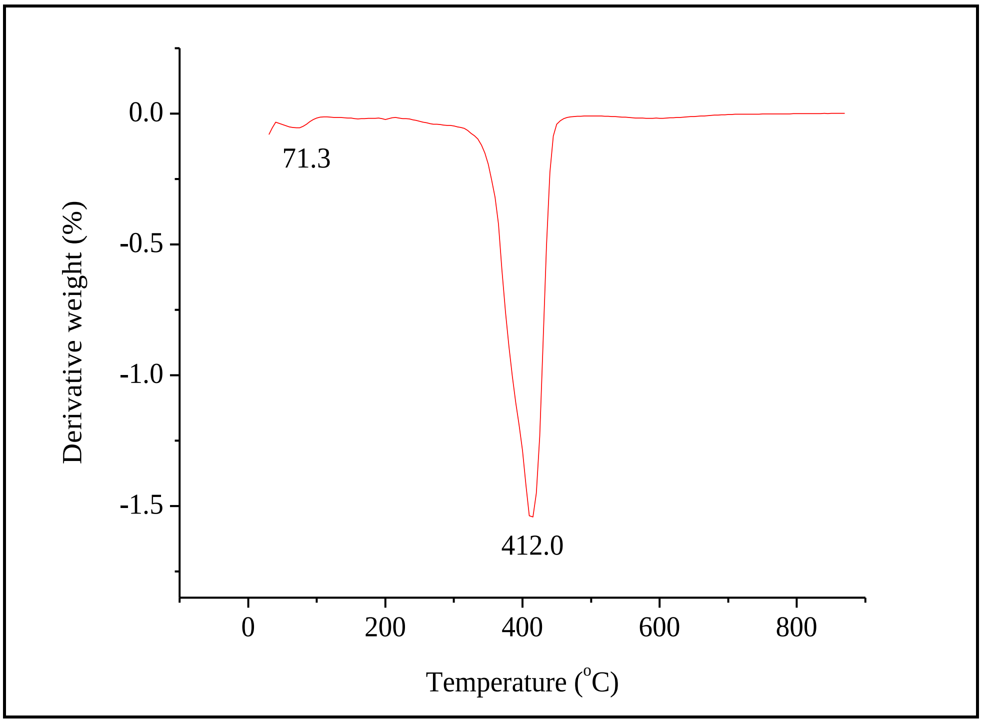


Figure 4. 11: DTG of gloss acrylic

From the Figure 4.11 above, the melting point of gloss acrylic is early which was at 71.3^oC, this point where water evaporates and the peak temperature for decomposition is on 412.0^oC. For matt acrylic (Figure 4.10), the first peak at 129.8^oC is attributed to the melting of acrylic and second peak at 401.9^oC is due to the thermal degradation of the matt acrylic.

Subsequently, the TGA curves of pure APP, PER, Melamine and combination of three ingredients is presented in Figure 4.12.

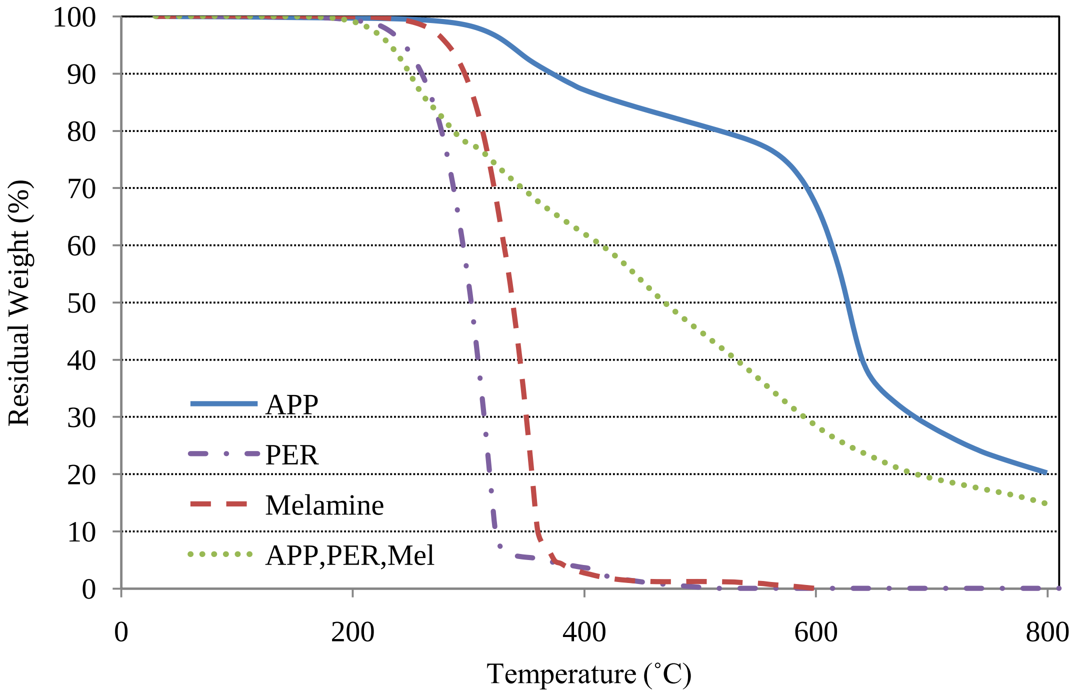


Figure 4. 12: TGA curves of pure APP, PER, MEL and combination of these three materials.

The APP begins to decompose in two main steps. The first step is between 260^oC and 450^oC, the weight loss gets to 20% and a second step between 450^oC and 780^oC with 20% residual weight. Based on Gu *et al.*, 2007 and Dravelle *et al.*, 2004 , the first step degradation is when the gas of NH_3 and H_2O is released and the second step corresponds to the evaporation of phosphoric acid and dehydration of the acid in P_4O_{10} [10], [40]. The TG curve for PER shows that the decomposition start at 210^oC, where the formation of crystal structure and decomposition of pentaerythritol occurred [20], [65] then at 460°C there is no residue of PER. The weight loss for Melamine begins above 260°C by decomposing Melamine and releasing the NH_3 [10]. There is no residue after 420°C. For the combination of three ingredients the decomposition begins at 200°C and left with thermally stable char at 690°C for about 20%.

According to Wang *et al.*, 2006a [20], the good char structure and efficiency of the FRC is when the acrylic binder decomposed at the same temperature range of interaction between APP, PER and MEL. This is because acrylic resin not only acts as a binder but also as an important carbonization agent in FRC. Thus, the APP also initiates the dehydration of acrylic resin besides PER to form the carbonaceous char.

The degradation temperature of APP, PER and MEL is between 260°C and 450°C due to the formation of protective char layer. The thermal decomposition of gloss acrylic is 250-450°C (Figure 4.9) which is the same temperature range for interaction between APP, PER and MEL. Meanwhile, the matt acrylic has two main steps of degradation process. The first step is 100-250°C then the second step is between 250°C to 450°C. The results show both acrylics have the same temperature range with those three components. Thus, the interaction of both acrylics with the APP, PER and MEL give the same weight residue of thermally stable material. This will be proven in the later part of the TG analysis.

Figure 4.13 shows the thermal degradation of formulation for both acrylics without vermiculite (F1 and F2). From these curves, it clearly shows that the overall thermal degradation of these two samples give similar profiles. However, at 500-720°C, sample F1 give slightly higher residue than F2 but in the end the residual weight of thermally stable char for both samples is about 20%.

