3.0 MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter encompasses three sections which include the materials, sample preparation methods and the tests that were carried out using different instruments in this study. The first section describes the flame retardant materials that were used to prepare the intumecent fire protective coating samples. Commercial crystal phase II ammonium polyphosphate (APP II) (n>1000) derivative acts as an acid source, melamine (MEL) acts as a blowing agent, pentaerythrithol (PER) acts as a carbon source, water-borne epoxy resin (ER) and silica fume (SF) act as binder and chicken eggshell (CES) acts as a filler.

The second section describes the sample preparation which includes processing of the CES. The preparation of the different compositions of intumescent fire protective coating systems i.e. (1) APP II, MEL and PER (AMP), (2) AMP+SF, (3) AMP+SF+CES and (4) AMP+SF+CES+ER systems, are also explained in detail.

The last section describes the methods and characterization techniques that have been conducted to investigate the fire protection performance, sticking ability, surface morphology, bonding strength and thermal stability of each intumescent coating samples using different instruments which are summarized in Figure 3.1 below.

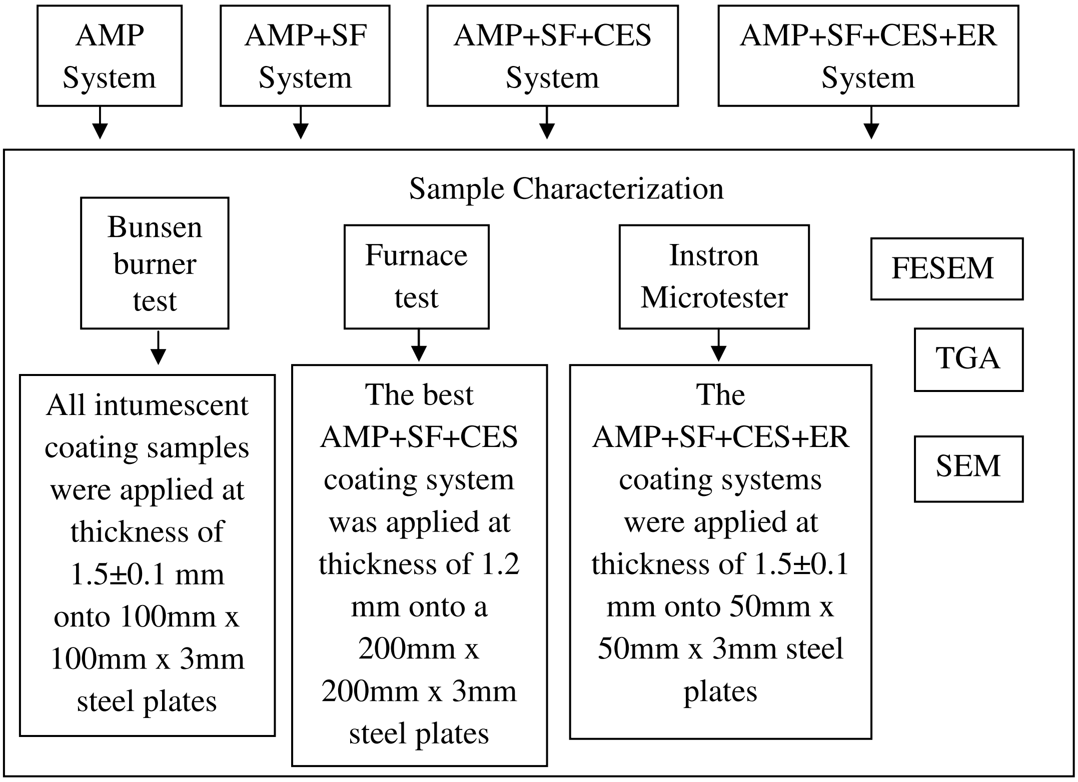


Figure 3.1 Flow chart of sample preparation and characterization of the four different intumescent coating systems

3.2 Materials

Three main halogen-free flame retardant additives were used in this experimental work for preparing the intumescent coating samples: (i) commercial crystal phase II ammonium polyphosphate (APP II), (ii) melamine (MEL) and (iii) pentaerythrithol (PER). In previous studies, many coatings containing halogen flame retardant additives have been developed and commercialized without taking into account the toxic effects on the environment when a fire occurs. These three halogen-free flame retardant additives have low smoke density and do not emit corrosive gases in a fire compared with halogen flame retardant additives. Moreover, the combination of AMP flame retardant additives leads to an effective intumescent flame retardant system in fire protection as mentioned in chapter two. Below is a brief description of the flame retardant additives. APP II was chosen as the best acid source for flame retardant additives after its properties were compared with that of APP I in terms of molecular weight, thermal stability and water solubility.

- Commercial crystal phase II ammonium polyphosphate (APP II) (n>1000) derivative acts as an acid source. APP II structure is cross linked as shown in Figure 3.2. The molecular weight of APP II is much higher than APP I with "n" value higher than 1000. APP II has a higher thermal stability where the decomposition starts at temperature more than 270°C and lower water solubility than APP I. The physical and chemical properties of APP II are presented in Table 3.1. The SEM image shows average particle size of APP II less than 15 μm as shown in Figure 3.3.

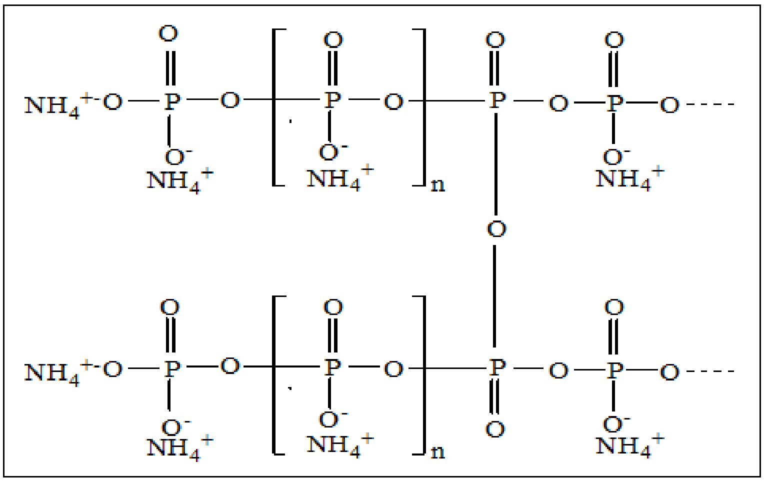


Figure 3.2 APP II structure

Table 3.1: Physical and chemical properties of ammonium polyphosphate phase II

Phosphorus %(w/w)	≥31
Nitrogen %(w/w)	≥14
PH value (10% suspension)	5.5-7.0
Water content %(w/w)	≤0.25
Thermal decomposition	°C ≥275
Density at 25°C kg/L	1.9
Apparent density kg/L	0.7
Viscosity(25°C in 10% suspension) mPa.s	≤100
Solubility in water (g/100cm^3) %(w/w)	≤0.5
Average particle size (μm)	≤15

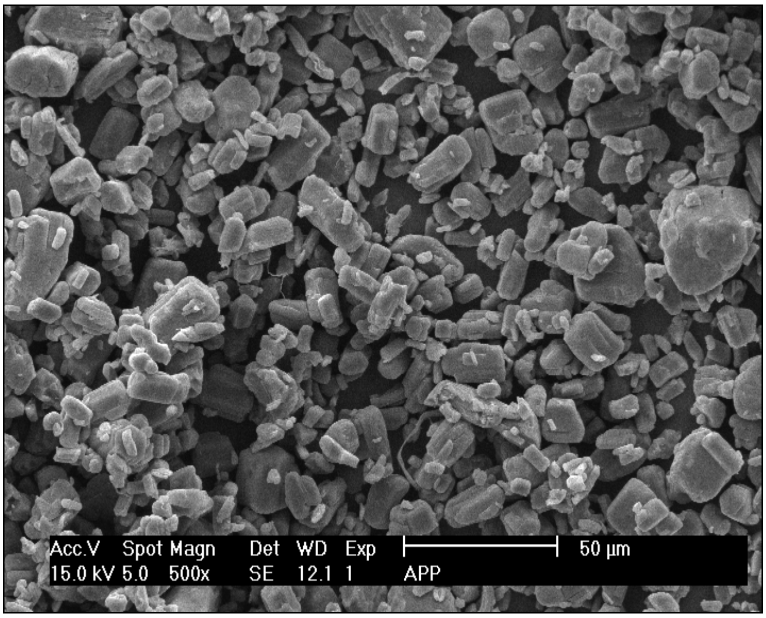


Figure 3.3 SEM image of ammonium polyphosphate phase II

- Melamine (MEL) acts as a blowing agent and its specification is presented in Table 3.2. The SEM image illustrates the particle size of MEL which is less than 40 µm as shown in Figure 3.4.

Table 3.2: Physical and chemical properties of melamine

Purity %	99.8min
Moisture %	0.1max
pH	7.5-9.5
Formaldehyde dissolve test	All dissolved in 10minutes
Ash	0.03max
Colority (platinum-cobalt color)	20max
Particle size (µm)	40max
Turbidity(Kaolin Turbidity)	20max

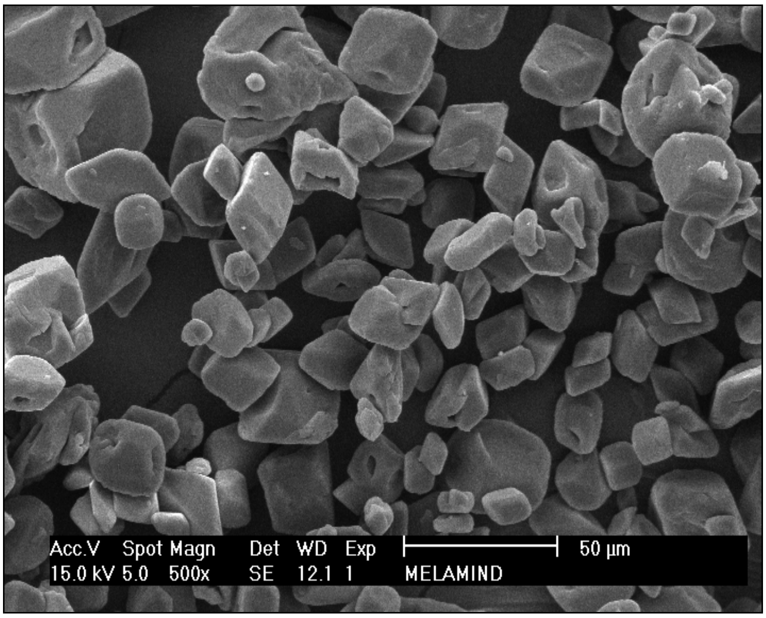


Figure 3.4 SEM image of melamine

- Pentaerythrithol (PER) acts as a carbon source and its specification is presented in Table 3.3. The SEM image illustrates the particle size of PER which is less than 40 µm as shown in Figure 3.5.

Table 3.3: Physical and chemical properties of pentaerythritol

Monopentaerythritol content %	98min
Hydroxyl group content %	48.5min
Water content %	0.2max
Ash content %	0.05max
Phthalic color	2max
Particle size (µm)	40max
Melting point °C	240min

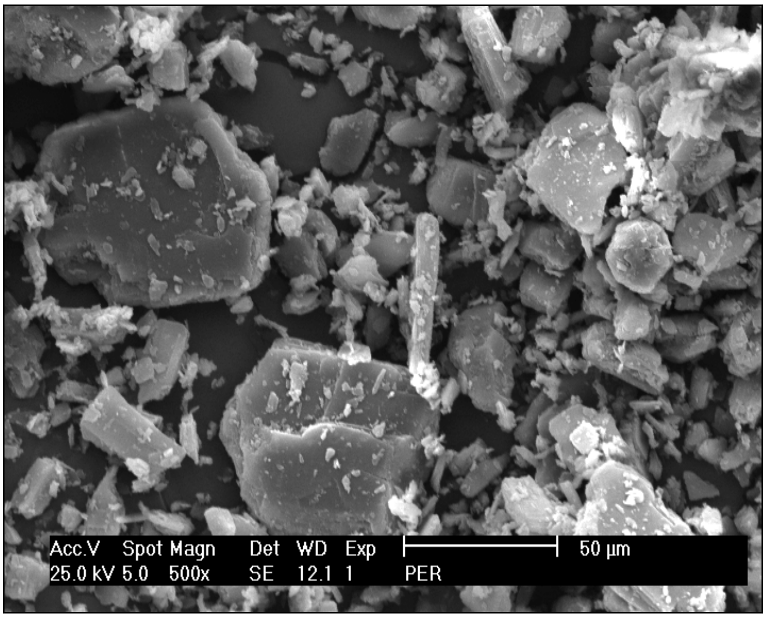


Figure 3.5 SEM image of pentaerythritol

In this study, the water-borne epoxy resin (ER) and silica fume (SF) were used as binder for preparing the water-borne intumescent fire protective coatings. A brief description of the properties of water-borne epoxy resin is shown in Table 3.4. The mixture uses a ratio by weight of 5:1 of resin to hardener for preparing the water-borne epoxy resin.