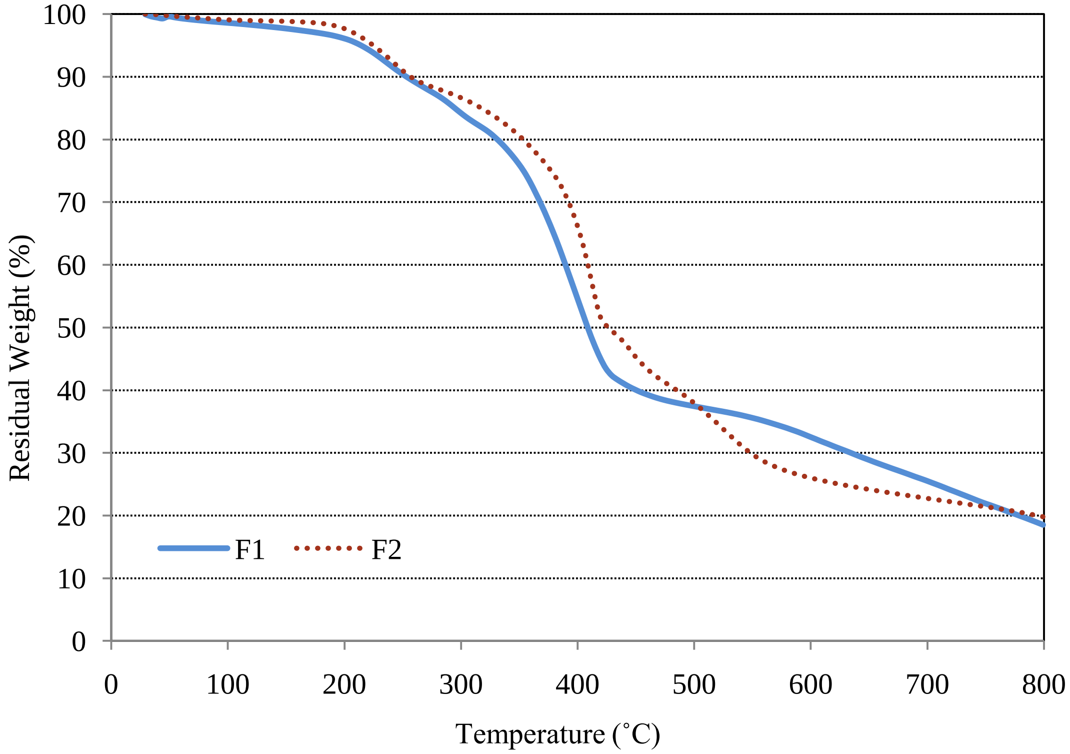


Figure 4. 13: TGA curves of F1 and F2

4.4.3.1 Effect of vermiculite addition on thermal degradation

The TG curves in Figures 4.14 and Figure 4.15 shows the comparison between the formulation without and with vermiculite. From these figures, the effect of vermiculite addition in this water-based acrylic FRC can be seen. The thermal degradation of F3 in Figure 4.14 shows a shift to the higher degradation temperature starting at 270^{o}C until the end. The thermal residue of F3 increases from 19% of F1 to 32% of residual weight.

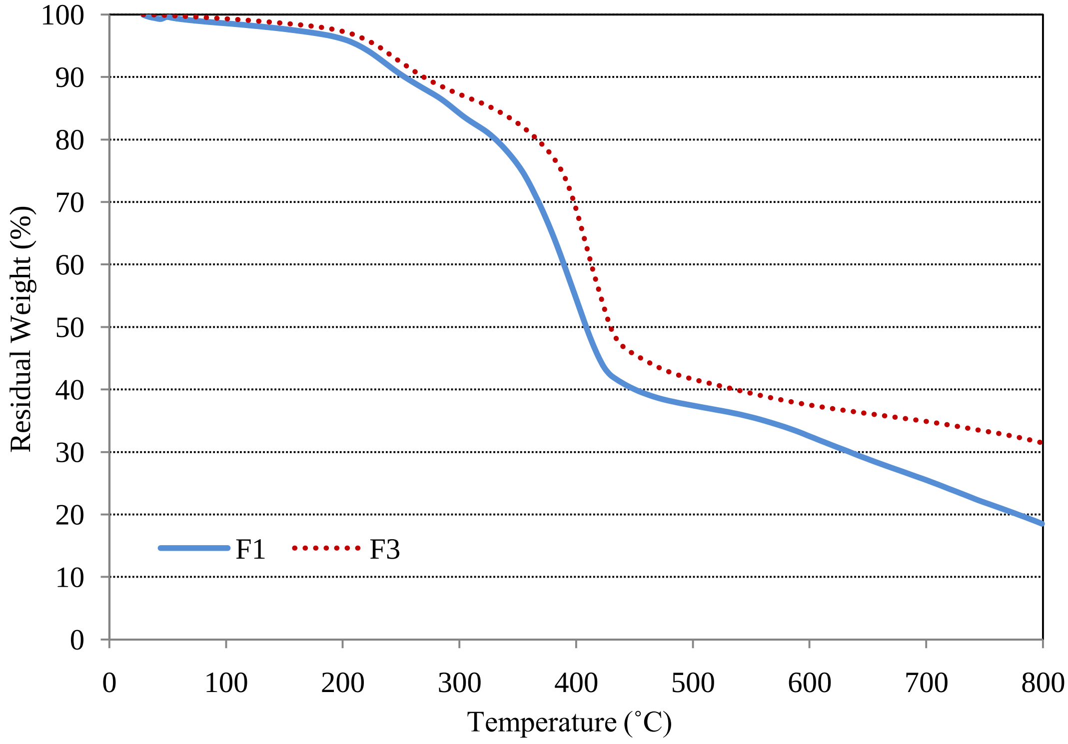


Figure 4. 14: Comparison of TGA curves between F1 (without vermiculite) and F3 (with vermiculite)

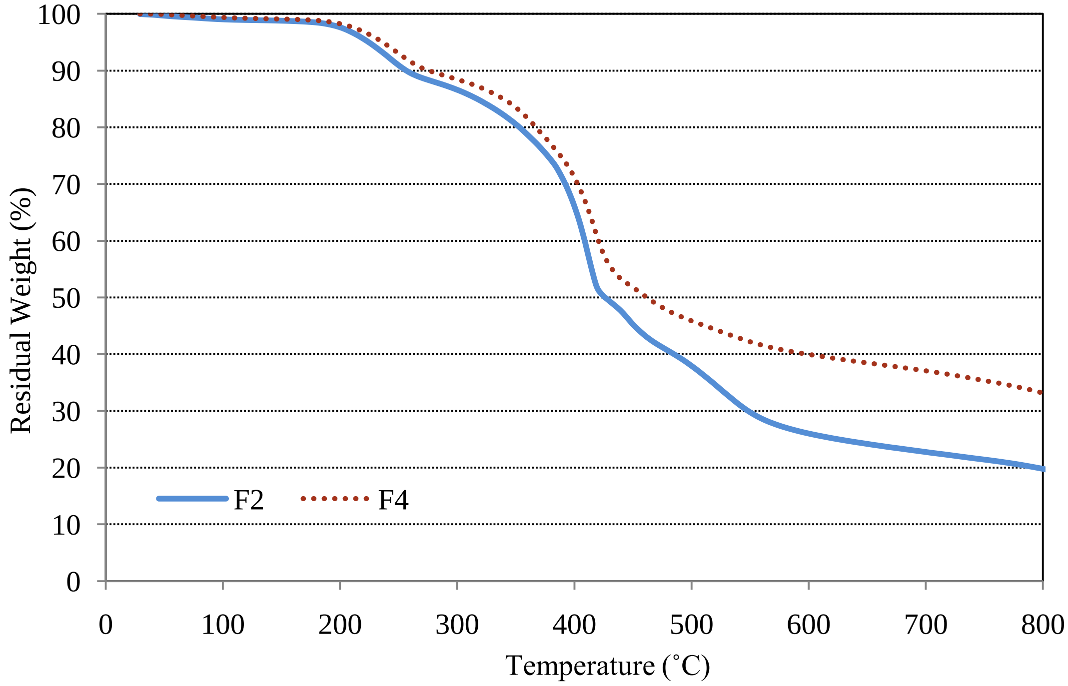


Figure 4. 15: Comparison of TGA curves between F2 (without vermiculite) and F4 (with vermiculite)