Table 3.4: Properties of water-borne epoxy resin

Mixing ratio by weight (epoxy: hardener)	100:20 (5:1)
Mix viscosity	1500 cPs@25°C
Pot life@25°C	About 2 hours
Shelf life	12 months
Touch dry	90 minutes
Fully cure	7 days
Specific gravity	1.5 g/cm^3
Coverage	0.3kg/m^2/150µm

The primary physical properties of SF are shown in Table 3.5. SF shows very good thermal stability in TGA test (Figure 3.6) and is more economical, besides having excellent dispersion and the ability to mix well in water (Figure 3.7 (a), (b), (c) and (d)).

Table 3.5: Physical properties of SF

Particle size (typical)	< 1 µm
Bulk density (densified)	600 kg/m^3
Specific gravity	2.2
Specific surface	20000 m^2/kg

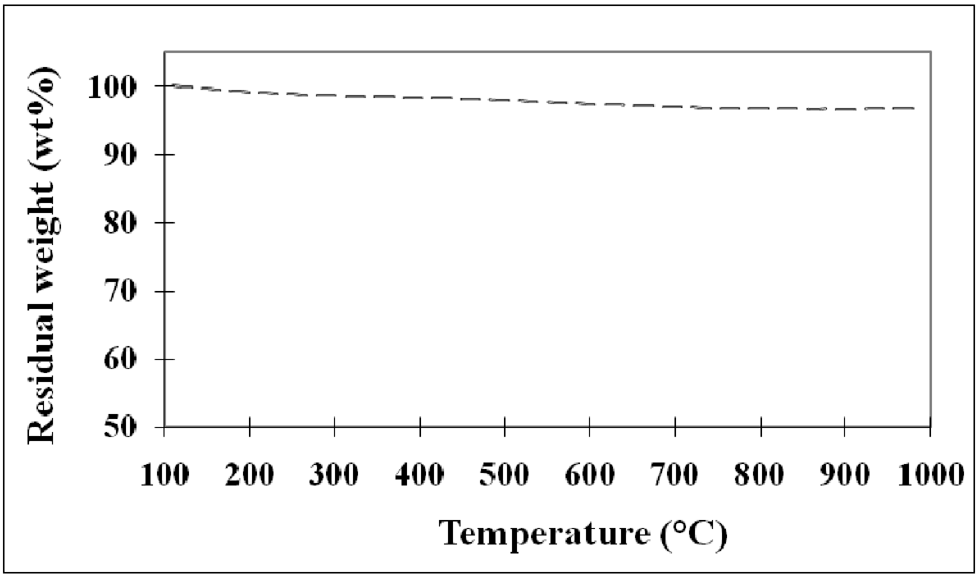
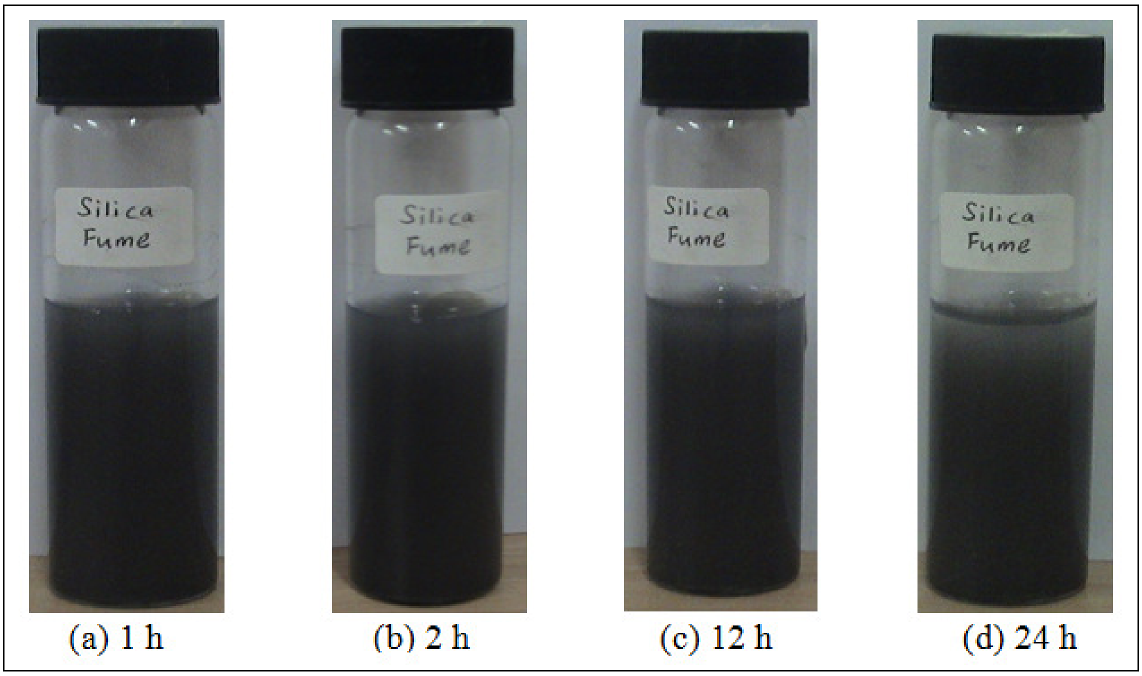


Figure 3.6 TGA curve of silica fume



(a) 1 h (b) 2 h (c) 12 h (d) 24 h

Figure 3.7 Dispersion of silica fume after (a) 1 hour, (b) 2 hours, (c) 12 hours and (d) 24 hours in water

Chicken eggshell (CES) was chosen as it shows better thermal degradation curve compared to commercial $CaCO_3$. The SEM image of CES before sieving is shown in Figure 3.8 where the particles of CES filler were in various, non-uniform sizes.

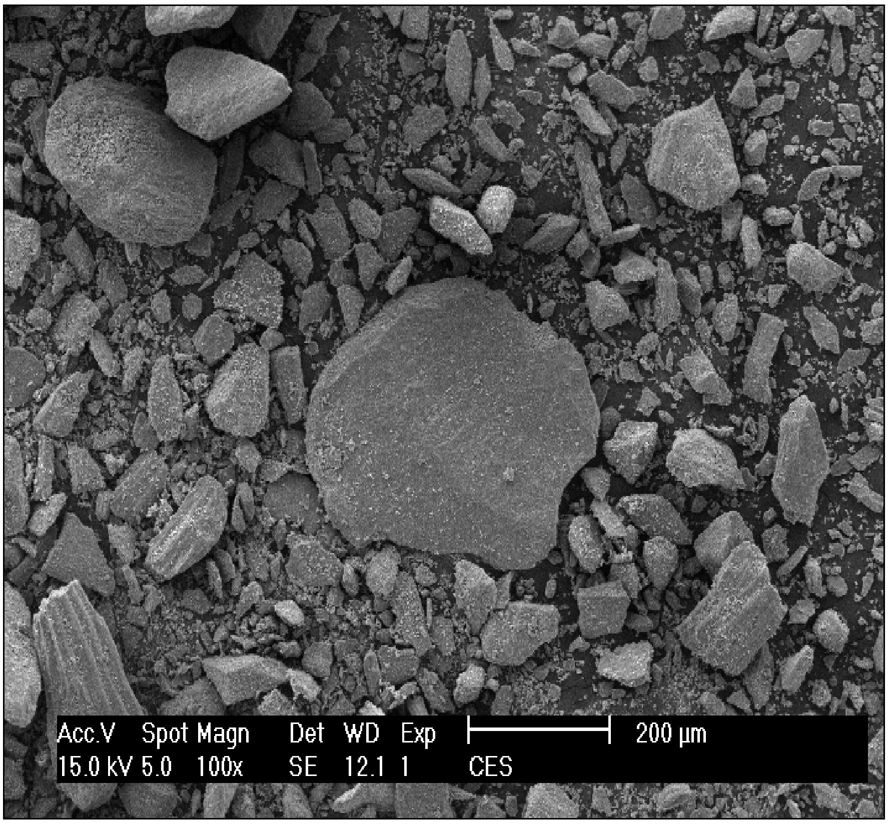


Figure 3.8 SEM image of chicken eggshell

3.3 Sample Preparation

The method and sample preparation for producing CES powder involves four stages. It includes cleaning, drying, grinding and sieving of eggshell powder.

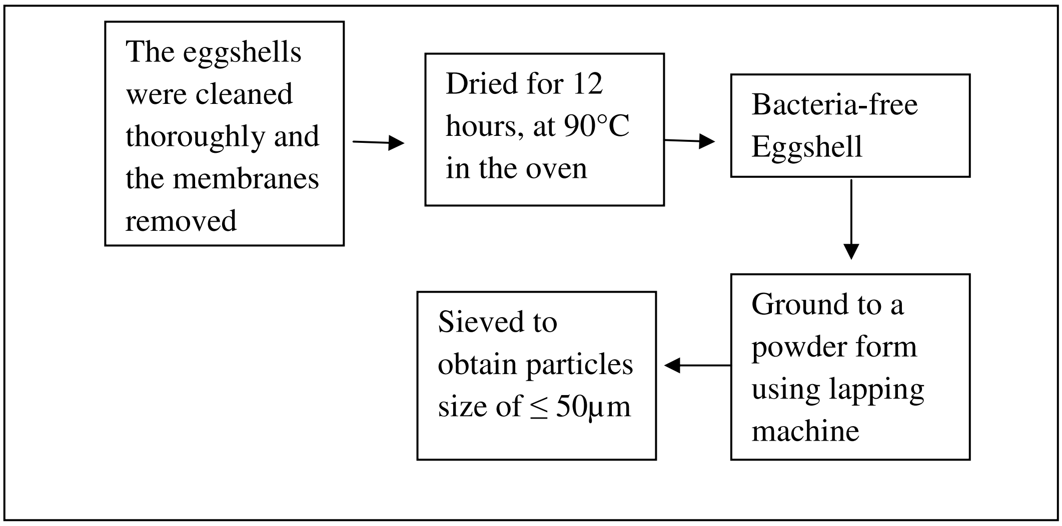


Figure 3.9 Flow chart of chicken eggshell powder preparation

The process is shown in Figure 3.9. Firstly, the eggshells were cleaned thoroughly with water and the membranes were removed from the eggshells. The eggshells were then dried for 12 hours, at 90°C in the oven to produce dry and bacteria-free eggshells (Toro et al., 2007). The dried eggshells were ground to a powder form by using a lapping machine. Finally the eggshell powder was sieved to obtain particles that are less than 50 µm in size.

The compositions of the AMP, AMP+SF, AMP+SF+CES and AMP+SF+CES+ER systems were prepared respectively for this study as shown in Table 3.6. Subsequently, the sections describe the detail compositions and preparation method of the samples.

Table 3.6: Composition and sample name of intumescent coating

Intumescent coating	**Sample name**	**Composition (wt.%)**
AMP system	A1	APP:MEL:PER (AMP) (60:20:20)
	A2	APP:MEL:PER (AMP) (50:25:25)
	A3	APP:MEL:PER (AMP) (45:30:25)
	A4	APP:MEL:PER (AMP) (40:30:30)
AMP+SF system	B1	A2:SF (95:5)
	B2	A2:SF (90:10)
	B3	A2:SF (85:15)
	B4	A2:SF (80:20)
AMP+SF+CES system	C1	B2:CES (90:15)
	C2	B2:CES (85:20)
	C3	B2:CES (80:25)
	C4	B2:CES (75:30)
AMP+SF+CES+ER system	D1	C3:ER (95: 5)
	D2	C3:ER (90:10)
	D3	C3:ER (85:15)
	D4	C3:ER (80:20)

3.3.1 AMP System

Four different ratios of the AMP system were prepared by solution blending method i.e. (1) 3:1:1 AMP (A1), (2) 2:1:1 AMP (A2), (3) 1.8:1.2:1 AMP (A3) and (4) 1.33:1:1 AMP (A4) as shown in Table 3.7.

Table 3.7: Constituents of the AMP samples

Designation	APP II (g)	MEL (g)	PER (g)	A:M:P (ratio)
A1	60	20	20	3:1:1
A2	50	25	25	2:1:1
A3	45	30	25	1.8:1.2:1
A4	40	30	30	1.33:1:1

The samples were mixed in beakers with 100 ml of distilled water using a high-speed disperse mixer (Figure 3.10) for 3-5 hours at room temperature until completely homogeneous. The total amount of the compounds is 100g. The mixture was then cast into Petri dishes and left to dry at room temperature until films were formed. The films were then dried at 60°C in the oven to produce completely dry films until required for TGA test. The AMP system sample with the highest thermal stability after TGA test was chosen and applied onto a steel plate (carbon steel, 100 mm x 100 mm x 3 mm) using a gun sprayer. This coating process was repeated 6 to 10 times until a 1.5±0.1 mm dry film thickness was attained. The steel plate coated with the AMP formulation was then dried for 3 days and tested using a Bunsen burner in order to investigate the fire protection performance of the coating. Subsequently, the best AMP coating formulation was applied onto a small piece of steel plate and left for 3 days at room temperature until completely dry. A gold film was then sprayed atop the dried coating to make the surface of the specimen electrically conductive before carrying out the SEM test. SEM (Hitachi XL 30) operated at 25kV at various levels of magnification was used to observe the morphologies of intumescent coating samples and the surface of the coating was characterized using SEM micrographs. The detailed flow diagram for the preparation process of the AMP system and characterization techniques are shown in Figure 3.11.