However, it is slightly differ in the degradation mechanism in F4 (Figure 4.15) where at the beginning of the decomposition process is similar but then at 400^{o}C and above, F4 which is added with vermiculite gives significant increase in high temperature residue at 800^{o}C from only 20% of F2 to 33%. It is shown that the significant effect of vermiculite addition, which indicates in the formation of high thermal stability residue in this water-based FRC is obvious. The increase in residue means the increase in the thermal stability of the material since vermiculite was added. The formation of thermally stable material at high temperature is an important parameter for fire retardant coating. In fact, the char formation is favorable to form a protective barrier and efficiently protect the substrate. These were supported by some studies on the fire retardant coating [4], [20] on the correlation of charring processes with flammability. According to Joseph and Ebdon, (2001), [31] the higher the amount of residual char, the less combustible the material and more efficient in heat resistance.

In order to further analyze the effect of vermiculite addition in enhancing the high thermally stable residue of FRC, the theoretical curve was calculated. The theoretical curve is the combination of individual additives which represents the degradation of the mixture without interaction amongst them occurred [62]. The theoretical curve was calculated as [13]:

$$M_{th(wt)}(T) = \sum_{i=1}^{n} \alpha_i M_{i(wt)}(T) \quad (4.1)$$

where α_i was the weight ratio of M_i, $M_{i(wt)}(T)$ was the weight of each component such as APP, PER, MEL, acrylic and vermiculite at certain instantaneous temperature. Then the summation of those is the theoretical curve of that whole component which represent by $M_{th(wt)}(T)$.

The theoretical weight % loss curves $M_{th}(T)$ were calculated according to Eq. 4.2 which is based on the ratio of each material in that formulation. This is to assess the synergetic effect of vermiculite addition by comparing the theoretical curve with experimental TG curve of formulations F3 and F4.

$$M_{th(wt)}(T) = 0.64M_{Acrylic}(T) + 0.32M_{APP/PER/MEL}(T) + 0.04M_{Vermiculite}(T) \quad (4.2)$$

Figure 4.16 and Figure 4.17 illustrates the synergetic effect of the vermiculite in F3 and F4. From Figure 4.16, the thermally stable residue for experimental curve is 10% higher than theoretical curve at temperature 800^{o}C. This clearly indicates there are synergetic reactions take place to enhance the char content within the FRC material with the presence of vermiculite.

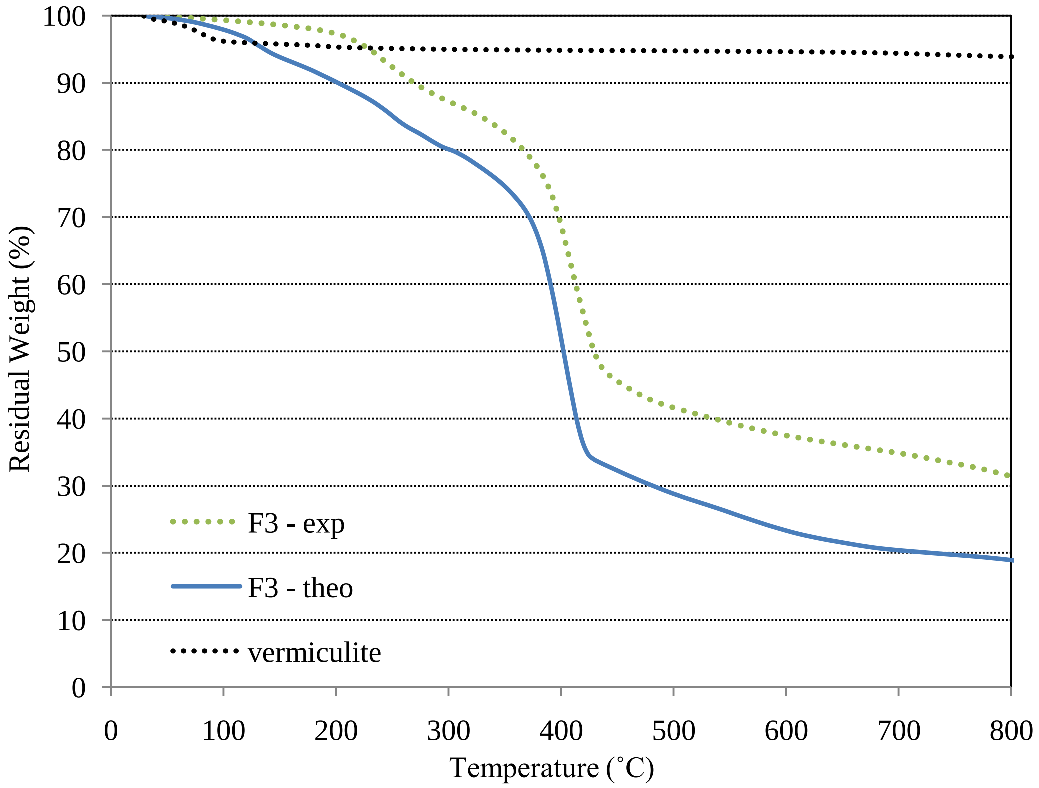


Figure 4. 16: Experimental and theoretical TGA curves of F3 and TG curve for vermiculite.

In Figure 4.17, there is also a shift to the higher degradation temperatures and increase of thermally stable residue where the different is about 24% of residual weight between these two curves. From these results, it is clearly shown that the pronounced synergetic effects amongst the additives are really there.

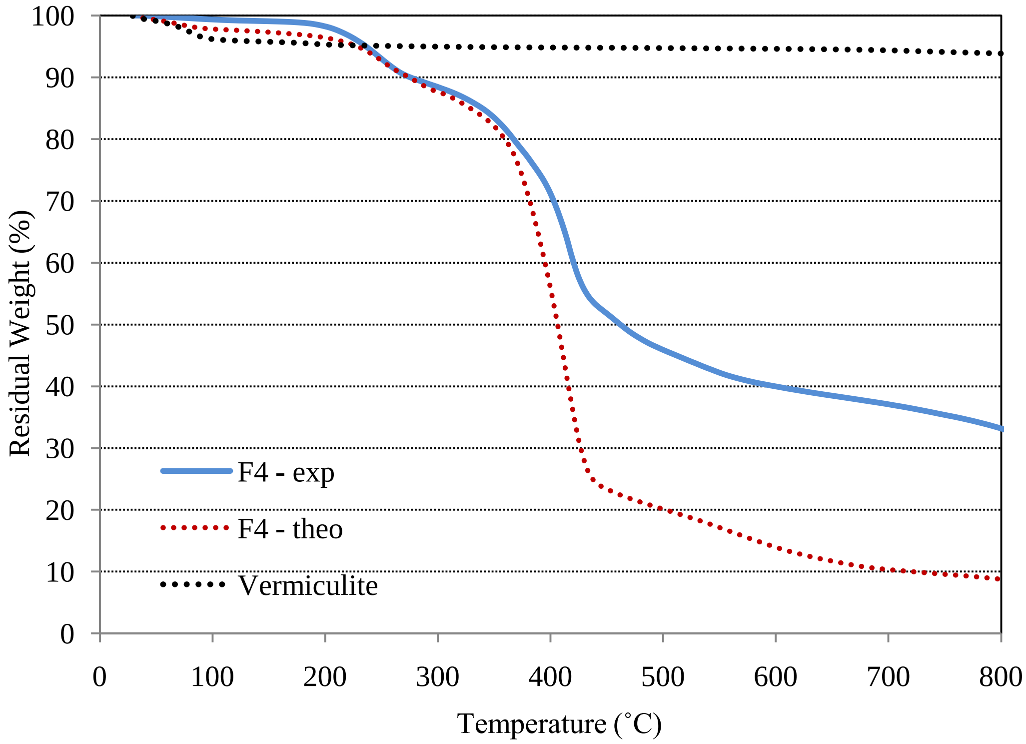


Figure 4. 17: Experimental and theoretical TGA curves of F4 and TG curve for vermiculite.

Thus, vermiculite addition significantly enhanced the formation of high temperature residue. This was supported from the previous study about the important compositions that act as an additional insulating layer and a barrier to heat and degradation of mass which are silicon dioxide, SiO_2 [66], [67] and aluminum oxide, Al_2O_3 [62]. Moreover, according to Chen *et al.*, 2008 [34], it was mentioned that, silicon dioxide produced from the reaction in the coating during fire is chemically stable at high temperature, thus it will enhance the integrity of the char. Besides that, the formation of silica layer protecting the coating materials to further decompose at high temperatures.

In addition, the iron element in the vermiculite and also in acrylic can slow down the exothermic chain reaction (*i.e* the process of oxidation of char layer to gases carbon dioxide) which stabilizes the residue at temperature higher than 630^{o}C [20], [68]. Thus, the formation of multi-layered carbonaceous alumino silicate [62] of the vermiculite platelets and the presence of iron in vermiculite and acrylic were helping in the stabilization of the material at high temperatures. Moreover, at high temperatures, silica-carbon compound also helped in forming protective silica layer and protect the residue from further thermal decomposition [34]. Therefore, these three elements are the major contributors in the extent of synergetic effect amongst the additives since the content of these compositions is high in vermiculite. It is then clear that vermiculite is expanding when heated at high temperature, consequently enhance the thermally stable char of FRC.

Figure 4.18 presents the comparison of the thermal degradation behavior of the two acrylic mediums when combine with the whole components.

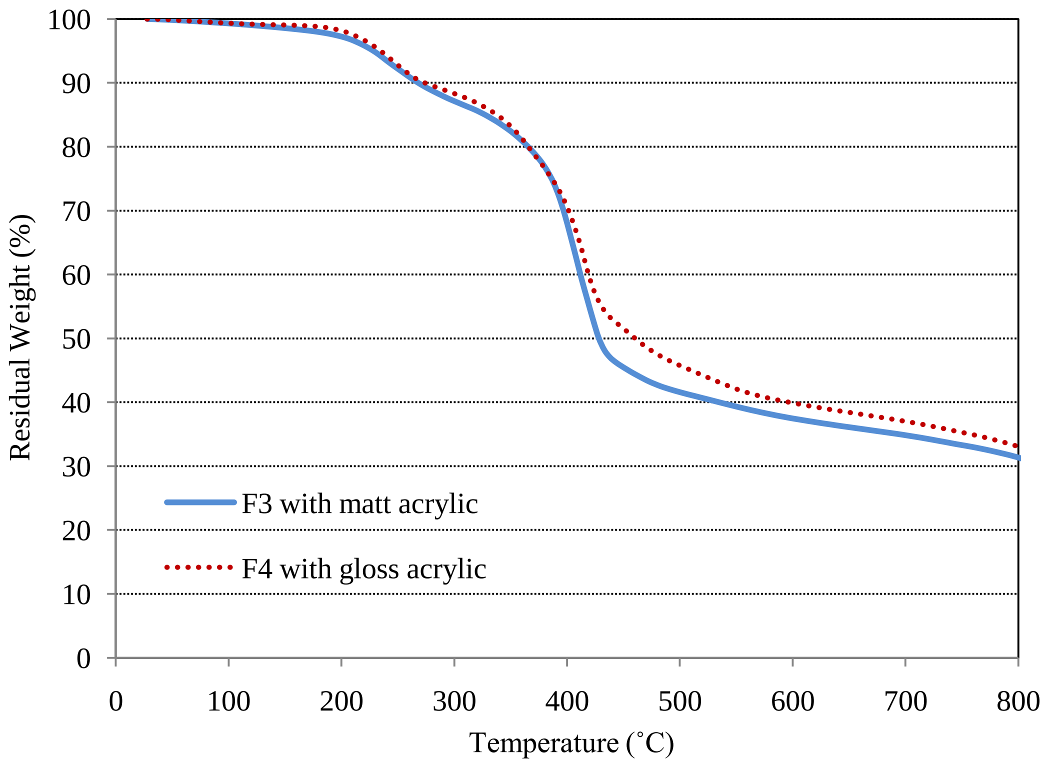


Figure 4. 18: TGA curves of F3 (with matt acrylic) and F4 (with gloss acrylic).

From the figure, it can be seen that the thermal degradation was slightly different for both acrylics where at 800^{o}C the residue for F3 was 34% while F4 was 33%. This was proven earlier (in Figure 4.9) when the thermal decomposition of acrylic medium is in the same temperature range with combination of APP, PER and MEL. Thus, from this degradation profiles, we can say that the interactions of matt and gloss acrylic with the other components were practically the same.

4.4.4 Scanning Electron Microscopy (SEM)

The SEM micrographs of the surface for the new formulation with and without vermiculite are shown in Figure 4.19 and 4.20, respectively. These figures are used to compare the surface morphology before fire test without vermiculite and also with vermiculite. The morphology of the formulations with vermiculite which are F3 and F4 shows relatively rough surfaces compared to that without vermiculite. Figure 4.19 (b) and Figure 4.20 (b) show the multi layers of the structure compared to formulation without vermiculite.

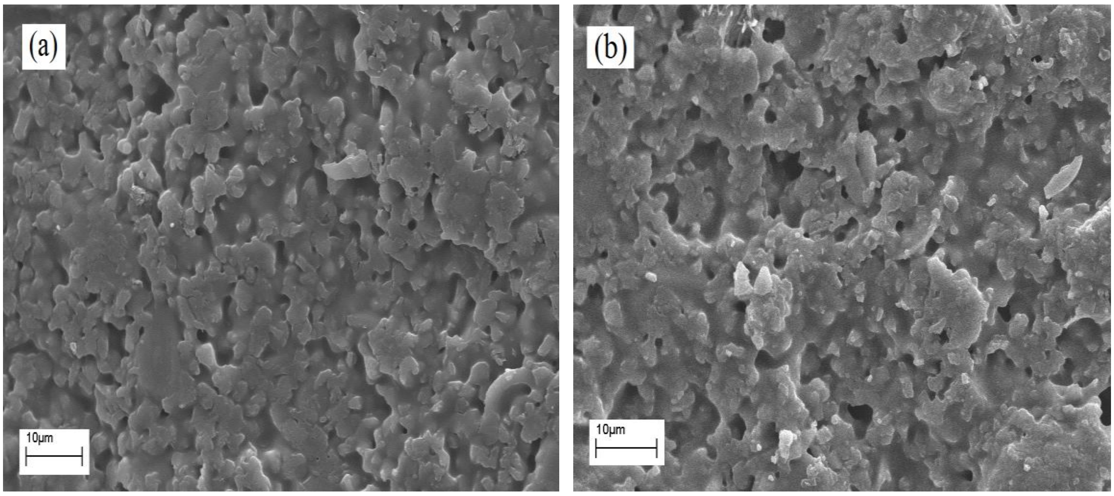


Figure 4. 19: SEM micrographs of the outer surface of a) F1 (without vermiculite) and b) F3 (with vermiculite)