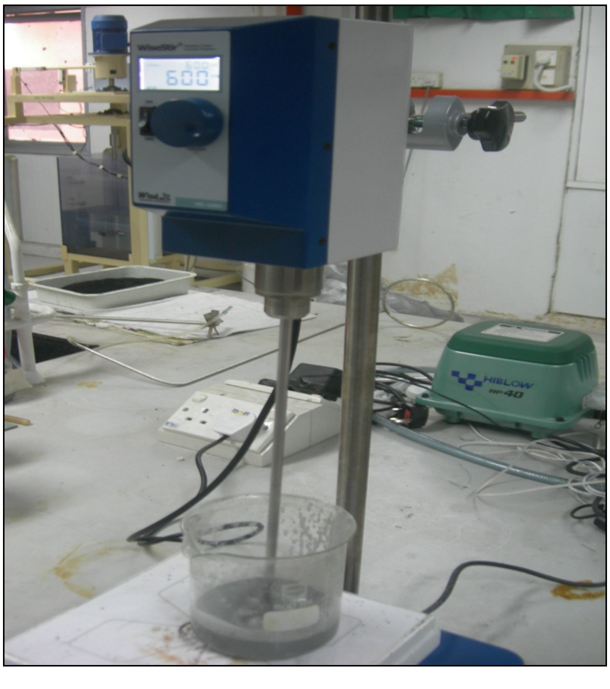


Figure 3.10 High speed disperse mixer

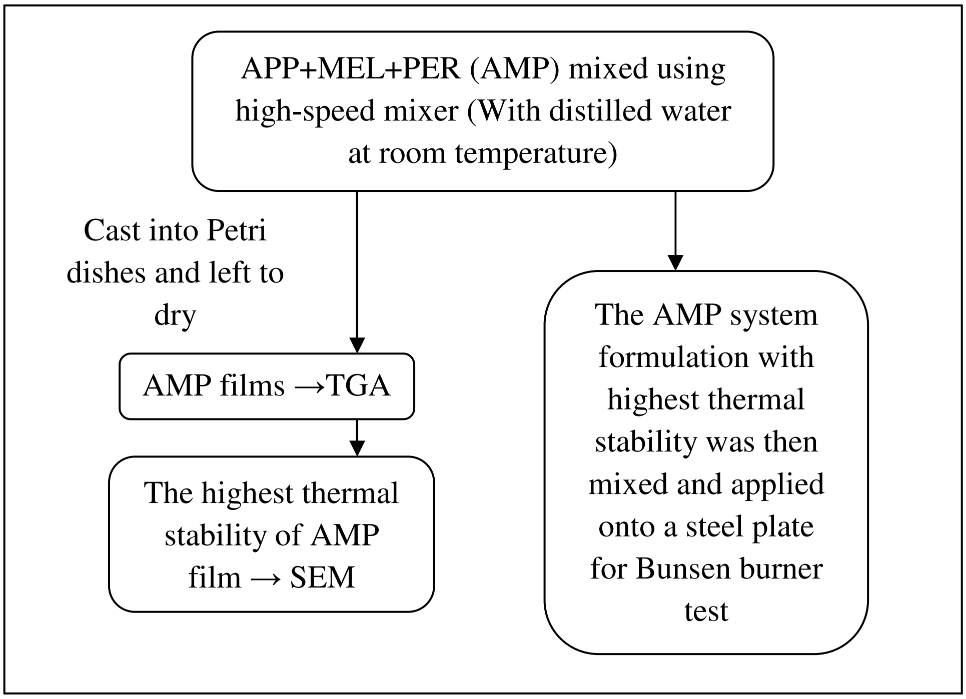


Figure 3.11 The flow diagram for the preparation process of AMP system

3.3.2 AMP+SF System

AMP formulation with the highest thermal stability i.e. sample A2 was added with 5, 10, 15 and 20 weight percent (wt.%) of SF, respectively as shown in Table 3.8.

Table 3.8: Constituents of the AMP+SF samples

Designation	A2 (g)	SF (wt.%)	SF (g)
B1	100	5	5.26
B2	100	10	11.11
B3	100	15	17.65
B4	100	20	25.00

The mixtures were then stirred using a high-speed disperse mixer for 3-5 hours at room temperature until completely homogeneous. Similar with the previous system, the four formulations were applied onto steel plates (carbon steel, 100 mm x 100 mm x 3 mm) using a gun sprayer until a 1.5±0.1 mm thick coating was obtained. The coated steel plates were then dried for 3 days at room temperature and tested using a Bunsen burner to investigate its fire protection performance. The AMP+SF formulation with the best fire protection performance and with good adhesion after the Bunsen burner test was then mixed and cast into a Petri dish and left to dry at room temperature until a film was formed. The film was then dried completely in the oven at 60°C for the TGA and SEM tests. The detailed flow diagram for the preparation process of AMP+SF system and characterization techniques is presented in Figure 3.12 as below.