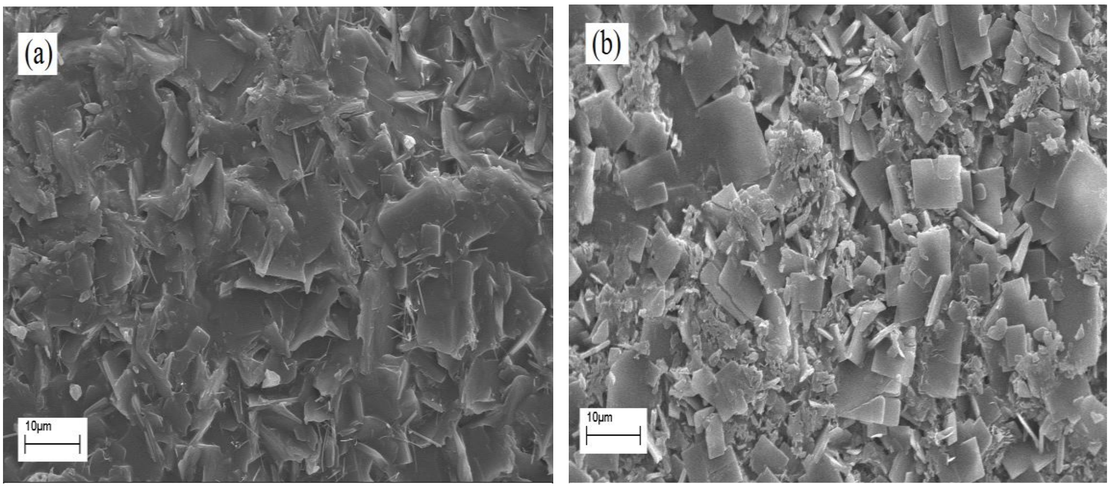


Figure 4. 20: SEM micrographs of the outer layer of a) F2 (without vermiculite) and b) F4 (with vermiculite)

The samples with vermiculite addition are 1) high strengthening effect which is inorganic reinforcement in the formulation; and 2) give better shielding effect when exposed to heat.

The SEM images of the sample after burning are shown in Figure 4.21 and Figure 4.22. The inner surfaces of char in Figure 4.21 (a) of F1 shows a thin surfaces with large holes for about 20 – 80 µm in diameter in the char structure. The existence of holes with diameter of 5-20 µm [30] is favorable as the heat transference from the flame to substrate through air inside the hole which is low. However, in Figure 4.21 (a) – F1, the diameter is larger than 30 µm that resulting in increases of speed of heat transference by air convection thus accelerate the degradation of binder and flame retardant materials [13], [29].

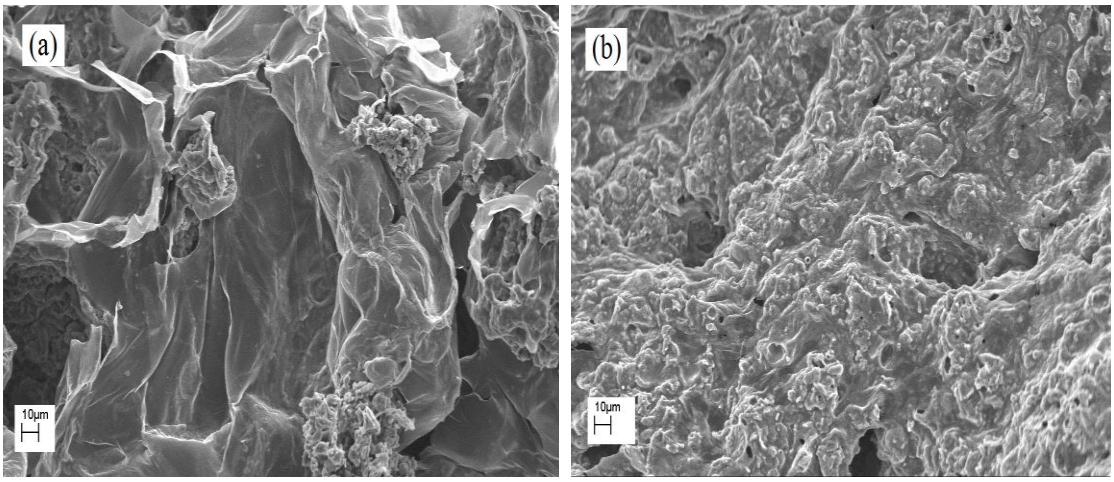


Figure 4. 21: SEM images of inner char surface of formulation (a) without vermiculite, F1 and (b) with vermiculite F3

The small holes are observed in Figure 4.21 (b) – F3 with diameter of 5-20 µm, which contain air that slow down the heat transference from the flame to substrate. This may be explained by the fact that, the presence of vermiculite enhance the formation of good char structure and resist to high temperature.

In Figure 4.22 (a) – F2, large holes are observed. Meanwhile, the continuous and dense “honeycomb” structure which is uniformly dispersed small closed holes for about 5-20 µm in diameter is present in Figure 4.22 (b) – F4. However, these two phenomena are unfavorable since in Figure 4.22 (a) – F2 the size of the holes larger than 20 µm while in Figure 4.22 (b) – F4, presence of totally large volume of small holes [13] in the inner surface of the char is also unfavorable. These phenomena can cause the increase of air convection, thus increase the speed of heat transference.

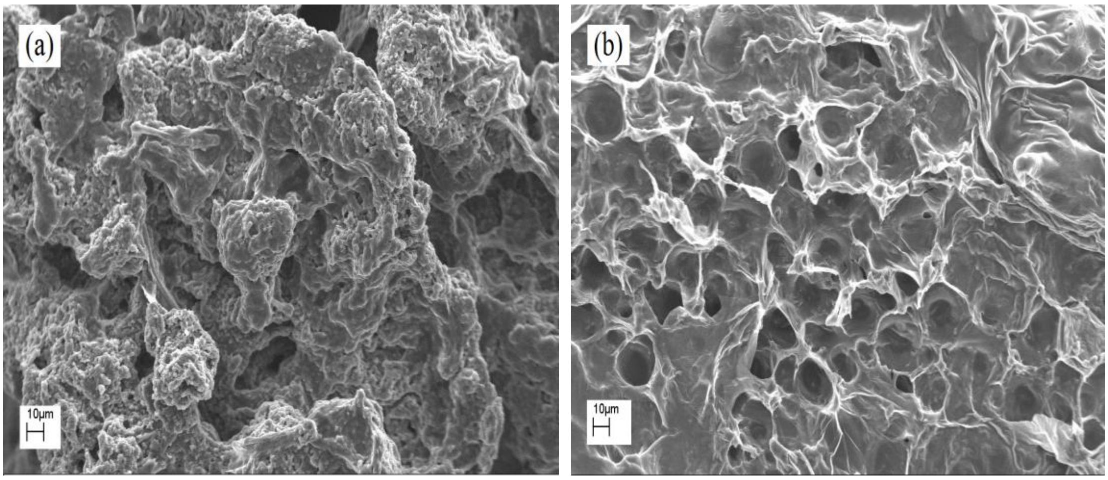


Figure 4. 22: SEM images of inner char structure of formulation with vermiculite (a) without vermiculite, F2 and (b) with vermiculite, F4

These SEM images further prove that the formulation with matt acrylic and addition of vermiculite (Figure 4.21 (b) – F3) give better char structures, thus improved heat insulation compared to formulation with gloss acrylic and without vermiculite.

4.5 Fire Protection Test

Figures 4.23 to Figure 4.26 show the physical appearance of the coating during the testing.

Figure 4. 23: After fire started, F1 starts to swell.

Figure 4. 24: After 5 – 10 minutes, it swelled bigger.

Figure 4. 25: From the top view of the char

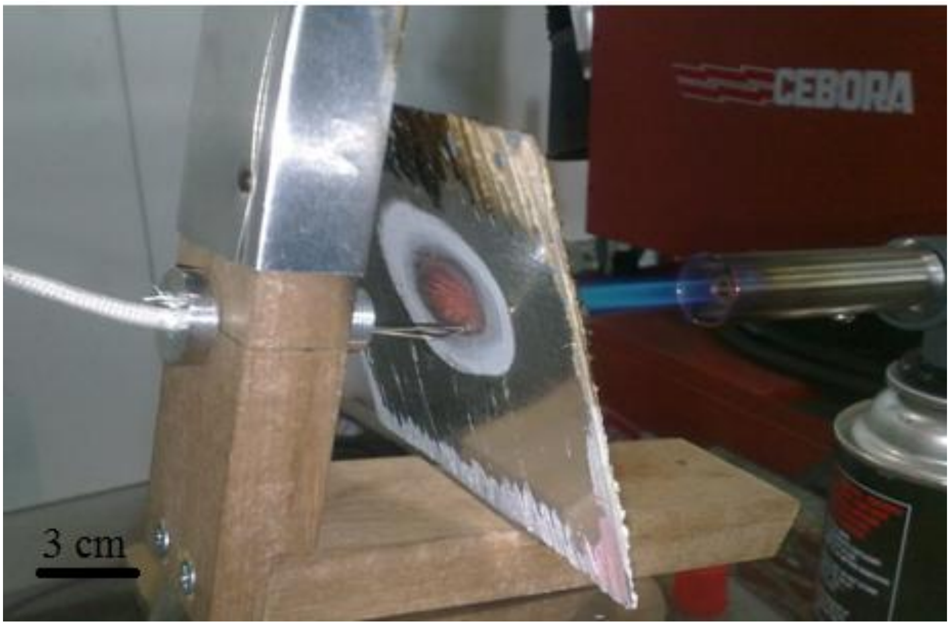


Figure 4. 26: The position of the thermocouple at the back of the substrate.

The curves of fire protection test are illustrated in Figure 4.27 and Figure 4.28. In these figures, F1 and F2 were the formulation without vermiculite while F3 and F4 with vermiculite. The back temperature of the galvanized steel at 100 minutes for Figure 4.27 are 400^{o}C for F1 while 200^{o}C for F3. The reduction in temperature which is the difference for formulation without vermiculite, F1 and with vermiculite, F3 was around 200^{o}C.

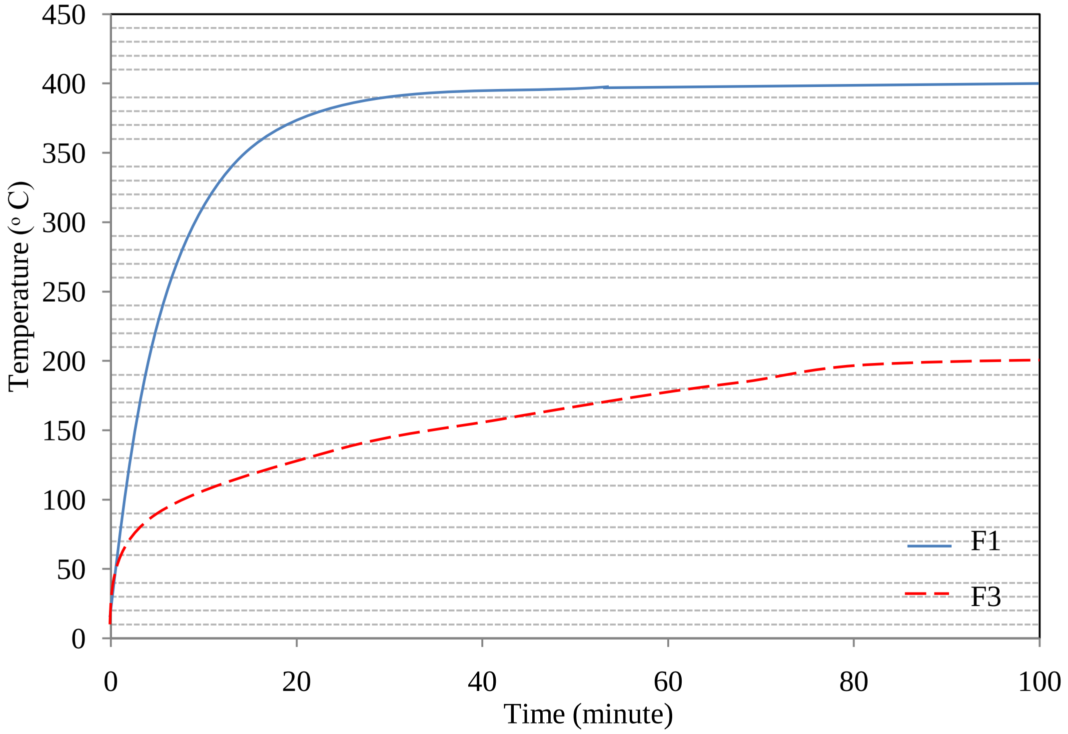


Figure 4. 27: Temperature-time curve for formulation with matt acrylic F1 (without vermiculite) and F3 (with vermiculite)

For Figure 4.28, the back temperature for F2 is 450°C, while F4 is 250°C. When comparing the formulations with vermiculite which is F3 and F4, the temperature curve of F3 is lower than F4. At 100 minutes, the temperature at the back of the galvanized steel of sample F3 was 200°C while for F4 was 250°C. This indicates that the difference constituents within the acrylic media plays important role in the fire retardant coating during a fire. Good heat insulation by F3 due to the main element in the acrylic which is silica that enhances the Si–O–Si network in the fire retardant material and vermiculite. According to Wang *et al.*, 2006b [37] and Chen *et al.*, 2008 [34], the Si–O–Si can protect the insulating material at high temperatures, give mechanical reinforcement and improves anti-oxidation in protective materials. Besides that, Chen *et al.*, 2008 [34] also mentioned Si-O-Si network forms a stable char residue which protects the underlying substrate at later stages of fire.