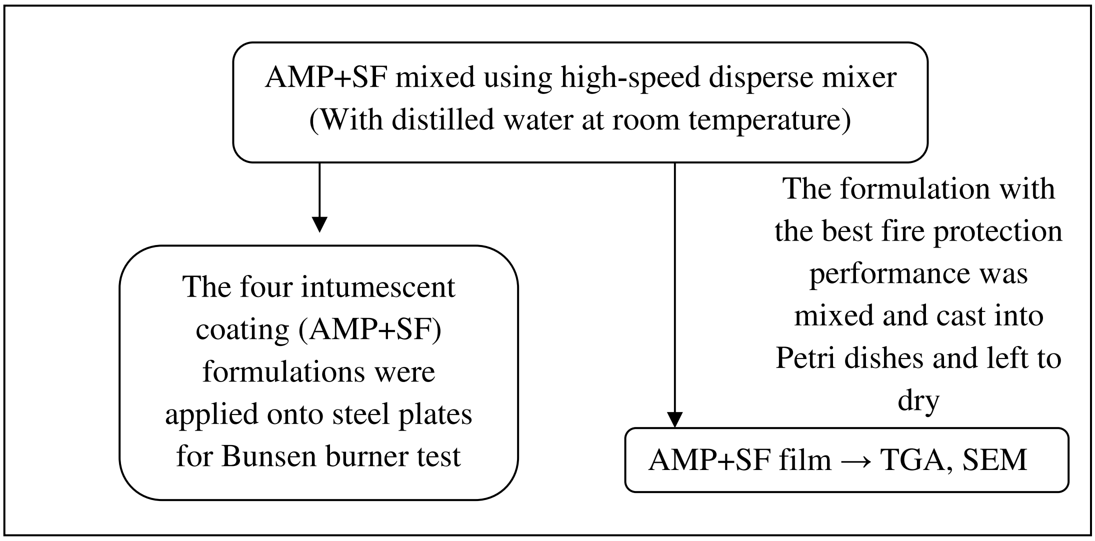


Figure 3.12 The flow diagram for the preparation process of AMP+SF system

3.3.3 AMP+SF+CES System

The AMP+SF formulation with the best fire protection performance obtained from the AMP+SF system i.e. sample B2 was added with 15, 20, 25 and 30 weight percent (wt.%) of CES, respectively as shown in Table 3.9.

Table 3.9: Constituents of the AMP+SF+CES samples

Designation	B2 (g)	CES (wt.%)	CES (g)
C1	111.11	15	19.61
C2	111.11	20	27.78
C3	111.11	25	37.04
C4	111.11	30	47.62

Figure 3.13 shows the preparation process of AMP+SF+CES system. The CES functions as a bio-filler. The steps used in the AMP+SF system were repeated for the

AMP+SF+CES system. After the Bunsen burner test, the formulation with the best fire protection performance was then applied onto a steel plate (carbon steel, 200 mm x 200 mm x 3 mm) using a gun sprayer for the furnace test.

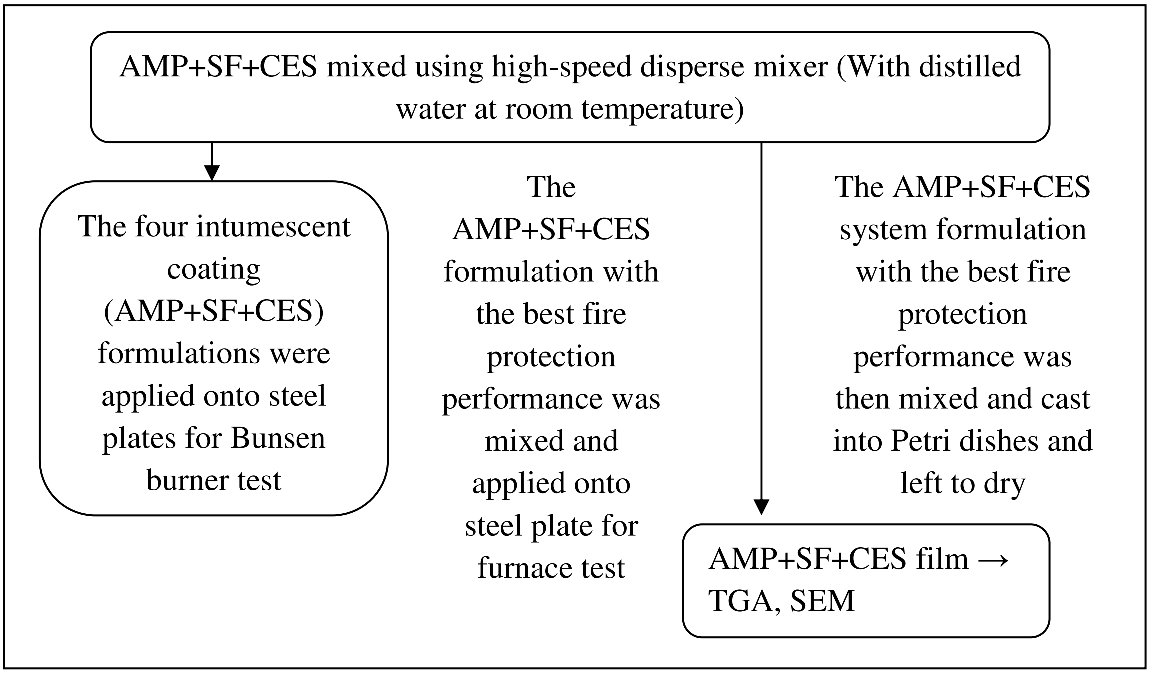


Figure 3.13 The flow diagram for the preparation process of AMP+SF+CES system

3.3.4 AMP+SF+CES+ER System

The AMP+SF+CES system formulation with the best fire protection formula i.e. sample C3 was added with 5 wt.%, 10 wt.%, 15 wt.% and 20 wt. % of water-borne epoxy resin (ER), respectively as shown in Table 3.10. ER functions as a binder

Table 3.10: Constituents of the AMP+SF+CES+ER samples

Designation	C3 (g)	ER (wt.%)	ER (g)
D1	148.147	5	7.76
D2	148.147	10	16.46
D3	148.147	15	26.14
D4	148.147	20	37.04

Figure 3.14 shows the flow diagram for the preparation process of the AMP+SF+CES+ER system. The steps used in the AMP+SF+CES system were repeated in the AMP+SF+CES+ER system. Then, a piece from the center of the char layer was cut out after the Bunsen burner test for observation using Field Emission Scanning Electron Microscope (FESEM). The FESEM was operated at various levels of magnification to observe the morphologies of the char layers and the foam structure was characterized using FESEM images.

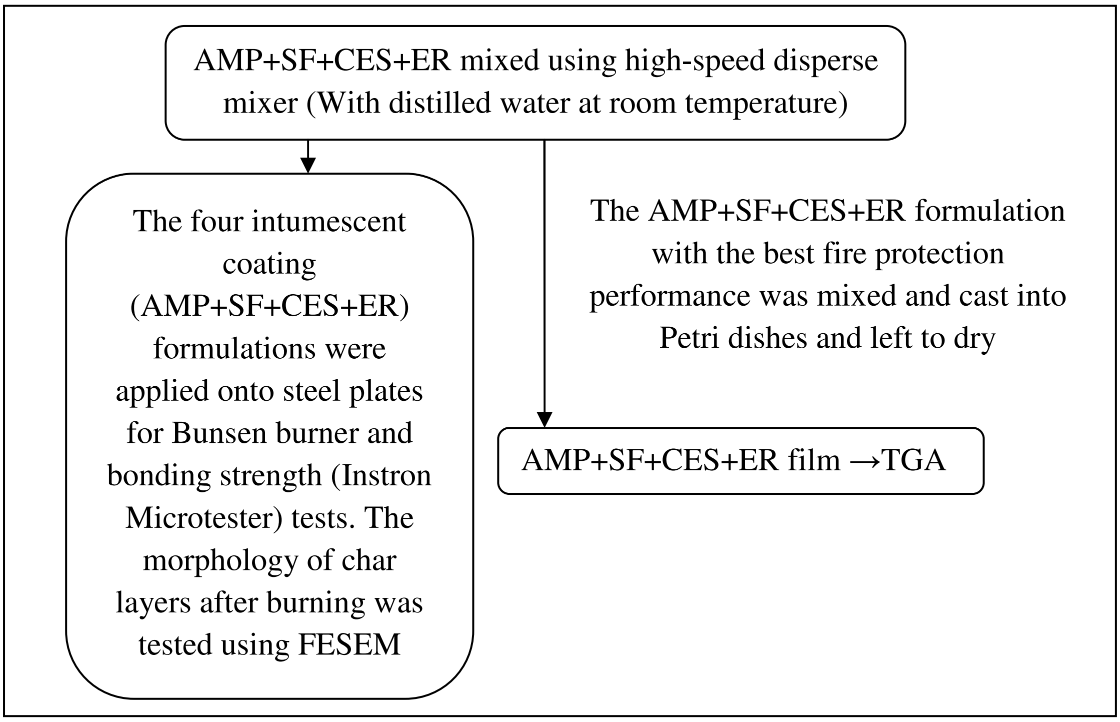


Figure 3.14 The flow diagram for the preparation process of AMP+SF+CES+ER system

3.4 Characterization and Measurement Techniques

The small scale lab tests and fire tests involved several techniques in order to characterize and determine the properties and behavior of the intumescent coatings. The techniques include Thermogravimetry Analysis (TGA), Scanning Electron Microscope (SEM), Instron Microtester, Field Emission Scanning Electron Microscope (FESEM), Bunsen burner test and furnace test.

3.4.1 Bunsen Burner Test

The Bunsen burner test was used to characterize the formation of char and the reaction of the intumescent coating in a fire. The temperature evolution of a steel plate without protection was also tested to determine the fire protection efficiency of the coating formulation. For each sample, the thickness of the char layer was measured using a digital caliper after the fire testing. The evolution of temperature between the virgin steel and the single-side coated steel plates were compared. The gas consumption of the Bunsen burner was at 126g/h. The formulation was applied using a gun sprayer onto grit blasted steel plates with dimensions of 100 mm x 100 mm x 3 mm until a coating thickness of 1.5±0.1 mm was obtained. The AMP, AMP+SF, AMP+SF+CES and AMP+SF+CES+ER coating systems were allowed to cure for three days before being exposed to fire for 90 minutes. Temperature changes during exposure to fire were measured using a handheld thermometer connected to a thermocouple plate welded to the back of the coated steel plate. Steel usually loses its main structural properties at around 550°C. In this study, 400°C has been chosen as the critical temperature for steel to ensure a higher level of safety and protection (Yew and Ramli Sulong, 2009). A high temperature flame (about 1000°C) was applied with a Bunsen burner to a virgin steel plate (Figure 3.15 (a)) and coated steel plate (Figure 3.15 (b)).

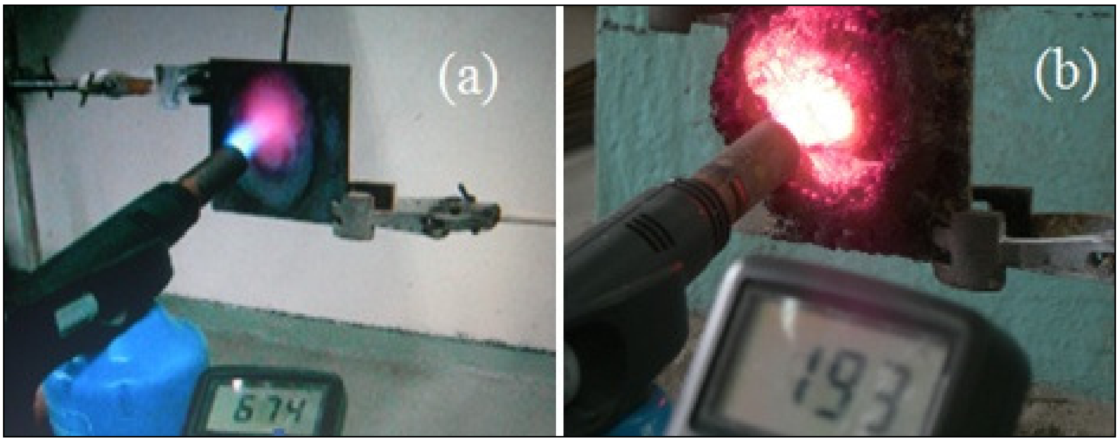


Figure 3.15 The Bunsen burner test (a) virgin steel plate and (b) coated steel plate

3.4.2 Furnace Test

The model UAF 16/10 ashing Lenton furnace has maximum operating temperatures of 1600°C with internal dimensions (H x W x D) 190 mm x 180 mm x 310 mm which provide rapid heating and cooling and low running costs as shown in Figure 3.16. The furnace test was carried out to investigate the fire behavior of protected and unprotected steel plates. In this study, the AMP+SF+CES formulation with the best fire protection performance was applied onto one side of a 200 mm x 200 mm x 3 mm grit blasted steel plate until a 1.2 mm thick coating was obtained. The specified coating thickness of 1.2 mm is to study the efficiency of a thinner coating under the furnace test. The evolution of temperature between the unprotected and protected steel plates was compared. The method of measurement of the temperature changes during furnace heating was similar to the Bunsen burner test. The coating was also allowed to cure for three days before fire testing. The furnace heating temperature rate was controlled to closely follow the Eurocode parametric time-temperature curve (EC3, 2002).

Figure 3.16 Furnace test

3.4.3 Thermogravimetry Analysis (TGA)

For materials that are candidates for elevated temperature applications it is important to investigate their decomposition with respect to temperature; this can be investigated by using TGA. TGA is a technique that permits the continuous monitoring of the mass of a sample as a function of temperature or time while being heated at a specific heating rate in an inert atmosphere or ambient atmosphere. In this study, TGA was carried out at 20°C/min under air flow in the temperature range of 30°C to 1000°C using a TGA/SDTA851^e model as shown in Figure 3.17. The samples were carefully weighed (around 3 mg) and placed into a high purity silica crucibles that is supported on, or suspended from an analytical balance located outside the furnace chamber. TGA is used to measure change in the weight of a material as a function of temperature, or time whilst being subjected to a constant heating rate. These measurements provide basic information about the thermal stability of a material and its composition.