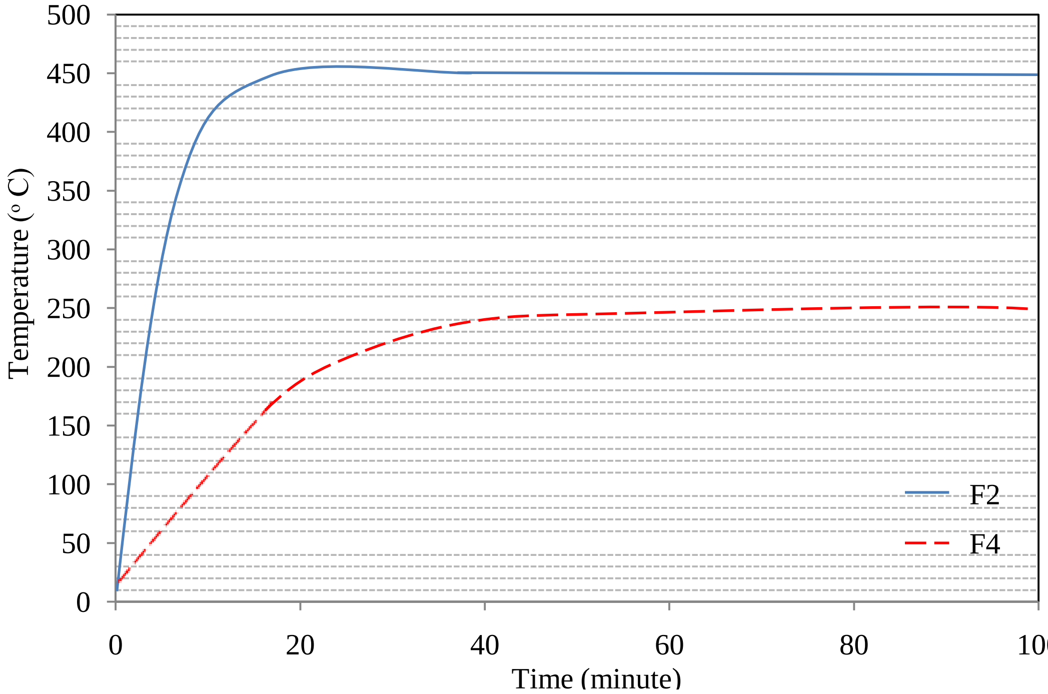


Figure 4. 28: Temperature-time curve for formulation with matt acrylic F2 (without vermiculite) and F4 (with vermiculite)

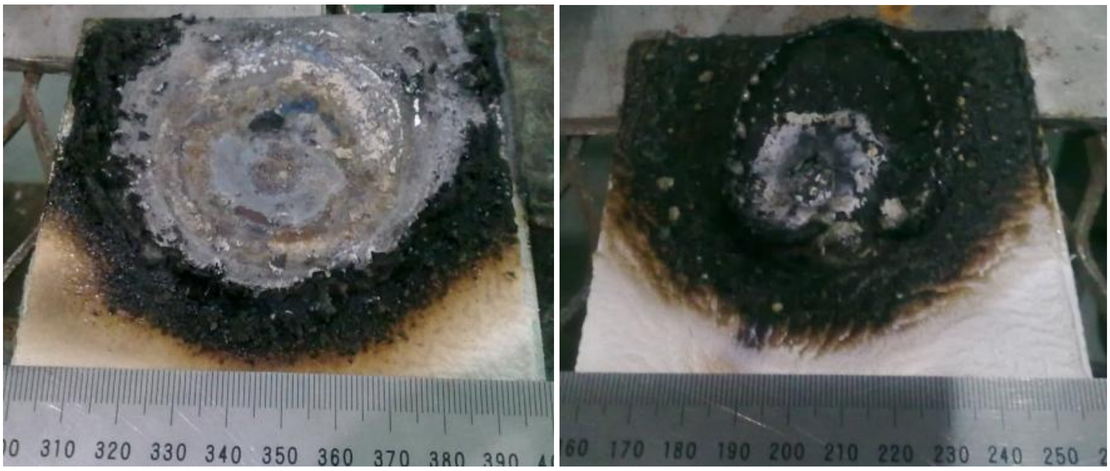
The results from the fire protection test were further proved by the TG analysis results where the formulation with the presence of vermiculite improves good heat insulation of the coating. As explained before the important compositions in vermiculite which are silicon dioxide, SiO_2 and aluminum oxide, Al_2O_3 which enhance the ingredients in the acrylic binder in forming a better insulation of the heat.

As comparison, for the formulation with vermiculite but different binder which are between F3 (matt acrylic) and F4 (gloss acrylic), F3 gives better thermal insulation. This is because the compositions of silicon was high (refer Table 4.5) which improved the Si-O-Si network. The composition can also protect the insulating materials at high temperatures and provide a mechanical reinforcement of the protective materials.

These were supported by the appearance of the char at the point of the flame in Figure 4.29 (b) – F3 and 4.30 (b) – F4 compared to the formulation without vermiculite in Figure 4.29 (a) – F1 and 4.30 (b) – F2. There were no char left at the point of the flame for Figure 4.29 (a) – F1 and 4.30 (c) – F2, due to the elements in acrylic and APP-PER-Mel only were not sufficient to sustain and stabilize the coating at high temperature.

(a) (b)

Figure 4. 29: The appearance of the char after fire test for formulation (a) without vermiculite, F1 and (b) with vermiculite, F3.



(a) (b)

Figure 4. 30: The appearance of the char after fire test for (a) without vermiculite, F2 and (b) with vermiculite, F4.

The thickness data of the swelling char is shown in Table 4.8. The thicknesses were taken at the point of the flame for maximum and minimum area.

Table 4. 7: The thickness of the char at the point of the flame after 100 minutes

Formulation	**The thickness of the coating before fire test (mm)** **±0.1 mm**	**The maximum thickness of the char (mm)**	**The minimum thickness of the char at the point of the flame (mm)**
F1	1	0 (vaporized)	0 (vaporized)
F2	1	0 (vaporized)	0 (vaporized)
F3	1	10.8	3
F4	1	11.1	3

From the results shown, the formulations with vermiculite (F3 and F4) expands about ten times and can sustain the high temperature until end of the fire protection test with the presence of the char compared to those formulation without vermiculite (F1 and F2) where the char was vaporized.

4.6 Shear test of FRC

Shear test was performed in this research work as the quantitative measurement on adhesion bonding between coating and galvanized steel substrate. The adhesion of the coating was calculated by the universal testing machine simultaneously during the execution of the experiment. The coating for this sample was applied onto the galvanized steel substrate without used any primer. Thus, the testing aimed to determine the strength of the coating to the galvanized steel substrate itself. The result of the shear test is shown in Figure 4.31 below:

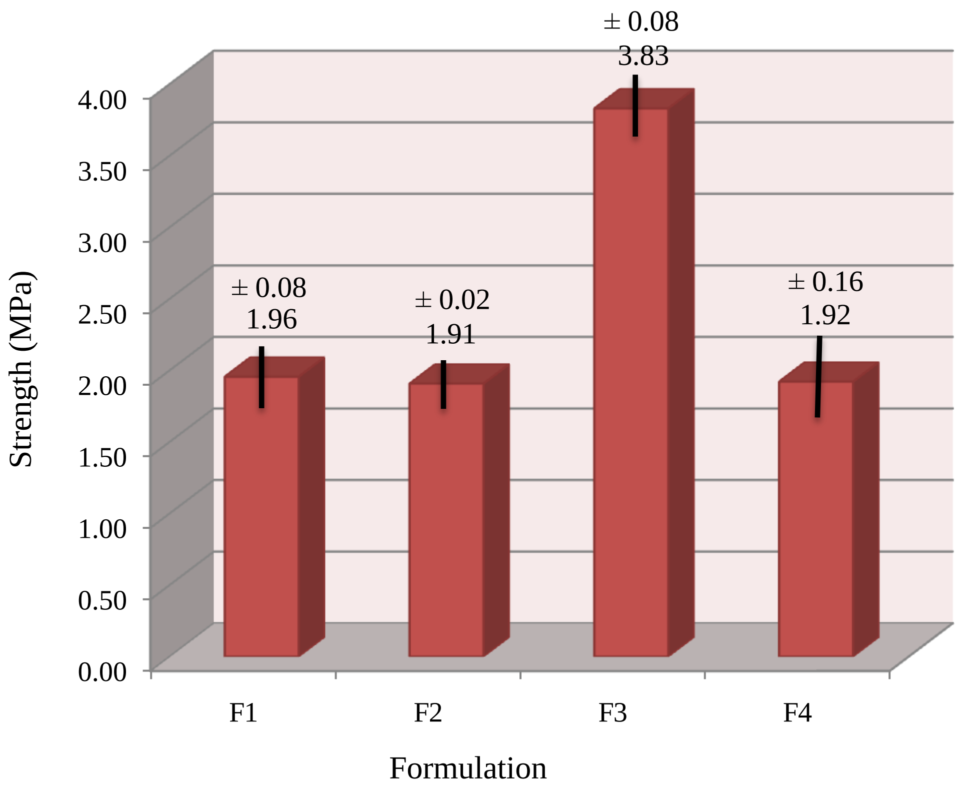


Figure 4. 31: The strength of each formulation from the shear test.

The tabulated data of the strength for the adhesion bonding is shown in Table 4.9 below:

Table 4. 8: The strength of the adhesion bonding of the coating

Formulation	Strength (MPa)
F1	1.96
F2	1.91
F3	3.83
F4	1.92

The failure modes in these four formulations were cohesive and interfacial. For F1 and F3, the interfacial failures were observed while in F2 and F4 both were occurred. Form the observation, the cohesive failures occurred for F2 and F4 because the textures of the formulations contained bubbles so that the adhesion within the coating was weakened. For F1 and F3, it showed that the cohesive bonding within the coating was strong compared than the adhesion bonding between substrate and coating. The Figure 4.33 below shows the interfacial failure of F4.

Figure 4. 32: The interfacial failure of F4

The expected results were F3 and F4 will be giving high adhesion bonding compared with other formulation without vermiculite. However, the result show F3 (matt acrylic and vermiculite) had the highest adhesion bonding of coating to the substrate as shown in the Table 4.9.

This is because the interaction of the vermiculite with matt acrylic which contains Al and Si elements as shown in the Table 4.5 that gives the strong adhesion between the interface layer of the coating and the substrate. This is supported by the previous researcher, Zhai *et al.*, 2007 [55] reported that with 0.2% of Al_2O_3 gave the highest strength of adhesion bonding among the other formulations.

From these result, it can be concluded that, Al and Si elements in matt acrylic does increase the adhesion strength about two times from the other formulations.

4.7 Chapter Summary

Findings of the research work were presented in this chapter. The chapter begins with preliminary results of compatibility test among the materials and the elements of the acrylic media and vermiculite were addressed.

The effect of vermiculite addition and acrylic media were presented and possible reasons for the findings were addressed. The effect of vermiculite was observed through thermogravimetry analysis, fire protection test, scanning electron microscopy and shear test. It was observed that with addition of vermiculite in the formulation gave good results in those testing. Besides that, the formulation with matt acrylic and presence of the vermiculite was the best formulation in this research work compared to others.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 Chapter Overview

This chapter explained on the findings that obtained from the overall research study and concluded the best formulation achieved. Besides that, the objectives of the research as outlined in chapter 1 are reviewed and the improvement for the future and better research work is also addressed.

5.2 Conclusion

In this research work, the fire retardant coating was formulated with an acrylic water-based binder and a natural mineral which is vermiculite. The acrylic resin is said to be a binder and also a carbonization agent in the fire retardant coating. Besides that, acrylic resin also improved the char layer when the degradation temperature is in the same range of the thermal degradation for APP-PER-Melamine. For vermiculite, it is a good additive to this water-based fire retardant coating as it gives the higher thermal residue weight in the TG curve. High thermal residue is indicator of a good material stability at elevated temperature. This was obtained in the TG curve and fire protection test by getting the low temperature at the back of the galvanized steel substrate for the formulation with vermiculite addition (F3 and F4) compared to the formulation without vermiculite (F1 and F2). Subsequently, the physical appearances of the char after the fire protection test were observed. The last testing was on adhesion bonding between the coating and galvanized steel substrate. Therefore, according to the analysis done and discussed, the following conclusions can be drawn:

1. The elements of the acrylic media were different to each other where the obvious element consist in matt acrylic were silicon and aluminium and none

in the gloss acrylic. The major compositions in vermiculite were, SiO_2, MgO, Fe_2O_3, Al_2O_3, and K_2O that were supported from the previous researcher that these were the major compound in the vermiculite. These compounds were played important role as proved in the TG analysis and fire protection test.

2. The thermal degradation curves were presented with the curve for all pure materials themselves and followed with the four formulations (F1-F4). From TG curves of matt and gloss acrylic were shown that the matt acrylic gave high thermal residue at high temperature compared to gloss acrylic. Then, comparison between formulation without vermiculite (F1 and F2) with formulation with vermiculite (F3 and F4) gave the significant increase of residue weight at 800^{o}C for F3 and F4. Besides that, to further proof the effect of vermiculite, the theoretical curves were calculated, to see the synergistic effect of vermiculite addition. The shifted to higher residue weight was obtained when compared the theoretical with experimental curve.

3. The fire protection test was performed on each formulation and the reduction temperature of 200^{o}C between F3 and F1 and F4 and F2. From the results of fire protection test, it clearly shown that the effect of vermiculite in enhanced the insulation of the heat from transfer to the galvanized steel substrate. Besides that, at the end of the fire protection test, the formulations with vermiculite (F3 and F4) still have the char residue at the point of the flame which indicates the compositions in vermiculite expand when exposed to heat and most important is it can sustain the high temperature.

4. The shear strength of F3 was the highest compared to other formulations by two times with 3.83 MPa due to presence of additional material of Si and Al in matt acrylic. Even though F4 is also with addition of vermiculite, the shear strength between the FRC and galvanized steel substrate is not strong enough compared to F3. This is because the compositions in gloss acrylic (which is in F4) not consist of Al and Si that can enhance those compositions in the vermiculite. However, the formulation F3 with matt acrylic and vermiculite have sufficient Al and Si content that help in stabilize the FRC at high temperature and also give better adhesion to the galvanized steel substrate.

As a conclusion, F3 is the best formulation with matt acrylic and presence of vermiculite. They gives high thermal residue at high temperature, the lowest temperature for the galvanized steel substrate in the fire protection test with 200^oC, good char structure and had shear strength of 3.83 MPa, two times higher than other formulations.

5.3 Recommendations

It is recommended to further improve the water-based acrylic fire retardant coating. For better fire retardant coating, other additives should be added to improve the fire resistance of the coating. Although the fire reduction from the coating is significantly reduced, further analysis on the use of other additives should be investigated. Subsequently, the strength of the char should be improved so that the structure of the char is strong, thus does not peel off from the substrate.

Thus, more additives that can enhance and helped in improving this water-based acrylic fire retardant coating should be explored. Besides that, the machine for testing the shear test also should be improved. The machine should have the offset forces in opposite direction to be applied onto the sample of shear test. Thus, more accurate result will be obtained.

5.4 Chapter Summary

At the beginning, the general idea of the research work was highlighted. Then, the reviews of all the important findings that met the objectives for the research were portrayed. Further improvement was also acknowledged for the better research work in this area including the proposed additives and shear testing.

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LIST OF PUBLICATIONS

1) W. A. W. Zaharuddin, B. Ariwahjoedi & P. Hussain,

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