Figure 3.17 Thermogravimetry analysis (TGA)

3.4.4 Scanning Electron Microscope (SEM)

Microscopic analyses were carried out using a scanning electron microscope (SEM) Hitachi XL 30 operated at 25kV at various levels of magnification as shown in Figure 3.18. All samples were ultra microtomed with a diamond knife on a Leica UltraCut microtome to obtain smooth surfaces for SEM analysis. All samples must be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. Nonconductive coating samples tend to charge when scanned by the electron beam, and especially in secondary electron imaging mode, this causes scanning faults and other image artifacts. The coatings were coated with an ultrathin gold coating as an electrically-conducting material which was deposited on the sample by using a low vacuum sputter coater. The sputter coater uses argon gas and a small electric field. The sample is placed in a small chamber in vacuum. Argon (Ar) gas is then introduced and an electric field is used to cause an electron to be removed from the Ar atoms to make the atoms ions positively charged. The Ar ions are then attracted to a negatively charged piece of gold foil. The Ar ions act like sand in a sandblaster, knocking gold atoms from the surface of the foil. These gold atoms now settle onto the surface of the sample, producing a gold coating. In this study, SEM operated at 25kV was used to observe the morphologies of the intumescent coating samples and the surface of the coating was characterized with SEM micrographs.

Figure 3.18 Scanning Electron Microscope (SEM)

3.4.5 Field Electron Scanning Electron Microscope (FESEM)

FESEM was introduced to improve imaging resolution available with conventional SEMs with a tungsten source as shown in Figure 3.19. The GEMINI® Based Field Emission SEM launched by ZEISS has been designed from the beginning as a high stability FESEM with a relatively large multi-ported chamber. All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. In this study, FESEM operated at 2kV was used to observe the morphologies of the char layers and the foam structure was characterized with FESEM images.

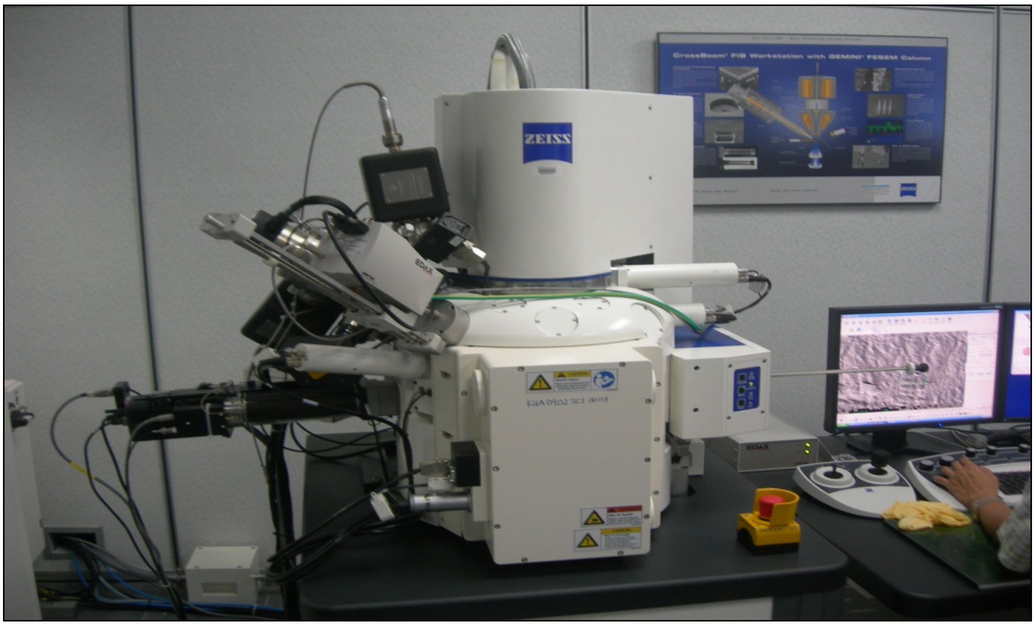


Figure 3.19 Field Emission Scanning Electron Microscope (FESEM)

3.4.6 Instron Microtester

The coatings were applied to one side of a 50 mm × 50 mm × 3 mm steel plate until a 1.5±0.1 mm thick coating was obtained. The steel plate with the dry film was stuck to a bare steel plate using epoxy glue. Then the two steel plates were pulled vertically with continuous extension rate of 1 mm/minute by using an Instron microtester as shown in Figure 3.20 until the coatings on the steel plate cracked and pulled off. The bonding strength, f_b (Nm^{-2}) of the coating was calculated by dividing the crack charge, F (N) of the coating with the sticking area, A (m^2) of the coating on the steel plate.

$$f_b = F/A \qquad (3.1)$$

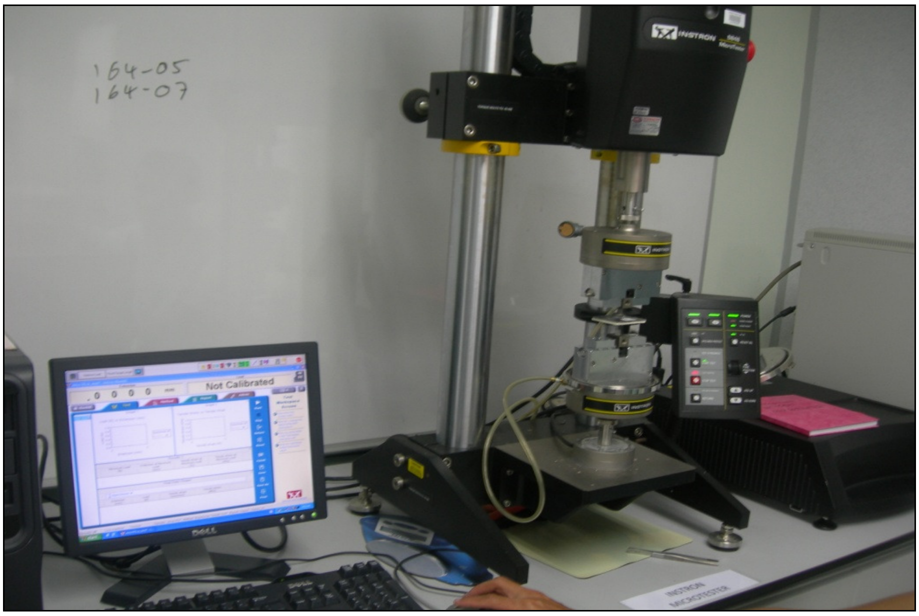


Figure 3.20 Instron Microtester